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FOR 1964

METALLURGY DIVISION

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9700 South Cass Avenue
Argonne, Illinois 60440

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Frank C. Footc, Director

Haim H. Chiswik, Associate Director

Robert E. Macherey, Associate Director

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Part I

Engineering Metallurgy

A. FAST REACTOR FUEL ELEMENT DEVELOPMENT AND FABRICATION

1. Properties of Metallic Fuels and Jacket Materials

a. Properties of Uranium-Plutonium-Fizzium Alloys (L. R. KELMAN, R. J. DUNWORTH, H. SAVAGE, AND H. V. RHUDE)

The uranium-plutonium-fizzium alloys are being studied⁽¹⁻⁶⁾ as possible metal fuels for fast breeder reactors. These alloys were selected for study because of EBR-II physics considerations as well as the pyrorefining fuel reprocessing scheme in the EBR-II hot cell.⁽⁷⁾ The fizzium composition used in our tests (2.8w/oZr, 2.7w/oMo, 3w/oRu, 0.5w/oRh, 1w/oPd)⁽³⁾ is an equilibrium alloy that represents the elements not removed by this reprocessing.

Out-of-pile property studies of these alloys were completed during the past year. The variation in properties with increasing plutonium (from 0 to 20w/o) and fizzium (from 0 to 15w/o) is shown in Table 1. Plutonium degrades the pertinent properties of the uranium-fizzium alloys whereas fizzium improves most of the properties of the uranium-plutonium alloys.

Phases and Transformation Kinetics (H. SAVAGE)

The influence of plutonium and fizzium on the transformation temperatures is summarized in Figure 1. The solidus and liquidus temperatures decrease with increasing plutonium and fizzium content; the solid state transformation temperatures are lowered.

Phase studies during the past year were made on U-10w/oPu-10w/oFz and U-10w/oPu-10w/oF alloys. These multicomponent alloys have a complicated structure in which two minor phases contain much of the fizzium elements. These phases generally do not transform or go into solution. The properties of these alloys depend, then, on the composition and structure of the matrix.

The composition of the matrix and predominant

⁽¹⁾ Dunworth, R. J., Kelman, L. R., Savage, H., Gilbert, E. R., and Rhude, H. V., *Properties of Uranium-Plutonium-Fizzium Alloys*, Trans. ANS, Vol. 7, No. 2, (Nov. 1964) p. 405.

⁽²⁾ *Annual Report for 1963 Metallurgy Division*, ANL-6868, pp. 11-23.

⁽³⁾ *Annual Report for 1962 Metallurgy Division*, ANL-6677, pp. 9-14.

⁽⁴⁾ *Annual Report for 1961 Metallurgy Division*, ANL-6516, pp. 9-16, 403, 406.

⁽⁵⁾ *Annual Report for 1960 Metallurgy Division*, ANL-6330, pp. 9-18.

⁽⁶⁾ *Annual Report for 1959 Metallurgy Division*, ANL-6099, pp. 9-11.

⁽⁷⁾ Koch, L. J., et al., *Hazard Report Experimental Breeder Reactor II*, ANL-5719 (1957) p. 50.

minor phases were determined for quenched specimens after annealing at 850°C for 60 days and seven days with a microprobe analyzer at Mound Laboratory. The microprobe results are given in Table 2 and microstructures of the fizzium alloys are given in Figure 2. The two predominant minor phases of the fizzium alloy (gray and white phases shown by arrows in Figure 2c) occupied about 20 percent of the structure. It is evident from Table 2 that the matrix of the casting contains practically all of the molybdenum and much of the ruthenium but practically none of the zirconium, palladium and rhodium. The light particles, after the seven day heat treatment, consist of about half uranium and plutonium and the balance mostly zirconium with some ruthenium. The ruthenium content of the light particles increases considerably on annealing at 850°C. The gray particles consist of plutonium, uranium, and palladium.

The phases and compositions of the fissium alloy quenched after seven days at 850°C are given in Table 3. The matrix composition was like that of the fizzium alloy. Two minor phases were found. One was similar to the gray particle of the fizzium alloy. The composition of the other particle was approximately that of U₂Ru.

The X-ray diffraction patterns of the heat-treated fizzium alloys were compared with known structures.⁽³⁾ The matrix was identified as γ° and the gray particles as θ . The light particles contained a ZrRu phase.

The U-10w/oPu-10w/oFz alloy transforms from γ to γ° on quenching from above 650°C to room temperature. On isothermally quenching to the range 400-550°C the final products of the transformation are α and γ' .⁽³⁾

Expansion, hardness,⁽²⁾ and elastic modulus were used to study the transformation kinetics of isothermally quenched specimens or quenched and reheated specimens. The elastic modulus, Figure 3, was the most reliable and sensitive of these methods. The alloy transformed most rapidly in the range 450-500°C. Transformation began almost immediately on quenching. The modulus approximately doubled in about 30 minutes after which it increased only slightly with time. An equivalent amount of transformation took about twice as long at 400°C.

The metallographic interpretation of the transformation is shown in Figure 2 for the 450-500°C temperature range. No clear end point could be detected

TABLE 1. PROPERTIES OF URANIUM-PLUTONIUM-FISSIUM ALLOYS

	Uranium	U-10Pu	U-10Pu-10Fz	U-15Pu-10Fz	U-20Pu-10Fz	U-20Pu-5Fz	U-20Pu-15Fz
Solidus, (°C)	1132	1025	910	≈865	820 ^(a)	860 ^(a)	805 ^(a)
Liquidus, (°C)	—	1060	1010	≈1000	990 ^(a)	≈1010	≈960
Transformation Range (°C)							
Start	668	585	550	520	510	510	500
End	775	740	630	605	605	700	550
Density, (g cm ⁻³ at 25°C)	19.07	18.7	16.8	16.5	16.8	17.7	16.1
Thermal Expansion							
Avg. Coef., (10 ⁻⁶ °C ⁻¹)							
20°C to start of trans.	19.4	19.3	16.3	16.5	17.5		
End of trans. to 720°C	25.6	23.8	20.5	22.5	21.7		
20°C to 720°C	24.2	23.8	21.2	20.6	21.2		
Transformation, (%)	0.45	0.28	0.45	0.36	0.33		
Enthalpy, 25°C to mp (cal gm ⁻¹)	52	46	44 ^(b)	≈43	≈42	≈43	≈42
Thermal Conductivity (cal sec ⁻¹ cm ⁻¹ °C ⁻¹)							
200°C	0.071	0.056	0.046	≈0.046	0.047	0.041	0.043
400°C	0.080	0.069	0.057	≈0.056	0.056	0.054	0.053
600°C	0.094	0.087	0.070	≈0.070	0.069	0.066	0.067
800°C	0.115	0.100	0.084	≈0.085	0.086	0.077	0.080
Thermal Cycling							
% change in density		-30	+1	0	-1		
% change in length	-7	+25	0	-1	+2		
Hardness, DPN, (kg mm ⁻²) ^(c)							
γ quenched	— ^(d)	— ^(d)	255		215		
α transformed	291	205	411	433	430		
Tensile Strength (kg mm ⁻²)							
200°C	37	26	58	42			
400°C	17	19	40	27			
600°C	5	9 ^(e)	8	6	3		
800°C	1	0.5	2		1		
Brittleness,							
Extreme fiber stress (kg mm ⁻²)							
γ quenched		— ^(d)	136		116		
α transformed		101	83		51		
% strain at fracture							
γ quenched		— ^(d)	1.3		1.0		
α transformed		0.7	0.9		0.4		

(a) These values were obtained on the fissium composition (low Zr).

(b) Four cal gm⁻¹ were added to the observed value to approximate the heat of transformation.

(c) Converted from Rockwell B and C scales by using the Steel Hardness Conversion Chart.

(d) Gamma phase cannot be retained in either U or U-10w/oPu by quenching.

(e) The high strength is probably caused by beta phase.

with metallography. Figure 2a shows the structure in a large-grained specimen after 30 minutes at 475°C. The matrix has not changed appreciably from the quenched appearance. There is a decomposition product at the boundaries of the quenched phase. Polarized

light (2b) revealed a banded structure which suggests the presence of non-cubic material. This was not found in specimens quenched to room temperature. After two hours at 450°C, the overaged matrix developed a peppered appearance as in 2c. The grain boundary product

did not grow. After one week at 450°C, the decomposition products developed into a partially lamellar structure (2d).

Enthalpy of the U-10w/oPu-10w/oFz Alloy (H. SAVAGE)

The measurements of the enthalpy (heat content) of the U-10w/oPu-10w/oFz alloy⁽²⁾ have been extended to include values in the liquid region. More enthalpy data of the solid alloy were obtained to improve definition of the curve. The smoothed results and a calculated equilibrium curve were plotted together with the U-10w/oPu alloy values (Figure 4). The heats of the α - β and β - γ transformations in the binary alloy were arbitrarily added to the measured data of the U-10w/oPu-10w/oFz alloy to obtain the calculated curve above the transformation temperature. The heat of fusion was found to be 9.5 ± 2.2 cal/g compared to 10.2 ± 1.0 cal/g for the binary alloy.

Thermal Conductivity (R. J. DUNWORTH)

The thermal conductivity of the U-10w/oPu alloy was determined by using the comparative apparatus previously described.⁽⁴⁾ As shown in Table 1, the thermal conductivity of this alloy is about 15 percent less than that of unalloyed uranium; the thermal conductivity of the U-10w/oPu-10w/oFz alloy is about 30 percent less. Additional increases in plutonium or fissionium have little significant effect.

Thermal Expansion (H. V. RHUDE)

Dilatometric measurements⁽⁴⁾ were made on injection cast rods, 10 mm in diameter by 26 mm long. Specimens were heated at 2°C per minute up to 720°C, then cooled at 2°C per minute.

All the cast U-Pu-Fz alloys listed in Table 1 have the general shape of the curve shown in Figure 5. In general they all have a slight decrease in slope of the expansion curve on heating from 400°C to 550°C. This behavior is attributed to transformation of the retained high temperature phase.

Thermal Cycling (R. J. DUNWORTH)

The change in dimensions and appearance of these alloys on repeated cycling through the transformations was also studied. Injection cast pins were thermally cycled 100 times between 475 and 700°C. They were held four hours at 475°C and one hour at 700°C with 15 minute transfer times. Since these alloys transform in less than 30 minutes, these holding times are sufficient to transform both the low and high temperature phases. This cycle resulted in large length increases and density decreases of the U-10w/oPu pins as shown

106-8078

FIG. 1. Transformation Temperatures in U-Pu-Fz Alloys. Upper shading shows interval between liquidus and solidus.

TABLE 2. COMPOSITIONS OF THE PREDOMINANT PHASES IN U-10w/oPu-10w/oFz ALLOY DETERMINED WITH A MICROPROBE ANALYZER (w/o)

Element	Total Specimen	60 Days at 850°C, Oil Quenched			7 Days at 850°C
		Matrix	Light Particle	Gray Particle	Oil Quenched Light Particle
U	80	88	22	18	41
Pu	10	7	18	56	7
Zr	2.80	trace	31	trace	40
Mo	2.75	3	trace	1	trace
Ru	2.95	2	26	1	11
Pd	1.00	0	2	24	—
Rh	0.50	trace	trace	trace	—

in Figure 6. The uranium pin contracted slightly; the fissionium alloy pins showed almost no change.

Tensile Properties (H. SAVAGE)

The tensile properties of the uranium-plutonium-fissionium alloys were measured from room temperature to about 800°C. Some of these data have been reported previously.⁽²⁾ All the tensile strength data are summarized in Figure 7, page 9.

The unalloyed uranium tensile strength drops off with increasing temperature from about 50 kg/mm² at room temperature to about 5 kg/mm² at 650°C. It increases abruptly in the β -uranium temperature region to almost 10 kg/mm² and drops again to about 1 kg/mm² in the γ temperature region.

The addition of plutonium greatly lowers the room temperature strength of uranium. The U-10w/oPu

FIG. 2. Transformed Structures in U-10w/oPu-10w/oFz Alloys

alloy tensile strength is about 25 kg/mm² from room temperature to about 300°C. It closely follows the uranium curve from there to 750°C.

The tensile strength of the U-10w/oPu-10w/oFz alloy depends on the prior heat treatment. In specimens quenched from 650°C or above, it is 55 to 60 kg/mm² between room temperature and 300°C and decreases to about 15 kg/mm² at 550°C. In specimens transformed at 550°C or below, the strength is 20 kg/mm² at room temperature and increases to 33 kg/mm² at

300°C, and then decreases to about 15 kg/mm² at 550°C. Between 600°C and 800°C it drops continuously from just under 10 to about 2 kg/mm².

The U-15w/oPu-10w/oFz alloy is somewhat weaker than the U-10w/oPu-10w/oFz alloy with the strength decreasing similarly with temperature.

Creep (R. J. DUNWORTH AND H. SAVAGE)

The uranium-plutonium-fizzium alloys were tested in creep under very light loads. The purpose of the in-

TABLE 3. COMPOSITIONS OF THE PREDOMINANT PHASES IN U-10w/oPu-10w/oFs ALLOY DETERMINED WITH A MICROPROBE ANALYZER (w/o) (7 Days at 850°C, Oil Quenched)

Element	Total Specimen	Matrix		Gray Particle Small	Gray Particle Large
		Area I	Area II		
U	80	87	80	29	79
Pu	10	4	13	50	1
Mo	3.76	4	4	—	1
Ru	4.10	3	3	2	16
Pd	1.44	1	—	19	1
Rh	0.66	1	—	—	2

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FIG. 3. Young's Modulus vs. Transformation Time for U-10w/oPu-10w/oFz Injection Castings.

vestigation was to determine if the fuel pins would collapse under their own weight before they were restrained by the jacket.

Most of the specimens were tested in compression for 200 hours in a dial gage dilatometer⁽⁴⁾ with weights added to the pushrod. The specimens were 50 mm long and 3.66 mm in diameter. Since the total strains were less than 0.5%, no corrections were applied for an increase in area with the compressive loading. The U-10w/oPu specimen bent slightly during the test at 850°C, and the strain values are apparently low. Tensile creep tests of the U-10w/oPu-10w/oFz alloy were made in a sealed quartz tube with weights hung on the end of the specimen. The specimens were 62 mm long and 3.66 mm in diameter with a 50 mm gage length.

The creep data in Table 4 show that little strain occurs—even at 750°C or 850°C. The strains obtained at 100 and 200 hours show a reasonable relation to temperature and load. The U-10w/oPu alloy is

stronger at 650°C than either of the fission alloys. At 750°C, however, all the alloys are in the gamma phase and the fission alloys are stronger because of solid solution strengthening.

b. Compatibility of U-Pu-Fz Fuel Alloys with Potential Cladding Materials (C. M. WALTER)

Studies on the extent of solid state diffusion between the uranium-plutonium-fission alloys and potential cladding materials were completed during the past year. The extent of penetration of fuel into the cladding is summarized here. Penetration of cladding ele-

106-8054

FIG. 4. Heat Content of U-10w/oPu and U-10w/oPu-10w/oFz above 25°C.

106-8079

FIG. 5. Thermal Expansion of As-Cast U-15w/oPu-10w/oFz Alloy.

ments into the fuel were also noted but they are of less importance to fuel element integrity and operating life.

The compatibility of U-10w/oPu, U-10w/oPu-10w/oFz, U-15w/oPu-10w/oFz and U-20w/oPu-10w/oFz alloys with chromium, Hastelloy-X, Type 304 stainless steel, molybdenum, niobium, Nb-1w/oZr, vanadium, V-10w/oTi and V-20w/oTi was investigated by annealing diffusion couples in the 550 to 750°C temperature range for times of 7 to 150 days. Penetrations were obtained by metallographic inspection of the couples and checked by microprobe analysis.

Figure 8 compares the cladding penetrations of a number of materials with U-10w/oPu-10w/oFz. If these cladding materials are arranged in order of decreasing compatibility with uranium-plutonium-fiz-

106-8084

FIG. 6. U-Pu-Fz Alloys after Thermal Cycling. These pins were cycled 100 times between 475° and 700°C. They were held 4 hours at 475° and 1 hour at 700°C with 15-minute transfer times.

zium, the following list is obtained:

1. V-20w/oTi
2. V-10w/oTi
3. Molybdenum
4. 304 stainless steel
5. Niobium and Nb-1w/oZr
6. Hastelloy-X

Table 5 compares the penetration coefficients (K) calculated (except where noted) from the expression

$$X^2 = Kt$$

where X is the cladding penetration in centimeters, t is the time in seconds and K is the penetration coefficient in cm^2/sec . This table summarizes (in order of decreasing compatibility) all the data obtained in our study.

Table 6 presents extrapolations of cladding penetration to a common time of one year for various cladding materials against U-10w/oPu-10w/oFz and U-15w/oPu-10w/oFz. Because the cladding material must at some point come in contact with structural components, usually made of austenitic stainless steel, it was also desirable to study the diffusion interaction between the cladding material and Type 304 stainless steel. Vanadium and V-20w/oTi were checked against 304 stainless steel because of their superior compatibility with the fuel. Bonding, but not serious penetration, did indeed occur between these materials so that one must be prepared to encounter this in disassembly of reactor components.

Some general conclusions which may be drawn from this study are as follows:

1. Of the cladding materials investigated, V-20w/oTi has been shown to be the most compatible with U-Pu-Fz.
2. Molybdenum was also found to be good, but, because of difficulty encountered in determining the direction of penetration, V-Ti alloys were judged to be somewhat better.
3. Hastelloy-X and 304 stainless steel show evidence of melting and accelerated penetration between 650 and 675°C. Their temperature limits of operation would, therefore, be considerably below 650°C.
4. As expected, an increase in plutonium content of the fuel results in poorer compatibility with all the cladding materials investigated.

The results of this investigation indicate that the compatibility of a given metal fuel with various cladding materials may be predictable, on a relative basis, by using the binary phase diagrams of the major elements in the fuel and in the cladding. In general, systems showing limited solid solubility, especially on the cladding side of the phase diagram, and no intermetallic

106-8053

FIG. 7. Ultimate Tensile Strength vs. Temperature for U-Pu-Fz Alloy Injection Castings.

TABLE 4. CREEP OF URANIUM-PLUTONIUM-FIZZIUM ALLOYS

Alloy, w/o U Pu Fz	Temp. (°C)	Stress (g/mm ²)	Strain × 10 ³ at 100 hrs	Strain × 10 ³ at 200 hrs
75 15 10	650	100	0.93	1.2
	650	12	0.39	0.50
	650 ^(a)	12	0.58	0.88
	750 ^(a)	12	1.36 ^(b)	2.1
	850 ^(a)	12	3.7	5.0
80 10 10 ^(c)	650	6	0.37	0.63
	750	6	0.97	1.16
	850	6	3.0 ^(d)	3.84 ^(d)
90 10	650	12	0.18	0.19
	750	12	1.6	2.83
	850	12	3.0 ^(d)	3.84 ^(d)

^(a) Tested in the cast condition—all other tests were on homogenized specimens.

^(b) Average value of two 100 hour runs, specimen cooled to room temperature.

^(c) 750 hour tensile creep tests.

^(d) Influenced by bending of the specimen.

compounds will have good compatibility. In contrast, systems having extensive solid solubility or intermetallic compounds will have poorer compatibility. In systems which form compounds, the closer in composition these compounds are to the cladding side of the diagram, the greater the cladding penetration.

2. Compatibility of Potential Cladding Materials with Molten Fuels (C. M. WALTER)

Safety considerations for EBR-II and other future fast reactors require information about the rate of pene-

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FIG. 8. Diffusion Penetration of U-10w/oPu-10w/oFz into Prospective Claddings at a Constant Time of 3.6×10^6 sec (42 days).

TABLE 5 PENETRATION COEFFICIENTS (K) IN CM²/SEC (EXCEPT WHERE NOTED)

Combination (w/o)	Temperature (°C)				
	550	600	650	700	750
V/U-10Pu-10Fz	(c) 7.5×10^{-14}	(c) 1.5×10^{-13}	(c) 4.0×10^{-13}		
V-20Ti/U-10Pu-10Fz	(a) 2.3×10^{-15}	1.3×10^{-14}	6.4×10^{-14}	3.1×10^{-13}	(a) 1.7×10^{-12}
V-20Ti/U-15Pu-10Fz		(a) 1.3×10^{-14}	8.1×10^{-14}	(a) 8.0×10^{-13}	(a) 3.0×10^{-12}
V-10Ti/U-10Pu-10Fz	4.7×10^{-15}	2.3×10^{-14}	1.1×10^{-13}		
Cr/U-10Pu-10Fz				(a) 3.5×10^{-13}	
Mo/U-10Pu-10Fz		4.5×10^{-14}	1.2×10^{-13}	1.9×10^{-13}	
Mo/U-15Pu-10Fz		(a) 7.5×10^{-14}	(a) 2.0×10^{-13}	(a) 4.0×10^{-13}	
304SS/U-10Pu-10Fz	6.9×10^{-14}	2.2×10^{-13}	1.1×10^{-12}		
304SS/U-15Pu-10Fz			(a) 3.4×10^{-12}		
Hast-X/U-10Pu-10Fz	1.8×10^{-13}	8.0×10^{-13}	3.6×10^{-12}		
Hast-X/U-15Pu-10Fz			(a) 1.1×10^{-11}		
Nb/U-10Pu-10Fz	1.3×10^{-13}	6.3×10^{-13}	(b) 2.2×10^{-9} cm/sec		
Nb/U-20Pu-10Fz	2.3×10^{-13}	1.8×10^{-12}	(b) 4.2×10^{-9} cm/sec		
Nb-1Zr/U-10Pu-10Fz	1.6×10^{-13}	4.0×10^{-13}	(b) 1.9×10^{-9} cm/sec		
304SS/V			(d) 3.4×10^{-13}		
304SS/V-20Ti			(d) 2.3×10^{-13}		

(a) Calculated from only one datum point assuming an $X^2 = Kt$ law.(b) Obeyed the $X = Kt$ rather than $X^2 = Kt$ rate law.(c) No cladding penetration. K 's represent band on the fuel side, believed to be (U,Pu)O₂. Vanadium contained 1300 ppm oxygen.(d) Total band width. Also calculated from only one data point assuming an $X^2 = Kt$ law.TABLE 6. CALCULATED PENETRATIONS FOR ONE YEAR (cm $\times 10^4$)

Combination (w/o)	Temperature (°C)				
	550	600	650	700	750
V-20Ti/U-10Pu-10Fz	3	6	15	30	75
V-20Ti/U-15Pu-10Fz		6	15	50	100
V-10Ti/U-10Pu-10Fz	4	10	20		
Cr/U-10Pu-10Fz				30	
Mo/U-10Pu-10Fz		10	15	25	
Mo/U-15Pu-10Fz		15	25	35	
304SS/U-10Pu-10Fz	15	25	60		
304SS/U-15Pu-10Fz			100		
Hast-X/U-10Pu-10Fz	25	50	110		
Hast-X/U-15Pu-10Fz			190		
Nb/U-10Pu-10Fz	20	45	700		
Nb/U-20Pu-10Fz	30	75	1300		
Nb-1Zr/U-10Pu-10Fz	25	35	600		

tration of prospective clad materials by molten uranium- and plutonium-containing fuels. Work has been reported earlier^(8,9,10) on the interaction of stainless steel and iron with molten U-5w/oFz alloy and with uranium. The formation of intermetallic compounds

(8) Annual Report for 1961 Metallurgy Division, ANL-6516, p. 21.

(9) Annual Report for 1963 Metallurgy Division, ANL-6868, p. 24.

(10) Walter, C. M. and Kelman, L. R., *Penetration Rate Studies of Stainless Steel by Molten Uranium and Uranium-Fissium Alloys*, J. Nuc. Matls., 6, 281-290 (1962).

during reaction in these systems played a dominant role in the mode and rate of penetration.

This study has been extended to cover the compatibility of vanadium with molten uranium, U-10w/oPu and U-10w/oPu-10w/oFz alloy in the 1100 to 1400°C temperature range. The preliminary results obtained on 750 μ thick samples are plotted in Figure 9. In uranium, the penetration rate is a linear function of the specimen thickness. The effect of specimen thickness has not yet been determined in U-10w/oPu and U-10w/oPu-10w/oFz alloys. As can be seen by the curve, uranium and U-10w/oPu act very differently towards vanadium than does molten U-10w/oPu-10w/oFz. The penetration rates of uranium and U-10w/oPu vary linearly with temperature, U-10w/oPu alloy is slightly more aggressive. The U-10w/oPu-10w/oFz versus vanadium results do not behave in such a predictable manner. As mentioned above, experience with the U-Fe system has shown that intermetallic compound formation during penetration can have a profound effect on the penetration rate. This suggested the possibility of compounds forming between the fission elements (Mo, Zr, Ru, Rh or Pd) and vanadium. Metallography of specimens tested in U-10w/oPu-10w/oFz indicated a band of what appeared to be a compound, forming on the surface of vanadium below 1300°C. An examination of the appropriate binary phase diagrams showed only two systems that form intermediate phases in the temperature range of interest, the Zr-V and Ru-V systems.

- Microprobe analysis of this band showed that it was composed of molybdenum and vanadium corresponding to a composition of about MoV_2 . There are no compounds in the Mo-V system so we have not been able to explain the effects seen in V vs. U-Pu-Fz alloy interactions. In light of these results we plan to run vanadium against U-10w/oPu with the appropriate singular additions of the fission elements to determine which of the elements is responsible for the observed penetration behavior and why. We plan to vary the plutonium content in U-Pu and U-Pu-Fz alloys to study the effect of increasing plutonium on penetration. Spot checks of cladding penetration rates using V-20w/oTi alloy (the cladding now under prime consideration as a container for U-Pu-Fz) will also be made.

d. Improved U-Pu Base Metal Fuels (L. R. KELMAN, H. V. RHUDE, AND C. M. WALTER)

As part of our continuing search for metallic U-Pu fuels capable of improved performance we have found that the U-Pu-Ti and the U-Pu-Zr alloys are very promising because of their relatively high solidus temperatures. Our ultimate goal is a fuel that will withstand higher burnup and/or higher operating temperatures. The melting temperature was selected as the criterion for screening in this study since a higher melting temperature should lead to improved swelling resistance. It should also permit a higher operating temperature, because of the greater temperature range before melting, and, it should be a safer fuel in the event of an excursion.

The alloys in the screening study were made of U-Pu in an atom ratio of 4 to 1 with additions of 30a/o and 10a/o of the following elements: Sc, Ti, Y, Zr, Mo, Pd, Th. The solidus temperatures were determined by heat-treating in vacuum, quenching in Nak and subsequent metallography. Thermal expansion coefficients were determined on the as-cast alloys and metallographic studies were made.

Only the 30a/oTi and 30a/oZr alloys had solidus temperatures over 1100°C , so it is planned to concentrate immediate studies on these two alloy systems. Alloys of U-Pu-Ti that are based on the U_2Ti compound appear to be particularly interesting. The compound has no transformations from room temperature to 900°C where it decomposes to gamma U-Ti alloy. Also there is evidence that appreciable amounts of the uranium in the compound can be replaced by plutonium. Metallographic studies indicate that the structure of alloys in the vicinity of the $(\text{U,Pu})_2\text{Ti}$ compound can be altered significantly by thermal treatment. Studies are now in progress to determine

106-8315

FIG. 9. Penetration of Vanadium by Molten Uranium, U-10w/oPu, and U-10w/oPu-10w/oFz.

to what degree pertinent properties can be influenced by heat treatment.

e. High-Temperature Physical and Thermal Properties of V-20w/oTi Alloy (H. V. RHUDE, F. L. YAGGEE, H. SAVAGE, AND R. J. DUNWORTH)

Thermal Expansion (H. V. RHUDE AND F. L. YAGGEE)

The thermal expansion of V-20w/oTi was measured over the temperature range 25 – 967°C . The experimental expansion curve is given in Figure 10 along with published curves for unalloyed titanium and vanadium.

Enthalpy of V-20w/oTi Alloy (H. SAVAGE)

The enthalpy of the V-20w/oTi alloy was measured to an accuracy of $\pm 1\%$ in an isothermal drop calorimeter⁽¹¹⁾ from room temperature to 1150°C . The results are given in Table 7. The mean values of the specific heat, given in Table 8, were calculated between the reference temperature (25°C) and multiples of 200°C . The mean specific heat values are comparable to those of vanadium.⁽¹²⁾ Between 25°C and 200°C , the alloy value is 0.119 compared to 0.121 cal/(gm- $^\circ\text{C}$) for

⁽¹¹⁾ Annual Report for 1961 Metallurgy Division, ANL-6516, p. 404.

⁽¹²⁾ Smithells, C. J., *Metals Reference Book*, 2nd Ed., Butterworth, London (1955).

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FIG. 10. Thermal Expansion of Titanium, Vanadium and V-20w/oTi Alloy. Ref. (a) Hamble, C. A., *Rare Metals Handbook*, 2nd Ed., (1961), p. 635, Reinhold Pub. Corp. (London). Ref. (b) Smithells, C. J., *Metals Reference Book*, 3rd Ed., (1962) Vol. 2, p. 697, Washington Butterworths (London).

TABLE 7. HEAT CONTENT OF V-20w/oTi ABOVE 25°C

Measured		Smoothed	
Temp. (°C)	ΔH_{25} (cal/gm)	Temp. (°C)	ΔH_{25} (cal/gm)
-80	-9.4	100	9.0
297	32.3	200	20.9
471	54.3	300	33.0
647	77.9	400	45.5
831	102	500	58.6
1001	127	600	71.8
1153	149	700	85.0
		800	98.2
		900	112
		1000	126
		1100	140
		1200	154 ^(a)

^(a) Extrapolated.

vanadium. Between 25°C and 1000°C the alloy value is 0.129 compared to 0.139 cal/(gm·°C) for vanadium.

Thermal Conductivity of V-20w/oTi Alloy (R. J. DUNWORTH)

The thermal conductivity of the vanadium-20w/o titanium alloy is being determined on the comparative type apparatus.⁽¹³⁾ Values to 600°C are listed in Table 9. The alloy was run against Inconel and Armco standards with good agreement between the two runs. The standard deviation of the data is 0.011.

⁽¹³⁾ *Annual Report for 1961 Metallurgy Division*, ANL-6516, p. 403.

TABLE 8. MEAN SPECIFIC HEAT OF V-20w/oTi ABOVE 25°C

Temperature Range 25°C to T°C	Mean Specific Heat, $\Delta H_{25}/T$ (cal/gm·°C)
200	0.119
400	0.121
600	0.125
800	0.127
1000	0.129

TABLE 9. THERMAL CONDUCTIVITY OF V-20w/oTi ALLOY

Temperature (°C)	Thermal Conductivity (watts cm ⁻¹ °C ⁻¹)
0	0.188 ^(a)
100	0.205
200	0.220
300	0.234
400	0.249
500	0.262
600	0.276

^(a) Extrapolated.

f. Properties of Zero-Power Uranium-Plutonium Metal Fuels (L. R. KELMAN, H. V. RHUDE, AND H. SAVAGE)

The search for satisfactory uranium-plutonium-base alloys for zero-power fuel critical experiments was continued during the past year. Based on this study a U-20w/oPu-2.5w/o(6a/o)Mo alloy was selected for the additional fuel required for the SEFOR* fast criti-

* SEFOR—Southwest Experimental Fast Oxide Reactor.

cal experiment to be performed in ZPR-III.⁽¹⁴⁾ This alloy has good overall properties so that it will also serve well for ZPPR* needs. It has good room-temperature air corrosion resistance, high ignition temperature, good thermal expansion characteristic, and high strength. It is, therefore, not expected to deteriorate on long-time storage or use. Furthermore, this alloy can be melted and cast into appropriate plate form, and it can be machined. Although molybdenum is not an ideal alloying additive from a physics standpoint, its effects can be compensated for in interpretation of results. A similar alloy, but with 25w/o Pu, appears also to satisfy the ZPPR fuel requirements. We are currently continuing our search for an even better fuel for ZPPR to learn whether other alloying elements, such as titanium, that are more desirable than molybdenum from physics considerations will impart the desired properties to the U-Pu binary compositions of interest.

The SEFOR and the ZPPR fuel alloys should have U²³⁸ to Pu²³⁹ atom ratios of 4 to 1 and 3 to 1, respectively, with as little dilution as possible from other elements. Considerations of fabrication cost and flexibility in critical tests have shown that a metal alloy is much preferred for both SEFOR and ZPPR. Unfortunately, the binary U-Pu alloys in the composition range of interest corrode badly in air and are extremely brittle. At best, solid castings of these alloys powder down completely with time in air, at worst they are pyrophoric—a U-30a/oPu alloy in the form of a 6.3 mm (0.25 inch) thick plate ignited spontaneously when exposed to air. These poor properties are caused by the presence of the zeta phase which is present in binary alloys containing over about 15% plutonium. We have, therefore, been seeking an alloying element which, in small enough amounts to be acceptable, will either suppress the formation of the zeta phase or improve its properties. Molybdenum appears to do both.

The following properties and characteristics are pertinent to zero-power fuel applications and have therefore been the bases for our studies of a number of alloying elements.

1. Adequate corrosion resistance to permit successful fabrication and jacketing and to assure that they will not burn or powder excessively if a hole or crack develops in the jacket.
2. Metallurgical stability—the alloy must not deteriorate with time.

3. A large, positive, and reliable expansion coefficient and no contractions from transformations or microstructural changes on inadvertent heating.
4. Enough strength to assure that the fuel will cause the thin stainless steel jacket to expand if inadvertent heating occurs.
5. Fabricability—thin plates of several sizes are required.

Al, C, Cu, Fe, Mo, Ti, V and Zr were chosen as alloying additions that might impart the desired properties to the binary uranium-plutonium alloys. Ternary alloys of uranium-plutonium and the above alloying elements were subjected to air corrosion tests and ignition tests⁽¹⁵⁾ as a preliminary weeding-out process. The results of the air corrosion tests are shown in Figure 11. The molybdenum alloy has the highest ignition temperature of the alloys that were studied, and it has shown excellent resistance to air corrosion even after a year-long exposure. The oxidation resistance of the uranium-plutonium-molybdenum alloys was found to be relatively insensitive to casting method and they do not deteriorate with time. The Al, C, Cu, V and Zr alloys were eliminated by the air corrosion tests.

Early tests on chill castings of a 1.5w/o(6a/o)iron alloy appeared to confirm French reports that iron is a very beneficial additive. Further studies, however, revealed that the corrosion resistance and the structure of the iron alloys are extremely sensitive to the method of casting. Also, they deteriorate with time. This helps to explain the poor corrosion resistance that Picton and Sackman reported for these alloys.⁽¹⁶⁾ Injection cast coarse grained specimens, Figure 12b, were found to have relatively low ignition temperatures and were completely disintegrated to powder in 12 days of exposure to room temperature air. However, the above described chill casting was very fine grained, Figure 12a, had a high ignition temperature, and only began to show appreciable corrosion after 11 weeks exposure to air. Also, the ignition temperature of the chill cast material was much lower after several months storage than when tested soon after casting.

Alloys of 14.3a/oFe [(U,Pu)₆Fe compound] had extremely good corrosion resistance in air, but were too brittle to be fabricated.

A very low titanium alloy, U-20w/oPu-0.6w/o(3a/o)Ti showed up well enough in the air corrosion test to justify continued study to determine the

⁽¹⁴⁾ Kelman, L. R., Rhude, H. V., and Savage, H., *Development of a Metal Fuel for the SEFOR Fast Critical Experiment and for ZPPR*, Summary in ANS Trans., Vol. 7, No. 2, November 1964, p. 401.

* ZPPR—Zero Power Plutonium Reactor.

⁽¹⁵⁾ Chemical Engineering Division Summary Report, January-June 1964, ANL-6900.

⁽¹⁶⁾ Picton, G. and Sackman, J. F., *The Corrosion and Ignition Behavior of Some Uranium/Plutonium/Iron Alloys*, AWRE O-58/64 (Aug. 1964).

106-8080

FIG. 11. Room-Temperature Air-Corrosion Tests at 25 to 56% Relative Humidity of U-Pu-X ZPR Fuel Alloys (Composition in Atomic Percent).

106-8108

(a) Chill cast. Original mag. 500X

(b) Injection cast. Original mag. 500X

FIG. 12. Chill Cast vs. Injection Cast Microstructure of U-27a/oPu-6a/oFe Alloy.

106-8083

FIG. 13. Thermal Expansion Curve for U-19a/oPu-6a/oMo.

optimum titanium composition. A chill cast alloy of U-20w/oPu-2w/o(8a/o)Ti is currently being air corrosion tested and a series of U-25w/oPu-Ti alloys are being studied for ZPPR.

The U-20w/oPu-2.5w/oMo alloy castings have excellent expansion behavior for the SEFOR critical experiments in ZPR-III. Dilatometric studies were made in which one-inch long cast specimens were heated and cooled through several cycles between 30 and 700°C to assure reproducibility. Typical heating and cooling curves are shown in Figure 13. The average coefficient increases from $15.3 \times 10^{-6}/^{\circ}\text{C}$ in the range 30 to 220°C to $24.8 \times 10^{-6}/^{\circ}\text{C}$ in the range 220 to 545°C. The density at room temperature of the as cast U-20w/oPu-2.5w/oMo alloy is 18.28 g/cm³. The

mean specific heat from 25 to 500°C for this alloy is $0.037 \text{ cal g}^{-1} ^{\circ}\text{C}^{-1}$ as determined from heat content studies in a drop calorimeter.

As indicated in Figure 14, the high compressive strength of the U-20w/oPu-2.5w/oMo alloy, 134,000 kg/mm² (190,000 psi) at room temperature, fell off approximately linearly with increasing temperature to 81 kg/mm² (115,000 psi) at 280°C and 29 kg/mm² (41,000 psi) at 480°C. The alloy is easily machined and is tough enough to permit normal handling. However, it had practically no detectable ductility in compression tests from room temperature to 380°C. Above 380°C the ductility increased rapidly to about 50% reduction in length at 480°C.

106-8081

FIG. 14. Ultimate Compressive Strength and Reduction in Length vs. Temperature for U-20w/oPu-2.5w/oMo.

2. Properties of Ceramic Fuels

a. UC-PuC Bodies (O. L. KRUGER)

Studies on the sintering characteristics of $(\text{U}_{0.8}\text{-Pu}_{0.2})\text{C}$ were conducted over the past year to define the sintering parameters so that this technique could be used for production of fuel pellets. Material for this investigation was prepared by melting pieces of U, Pu and C in an arc furnace. This starting material usually contained <0.02w/o of both oxygen and

nitrogen. Powders prepared from this material were handled in a nitrogen atmosphere with impurities of oxygen and water vapor of about 0.005 and 0.01w/o respectively.

Preliminary work showed that pellets from the solid-solution material lost plutonium when fired under vacuum from 1600°C to 1800°C for two hours. To reduce plutonium vaporization, pellets were fired in a

FIG. 15. The Change in Density with Sintering Temperature for $(U_{0.8}, Pu_{0.2})$ Pellets Prepared from $<44\mu$ Powder and Fired in Argon.

TABLE 10. CHANGE IN DENSITY WITH TIME FOR $(U_{0.8}, Pu_{0.2})C$ PELLETS PREPARED FROM <44 MICRON POWDER AND HELD AT $1900^{\circ}C$ IN ARGON

Time (hours)	Density (Percent Theoretical)
1	83.4
2	84.9
4	85.7
8	86.7
16	87.7

flowing high-purity argon gas. No plutonium loss was detected, therefore, all subsequent studies were carried out under these conditions.

The changes in density of the pellets were investigated as a function of particle size and sintering temperature. Pellets prepared from powder with a particle size of $<8\mu$ attained densities of 80 to 85% of theoretical when sintered in argon for two hours at $1600^{\circ}C$. Densities of 90% of theoretical were obtained when the sintering temperature was increased to $2000^{\circ}C$ for two hours. The fine particle size of the powder was apparently conducive to oxygen pickup because these pellets contained from 1 to 2w/o oxygen. Their carbon contents were low (3.2 to 3.9w/oC) which indicated loss by reaction to form CO gas. In comparison, pellets prepared from powder with a particle size of $<44\mu$ and sintered at $1600^{\circ}C$ had lower densities, about 76% of theoretical, but the oxygen content was usually $<0.15w/o$ and the amount of carbon was always about the same as that present in the arc-melted material. Because of the problem of the high oxygen contamination in powders with maximum particle sizes near about 10μ , all further work was conducted on the $<44\mu$ powder. This powder was coated with 0.5w/o Carbowax binder and pressed into pellets

at a pressure of about 21 kg/cm^2 . These pellets were sintered at increasing temperatures for two hours. The changes in density with sintering temperature are shown in Figure 15. Pellets 90% of theoretical density were obtained by sintering at $2100^{\circ}C$. Metallographic and X-ray examination showed that only the solid solution $(U,Pu)C$ phase was present. There was no detectable loss of plutonium from sintering under argon at this temperature.

The above procedure was used to make pellets 0.634 cm in diameter by 1.2 to 1.5 cm long for instrumented irradiation studies in MTR and test fuel elements for EBR-II. For these experiments, pellets with a density about 85% of theoretical were required. This density was thought best for high burnup on consideration of fission gas retention and swelling, combined with the desire to retain a high thermal conductivity in the pellets throughout the tests. From the curve of Figure 15, it can be seen that a density of 85% of theoretical is obtained after sintering at about $1900^{\circ}C$ for two hours. The shrinkage of these pellets had to be controlled to $\pm 0.003\text{ cm}$ so that they could be loaded into fuel jackets without grinding to size. Therefore, the change in density with time at $1900^{\circ}C$ was investigated and the results are shown in Table 10. The changes were slight, consequently, precise control of time was not considered an important factor in the production process. Pellets for EBR-II of the composition $(U_{0.8}Pu_{0.2})C$ were made from 50% enriched U. Their total length was 157 cm of fuel. The same composition pellets were also made using depleted uranium, total of 80 cm. One-quarter of these pellets had axial holes to accommodate thermocouples. In addition to this work pellets are now being prepared for use in compatibility studies.

b. Interaction of Uranium-Plutonium Mixed Carbides with Potential Refractory Metal Claddings (C. M. WALTER AND T. W. LATIMER)

The need for compatibility between fuel and cladding is a prime consideration in the selection of an optimum cladding material for $(U,Pu)C$ fast reactor fuels. Extensive interaction could cause rupture of the fuel element cladding, thereby allowing a release of fuel into the coolant. Also, less extensive, but appreciable, interactions could adversely affect pertinent properties of the cladding, such as mechanical strength and thermal conductivity. Therefore, a systematic study of potential claddings in the temperature range 650° to $1100^{\circ}C$ has been started. The study will cover pure metals as well as alloys based on iron, nickel and a number of refractory metals.

The initial phase of this program is under way and consists of annealing carefully prepared diffusion

couples of $(U_{0.8}Pu_{0.2})C$ and various cladding materials (Cr, Mo, Nb, Ta, V, W, Hastelloy-X, Type 304 stainless steel, V-20w/oTi and Ta-10w/oW) in the 800° to 1100°C range. The couples will be evaluated by using metallography, microhardness, and microprobe analysis. Preliminary annealings of four

(U,Pu)C/cladding diffusion couples at 800° and 1100°C indicate that the experimental techniques are sound. An evaluation of pertinent literature information associated with the compatibility of cladding materials with uranium-plutonium carbides is progressing in conjunction with the experimental portion of the program.

3. Corrosion of Refractory-Metal Alloys in Sodium

a. Corrosion of Fuel Cladding Materials for Sodium Cooled Reactors (H. A. LEVIN AND S. GREENBERG)

Preliminary studies⁽¹⁷⁾ had indicated that V-Ti alloys had superior corrosion resistance to niobium-base alloys in oxygen-contaminated sodium at 650°C. The next objectives of the program are twofold and are closely related:

(1) To determine if V-20w/oTi does, in fact, have adequate corrosion resistance to serve as fuel cladding material for sodium-cooled reactors.

(2) To determine the effect on corrosion behavior of important variables, e.g., temperature, sodium impurity concentration, and hydrodynamic conditions.

Consideration of the system, including study of the literature, lead us to the conclusion that the effect of impurities, particularly of oxygen concentration, was of prime importance and it was therefore decided to investigate this parameter first. Unfortunately, as will be evident from the following discussion, our ability to control and characterize the environment with respect to oxygen concentration has not been adequate for these purposes and the objectives have not been achieved. This inadequacy makes quantitative discussion of results obtained during the past year unwarranted. Efforts are now being intensified to solve the problems of adequate control and characterization of the experimental conditions.

Exposure at 650°C for nine days of V, V-10w/oTi, and V-20w/oTi to flowing (15 cm/sec) sodium containing 75 to 100 ppm oxygen showed that addition of titanium to vanadium resulted in appreciably smaller weight gains. For example, pure vanadium gained six times as much weight as V-20w/oTi. Microhardness traverses of exposed samples indicated that titanium additions greatly reduced the rate of oxygen diffusion through the alloys.

Corrosion studies were then initiated in a static isothermal (with respect to the test chamber) system in-

corporating a cold leg maintained at a preselected lower temperature to control the oxygen concentration in the sodium. At equilibrium the concentration of oxygen in the system should be that corresponding to the solubility of oxygen in sodium at the temperature of the cold leg.

Subsequently, calculations have shown that in the absence of agitation (either thermal or mechanical), diffusion rates are so low that the time to reach equilibrium is prohibitively long. Of greater importance is the possibility that slow diffusion rates could result in oxygen depletion at the sample surface. In such a case, corrosion would be controlled by the rate of diffusion of oxygen to the surface and bulk oxygen concentration (even if determined accurately) would be of only secondary importance.

Although it is not believed that the system is free of convection currents, future runs will incorporate more positive means of maintaining the oxygen concentration.

A series of V-20w/oTi samples (stress relieved at 650°C) were tested at 650°C for times up to 23 days. The cold-leg temperatures were maintained at 132°C and 232°C for two separate runs. The equilibrium solubilities of oxygen in sodium at these two temperatures are 6 (Run 1) and 50 ppm (Run 2), respectively. Samples from the same ingot were used for both experiments.

Samples were removed periodically, cleaned of sodium, weighed, and either returned to test or saved for detailed examination. Some samples received in one continuous exposure the same total time in test as others received in a series of interrupted exposures. There was no difference in behavior of samples tested in these two different manners.

Samples from both experiments behaved in the expected fashion. They gained weight at a decreasing rate. The magnitude of the weight gains in the nominally 50 ppm oxygen run were about twice those in the nominally 6 ppm oxygen run.

It was then attempted to reproduce some of the results obtained in the nominally 50 ppm oxygen test

⁽¹⁷⁾ Levin, H. A., and Greenberg, S., *An Exploratory Study of the Behavior of Niobium and Vanadium Base Alloys in Oxygen Contaminated Sodium*, ANL-6982 (1965).

FIG. 16. Electron Photomicrograph of V-20w/oTi Exposed for 20.9 Days at 650°C to Sodium Containing 6 ppm Oxygen.

(Run 2) as the first in a series of experiments designed to study the effects of hydrodynamic conditions. (Velocity would be imparted by rotating the samples in the same apparatus previously used.) Results were markedly different from those previously obtained. The samples had high weight losses (as contrasted with previously obtained small weight gains) and were covered with a readily visible corrosion product. The samples in this experiment (Run 3) were also tested as stress relieved at 650°C but were from a different ingot than those used in Runs 1 and 2.

The difference in behavior is illustrated in Figures 16, 17, 18, and 19. Figure 16 is an electron photomicrograph of a replica of a transverse section of a sample exposed in Run 1 for 20.9 days. No surface oxide could be detected although a sub-surface precipitate was formed. The same behavior was found in samples from Run 2. The appearance of the stress relieved alloy before exposure to sodium is shown in Figure 17. Figure 18 shows a sample from Run 3 after an exposure of 3.1 days. The nonadherent surface film (not observed in previous experiments) is apparent. Figure 19 is a photomicrograph of a transverse section of a sample exposed for 2.0 days in Run 3. Two phases are present on the surface and a sub-surface precipitate can be seen. The surface film has been identified as $\text{VO}_{0.9}$ and $\text{VN}_{0.35}$. This is the first time in this work that a nitride has been identified on the surface of vanadium alloys exposed to sodium.

In an effort to learn whether the unexpected results of Run 3 were primarily the results of unknown changes in environment or in material, a short experiment (Run 4) was performed under as identical conditions as possible to Run 3. Two samples were exposed to sodium at 650°C for 2.7 days. One sample was previ-

FIG. 17. Stress-relieved Alloy before Exposure to Sodium Containing 50 ppm Oxygen.

FIG. 18. Sample Showing Nonadherent Surface Film on V-20w/oTi (Run 3, 3.1 days).

ously unexposed material from the same sheet used to prepare the samples for Run 3. No unexposed material was available corresponding to the samples of Runs 1 and 2. The second sample (for the Run 4 experiment) was a sample previously exposed for a short time in Run 1. This sample was reground to a depth considerably below that of the measured hardened case and could reasonably be considered a new sample.

Both samples lost weight. Two measurements of the oxygen concentration gave values of 125 and 116 ppm using the mercury amalgamation method. This may be evidence that our techniques of sampling and analysis are achieving the required standards. Subsequent analyses indicated that the oxygen concentrations in Runs 2 and 3 were comparable to that in Run 4, i.e., about 95 ppm.

It thus appears reasonable to explain the results of Run 3 in terms of environmental rather than material changes. However, there are at least two problems in this regard:

(1) The presence of nitride.

(2) Previously reported results,⁽¹⁷⁾ as well as the results of Run 2, had indicated that the V-Ti alloys had much better corrosion resistance in sodium of the oxygen concentration measured in Runs 3 and 4.

Work is progressing to solve these problems within the framework of the objectives stated earlier in this discussion.

The effect of the contaminated-sodium environment on the mechanical properties of cladding materials is of obvious importance. Thus, a cooperative program (with the Physical Metallurgy Group) is in progress and preliminary results are available. As is the case of the experiments discussed previously, results are clouded by lack of definition of the environment.

Flat tensile samples of recrystallized V-20w/oTi were exposed to flowing (15 cm/sec) sodium at 650°C for 7.0 days. The samples were preloaded to a value that produced a permanent strain of approximately 1.5%, i.e., the samples underwent creep during test. The oxygen content is thought to have been very low. Plugging meter analyses before and after the experiment indicated 10 ppm or less of oxygen. Analysis of a sodium sample taken at time of removal of the tensile specimen awaits modification of the analytical apparatus.

All samples (as did those in Runs 3 and 4 discussed previously) lost weight. In addition the region near the surface (about 12–25 microns thick) was apparently subject to intergranular attack. These preliminary results make it mandatory that the conditions under which V-20w/oTi may be subject to intergranular attack be defined. Previous work⁽¹⁷⁾ gave no evidence

40428

As Polished

750X

FIG. 19. Alloy Specimen (Run 3, 2.0 days) Showing Surface Film Consisting of $\text{VO}_{0.9}$ and $\text{VN}_{0.35}$.

that material in the recrystallized condition was subject to intergranular attack.

b. Development of Refractory Metal Alloys for Service in Oxygen Contaminated Sodium (W. E. RUTHER)

Many of the refractory metals possessing good mechanical properties are compatible with high temperature ($\sim 650^\circ\text{C}$) pure sodium that is free of contaminants such as oxygen, nitrogen and hydrogen. In large sodium cooled reactors it may not be feasible to maintain sodium oxygen free but rather within a range of 10–100 ppm. At the greater concentration, most of the existing refractory metal alloys tested have shown high attack rates and severe oxygen embrittlement. This program is directed towards developing a refractory metal alloy which will minimize the damage incurred in exposure to oxygen contaminated sodium.

Because of the encouraging results reported last year by H. Levin (Annual Report for 1963—ANL-6868) the initial experimentation has been with vanadium base alloys.

Preliminary experiments quickly exposed three basic problem areas in the program. The first was concerned with sampling and analysis of sodium samples for oxygen content. The second was a lack of homogeneity in arc melted alloys. The last area involved the quantitative evaluation of the corrosion performance of the refractory metal alloy.

In order to minimize the air contamination of sodium samples, a vacuum transfer cutoff device has been constructed and is operating in a very satisfactory manner. A modified mercury amalgamation analysis technique for oxygen in sodium has been devised and is currently being checked against known oxygen additions to the sodium samples. Results appear to be encouraging.

The problem of preparing small homogeneous alloys appears to be solved by first briefly arc melting the components to hold them together and then remelting the buttons in a levitation induction furnace. The melts are cast into copper molds.

The third problem area, associated with the quantitative evaluation of the corrosion behavior, is created by the relatively large diffusion of oxygen into the interior of the refractory metal samples. A vanadium alloy after exposure at 650°C to sodium containing ~100

ppm oxygen may have an exterior oxide coating that is only partially adherent. Weight gains can thus be unreliable. Even if a satisfactory method were developed for completely removing the exterior coating without attacking the base metal, the weight change (probably a loss) would be unreliable as a measure of the metal loss since a significant weight of oxygen has diffused into the interior of the specimen. Thus it appears that the usual gravimetric techniques will not be useful and evaluation by microscopic dimensional measurements coupled with microhardness traverses to determine the depth of oxygen penetration will have to be substituted.

For example, early experiments in which samples of arc melted binary alloys were exposed at 650°C to static sodium containing about 100 ppm oxygen indicated that titanium, chromium and molybdenum alloys were most corrosion resistant of the ten binary alloys tested. These results were based on defilmed weight loss measurements. When the specimens were examined by microhardness traverses for oxygen penetration the titanium containing alloy was still the best and molybdenum was the poorest of the binaries tested.

These early experiments are suspect because of poor oxygen analytical techniques and nonhomogeneous arc melted alloys and will be repeated under adequately controlled conditions as soon as new equipment is operating in a satisfactory manner.

4. Irradiation of Fast Reactor Fuel Elements and Structures

a. Postirradiation Annealing Study of Uranium-Fissium and Uranium-Fissium-Zirconium Alloys (K. MATSUMOTO* AND J. H. KITTEL)

In connection with the development of metallic fuels for the Experimental Breeder Reactor (EBR-II), a postirradiation annealing study was made of six fuel alloys. The alloys included both uranium-fissium and uranium-fissium with extra zirconium, in which the fissium fraction in weight percent was 1.0 Zr, 49.2 Mo, 40.2 Ru, 6.0 Rh, and 3.7 Pd. The specimens had been irradiated in NaK capsules to burnups ranging from 1.0 to 2.5a/o. A 3.66 mm diameter by 25.4 mm long specimen of each alloy was annealed for 24 hours in purified argon at progressively increasing temperatures between 400°C and 775°C. Immersion densities and dimensions were measured after each anneal.

* On loan from Atomic Fuel Corporation, Tokai-Mura, Japan.

Figure 20 summarizes the results obtained, in terms of the ratio volume change/burnup. The alpha phase alloy U-3.7w/oFs began to swell before any of the other alloys, as expected. However, it showed the lowest total volume change of any of the alloys at temperatures above 700°C. The reference alloy for EBR-II, U-5w/oFs, showed the greatest rate of volume change in the temperature range 575°C to 650°C. All of the alloys showed a steep increase in swelling rate at some characteristic temperature between 500°C and 725°C. After this sharp increase the specimens either decreased in density at a much slower rate or slowly gained in density.

The temperature interval during which each specimen rapidly decreased in density was accompanied by considerable surface cracking. The changes in a typical specimen are shown in Figure 21. It appeared that after extensive surface cracks developed, the specimens no longer contained sufficient gas to promote

FIG. 20. Cumulative Rates of Volume Increase in U-Fs and U-Fs-Zr Alloys during Postirradiation Annealing.

additional swelling. Metallographic studies, however, failed to show extensive cracking within the specimens, but only relatively shallow cracks that were already evident on the surface of the specimens. A typical specimen is shown in Figure 22. Figure 23 shows the differences in bulk volume and immersion volume which developed in a typical specimen as cracking increased. Also, as shown in the figure, isotropic expansion no longer held after extensive swelling occurred.

b. Irradiations of Refractory Alloy-Clad Uranium-Plutonium-Fissium Alloys (W. N. BECK)

Irradiation experiments are being conducted in CP-5 on jacketed, sodium-bonded U-Pu-Fs alloy fuel rods as potential fuels for use in fast reactors. The configuration of the irradiation-test specimens generally duplicates an EBR-II type fuel rod, but the pin length has been scaled down to 50 mm. The fuel diameter is 3.66 mm. Earlier experiments were performed on U-20w/oPu-10w/oFs jacketed in tubing having a wall thickness of 0.23 mm. The parameters presently being investigated are: (1) variable plutonium concentration in the fuel pin, (2) the effect of increasing the jacket wall thickness, (3) irradiation temperature, (4) vented jackets, (5) duplex tubing as jacket material, and (6) the determination of maximum attainable fuel burnup.

The different fuel compositions that have been undergoing irradiation are U-20w/oPu-10w/oFs, U-15w/oPu-10w/oFz, and U-10w/oPu-10w/oFz. A total

of 60 specimens are presently being tested. Some have been examined, but the majority are still being irradiated or awaiting metallographic examination.

Increasing the jacket thickness had a marked effect in extending the attainable fuel burnup of the specimen before the jacket failed. The first irradiations were performed with jacket thicknesses of 0.23 mm. By increasing the thickness to 0.38 mm, attainable burnup values were increased by a factor of ~ 2 to heavy metal burnups of at least 4.0a/o. Fuel specimens in 0.64 mm thick jackets have been irradiated at 615°C maximum jacket temperatures for 4.2a/o burnup and were recovered intact. The irradiation period of these specimens will be continued to establish the operating limit of the jacket. Specimens jacketed in the 0.38 mm wall thickness tubing and loaded with U-15w/oPu-10w/oFz are now being irradiated at 550°C maximum jacket temperature for a burnup of 5.5a/o without apparent failure of the jacket.

Specimens were also tested with preselected gas void volumes as well as with vented jackets. The EBR-II type sodium bonded fuel pin is provided with a gas filled void to accommodate pressure buildup due to expansion of the fuel alloy and sodium as well as fission gas release. The ratio of the gas void to the fuel volume is referred to as the percent void volume. Jacket failures were experienced after burnups of only ~ 1.1 a/o where the void volumes were from 13 to 28 percent. In addition, the fuel pin showed little elongation within the jacket. By increasing the void volume to 50 percent, the fuel tended to elongate and

achievable burnup increased to approximately 3.0a/o. Some specimens were irradiated with vented jackets. The results indicated that venting as an internal pres-

700°C

725°C

750°C

106-7953

FIG. 21. Surface Changes in Irradiated U-10w/oFs-5w/oZr Alloy Specimen after Annealing at Indicated Temperatures. Magnification 8X.

106-7979

FIG. 22. Typical Surface Crack in U-3.3w/oFs-2.5w/oZr Alloy after Postirradiation Annealing.

106-7943R

FIG. 23. Comparison of Volume and Dimensional Changes during Postirradiation Annealing of U-5w/oFs Alloy.

sure relief technique was no more effective than void volumes of 50 percent.

Four specimens of U-20w/oPu-10w/oFs alloy were irradiated which had 1.4 mm axial holes. These were in a capsule which also had two fuel pins with diameters which had been reduced so as to provide comparable

fuel volumes to the vented fuel pins. The fuel was jacketed with 0.38 mm thick Nb-1Zr alloy. The specimens were irradiated at a maximum jacket temperature of 635°C for 3.1a/o burnup. Periodic neutron radiographs of the capsule showed a progressive closing of the axial holes accompanied by a reduction of pin length. The pins having the reduced diameter experienced isotropic swelling of the fuel until the fuel made contact with the jacket. The experiment was terminated when it was apparent that more than one jacket had failed.

Several cladding materials other than Nb-1w/oZr alloy are also being irradiated. One group consists of duplex tubing and includes type 304 stainless steel lined with vanadium or tungsten and Hastelloy-X lined with vanadium or tungsten. The second group also includes the promising jacket alloy V-20w/oTi.

The duplex tubing irradiations have been successful under conditions where the maximum jacket irradiation

temperatures have been below the eutectic temperature of the particular fuel-jacket combination. It has been difficult to obtain defect-free duplex tubing that did not have a pinhole in the barrier layer that could be penetrated by the fuel.

Figure 24 shows the specimens with the highest burnup that have been removed from the reactor. As can be seen, one specimen failed. Figure 25 shows an enlarged view of the jacket failure.

In metallographic examinations of irradiated specimens, all jacket materials have been characterized by incipient cracking which originated on the inside diameter of the tubing. These cracks appeared at random places and propagated from 10% to 100% of the jacket wall thickness. Cladding fractures appeared to be of a brittle nature. (See Figures 25 and 26.)

Specimens that had been irradiated in Nb-1w/oZr alloy at maximum jacket temperatures of 635°C showed a fuel-clad reaction layer on the ID of the

FIG. 24. Effect of 4.2% Heavy Atom Burnup on U-20w/oPu-10w/oFs Alloy Specimens Jacketed with Nb-1w/oZr Alloy.

jacket tubing. The thickness of the layer varied from 0.03 to 0.18 mm, and was directly related to the maxi-

EI-2705

7.6×

FIG. 25. Enlarged View of Jacket Failure in Nb-1w/oZr Alloy Jacketed Specimen after 4.2a/o Burnup. (See Figure 24.)

Jacket

Fuel

EI-3003

130×

FIG. 26. Incipient Cracking of the ID of Nb-1w/oZr Tubing Having a Wall Thickness of 0.23 mm. The specimen had been irradiated at a maximum jacket temperature of 615°C for 3.1 a/o burnup.

Jacket

Fuel

EI-3166

100×

FIG. 27. Reaction Layer Between U-20w/oPu-10w/oFz Alloy and Nb-1w/oZr Alloy. The jacket was irradiated at a maximum temperature of 635°C.

imum temperatures of the jacket. An area of extensive fuel-clad reaction is shown in Figure 27.

V-20w/oTi alloy as a jacket material is attractive for its nuclear as well as its metallurgical properties. Twelve specimens are presently being irradiated in V-20w/oTi alloy tubing having a wall thickness of 0.4 mm and ID's of 4.0, 4.1, 4.2, and 4.3 mm. The maximum jacket temperature of the specimens is being maintained at 600°C.

One capsule containing six specimens is being irradiated to measure the effect of swelling on fission gas release of U-15w/oPu-10w/oFz alloy. Each specimen is jacketed in Nb-1w/oZr alloy tubing having ID's of 4.0, 4.2, 4.4, 4.6, 5.0, and 5.5 mm to permit variable amounts of fuel swelling. The internal dimensions were calculated to provide an internal pressure of 10 atmospheres when the fuel has expanded and contacted the jacket. The specimen jackets will then be punc-

EI-3148

FIG. 28. Failure in Nb-1w/oZr Alloy-Jacketed U-20w/oPu-10w/oFz Alloy Specimen after 2.4a/o Burnup at a Maximum Jacket Temperature of 505°C. 1.3X

tured and the gas will be recovered and analyzed. The specimens are being irradiated at a maximum jacket temperature of 595°C.

c. Irradiation of Full-Length EBR-II Fuel Elements of Refractory Alloy-Jacketed Uranium-Plutonium-Fissionable Alloys (W. F. MURPHY AND C. C. CROTHERS)

Capsules containing full length [45 cm (18 in.)] EBR-II fuel elements of refractory alloy-jacketed U-Pu-Fz alloys are being irradiated in the MTR. The temperature in the capsules is controlled by varying the composition of a helium-nitrogen mixture in an annulus of the capsule containing the fuel specimens.

Capsule ANL-55-5 contains one fuel element of U-20w/oPu-10w/oFz alloy jacketed in Nb-1w/oZr alloy tubing with a 3.96 mm ID and 0.23 mm wall thickness. The fuel pin was 361 mm long and 3.66 mm in diameter. The fuel was bonded to the jacket with sodium. The capsule was put into the MTR on August 19, 1963, and removed on June 18, 1964, after a temperature spike on the control thermocouple had given an indication of jacket failure on June 13. The maximum calculated burnup was 2.4 percent of heavy metal atoms. The jacket temperature was about 550°C at the hottest section.

A neutron radiograph taken of the encapsulated fuel element after irradiation showed two areas of jacket failure accompanied by drastic swelling of the fuel. Both areas were on the upper third of the length of the fuel pin and were about 32 mm apart. The uppermost failure was about 19 mm from the end of the fuel pin. A detailed examination will be made when the fuel element is removed from the capsule.

Capsule ANL-55-6 contained three identical fuel elements similar to the one in capsule ANL-55-5. The fuel was U-20w/oPu-10w/oFz alloy jacketed in stress relieved Nb-1w/oZr alloy tubing 3.96 mm ID and with 0.23 mm wall thickness. This capsule was put into the MTR on April 15, 1963, and removed on July 20, 1964, after 2.4 atom percent burnup. Jacket temperatures were about 505°C at the hottest sections. Tem-

perature data for this irradiation experiment had given no indication of any failure.

When the capsule was returned to the Illinois site it was neutron radiographed. One fuel element showed evidence of a fairly long split in the jacket on the lower half. There was only slight evidence of fuel swelling on this element. The other two elements appeared to be intact. In all three elements the fuel pins were displaced about 20 mm off of the bottom plug within the jackets.

The capsule was taken apart in the Alpha-Gamma Hot Cell and the fuel elements were removed without difficulty. Figure 28 shows a view of the split fuel element. The crack extends from about 25 mm above the lower end of the element for 115 mm total length. The crack extends into the fuel for a short distance and has the appearance of a rip or a tear. The spacer discs appear to have had only a slight restraining effect on the splitting action. Further examination is under way.

Capsule ANL-55-7 also contains three fuel rods. The fuel pins are all U-15w/oPu-10w/oFz alloy with 7.7% enriched uranium. Jacket materials are as follows: Nb-1w/oZr alloy, stress relieved, 3.96 mm ID, 0.38 mm wall; vanadium, stress relieved, 3.96 mm ID, 0.38 mm wall; and Hastelloy X tubing with a vapor deposited tungsten liner, 3.88 mm ID, 0.23 mm wall. Sodium is the heat transfer medium between the fuel and the jacket. This capsule was put into the MTR on February 3, 1964. The fuel has accumulated about 1.6 atom percent burnup with a maximum jacket surface temperature of 555°C.

Capsule ANL-55-8 contains three fuel rods as follows: U-15w/oPu-10w/oFz alloy jacketed with Nb-1w/oZr alloy, U-10w/oPu-10w/oFz alloy jacketed with Nb-1w/oZr alloy, and U-15w/oPu-10w/oFz alloy jacketed with vanadium. The uranium in the 15w/oPu alloy is 7.7% enriched and in the 10w/oPu alloy is 15.5% enriched. The fuel pins were all 330 mm long and 3.66 mm in diameter. The jacket materials were initially in an annealed condition. The ID of the jackets was 3.96 mm and the wall thickness was 0.38 mm for all three elements. They were all sodium bonded. This

capsule was put into the MTR on June 8, 1964. The fuel has accumulated about 1.1 atom percent burnup at a maximum jacket surface temperature of 555°C.

d. Development of Experimental Metallic Fuel Irradiations in EBR-II (W. F. MURPHY AND J. H. KITTEL)

A total of sixty-five experimental EBR-II type test fuel rods have been made by the Plutonium Fabrication Group for irradiation experiments in EBR-II. The fuel materials are U-Pu-Fz alloys with 10, 15 and 20w/o plutonium and various enrichments of uranium-235. All alloys contain 10w/o fissionium. Jacket materials include vanadium, niobium-4w/o vanadium, niobium-1w/o zirconium, and Hastelloy X with a tungsten liner. Other variables include heat treatment of the jacket (stress relieved or annealed), and jacket wall thickness (0.23 mm to 0.64 mm). The fuel pins are 330 mm long and 3.66 mm in diameter. The jacketed fuel elements are 450 mm long and the ID of the cladding is 3.96 mm. All fuel elements are sodium bonded, and the bonds were checked by eddy current techniques.

Nineteen of the fuel rods have been encapsulated in stainless steel for irradiation in EBR-II. A vanadium barrier was incorporated into the capsule. Sodium was provided as a heat transfer medium between all elements of the capsule. The capsules were vibrated at 500°C for four hours to promote sodium bonding, after which they were both eddy current tested and radiographed at a temperature (140°C) above the melting point of the sodium. Seven capsules showed no evidence of any voids. Bubbles in the outer annulus between the vanadium barrier and the capsule wall as detected by eddy current were generally small, barely exceeding 1.6 mm in maximum dimension. Bubbles detected by radiography in the annulus between the fuel jacket and the vanadium barrier were generally about 1.6 mm in length. It is expected that this group of 19 fuel rods will be put into a subassembly for irradiation in the seventh row (inner blanket) of the EBR-II.

Because of the excellent results being obtained from current fuel specimen irradiations in CP-5, full size EBR-II type fuel rods with various gas void volumes have been scheduled for fabrication. The fuel pins in this group will have the following compositions: U-10w/oPu-10w/oFz, U-15w/oPu-10w/oFz, U-15w/oPu-10w/oTi, and U-15w/oPu-10w/oZr. The uranium will be enriched by various amounts to provide for variation in the rate of heat generation. All the pins in this group will be jacketed with vanadium-20w/o titanium alloy and sodium bonded. The new variables introduced in this group are optimistically expected to permit burnups of perhaps 8a/o at cladding temperatures as high as 650°C.

A shielded shipping cask has been designed for the shipment of irradiated experimental fuel elements from Idaho to Lemont. The design is in accordance with new regulations and has been approved by both the AEC and the Bureau of Explosives. Construction is expected to start soon.

e. Irradiation of PuC and UC-20w/oPuC (L. A. NEIMARK AND C. C. CROTHERS)

Two vibratorily compacted PuC powder specimens and ten vibratorily compacted UC-20w/oPuC mixed-powder specimens are under irradiation in the MTR reactor. The specimens are in capsules ANL-56-7, ANL-56-8, ANL-56-9, and ANL-56-11. The capsules are the temperature-controlled type in which the specimen temperatures are controlled by varying the helium-nitrogen ratio in a 0.25 mm annulus between the inner and outer capsule walls. Specimen temperatures are measured by a thermocouple next to each specimen.

The two PuC and four UC-20w/oPuC specimens in capsule ANL-56-7 have jackets of 0.23 mm thick Nb-1w/oZr alloy. The fuel diameter is 3.96 mm. These specimens have achieved estimated burnups of from 1.1×10^{21} to 1.4×10^{21} fissions/cc. They are presently operating at cladding surface temperatures of from 600° to 650°C, the design range. Target burnup for these specimens is 2.6×10^{21} fissions/cc (10a/o burnup of U + Pu).

Six vibratorily compacted UC-20w/oPuC mixed-powder specimens are distributed in capsules ANL-56-8, ANL-56-9, and ANL-56-11. These specimens have 0.30 mm thick Nb-1w/oZr alloy jackets and a fuel diameter of 6.53 mm. The carbide specimens in capsule ANL-56-8 are scheduled for a burnup of 3.9×10^{21} fissions/cc (15a/o burnup of U + Pu). Burnup to date is estimated at 4.4×10^{20} fissions/cc. Cladding surface temperatures are at the design level of 650°C. The carbide specimens in capsule ANL-56-9 have achieved 3.0×10^{20} fissions/cc of a scheduled burnup of 2.6×10^{21} fissions/cc. Cladding surface temperatures are presently 100° below the design temperature of 850°C. This will be corrected by moving the capsule to a position of higher flux. The carbide specimens in capsule ANL-56-11 are scheduled for a burnup of 2.6×10^{21} fissions/cc at a design temperature of 650°C cladding temperature. These specimens have reached a burnup of 3.4×10^{20} fissions/cc and are operating within range of the design temperature.

f. Irradiation Surveillance Program for EBR-I Structural Materials (W. F. MURPHY)

The Metallurgy Division and the Reactor Engineering Division are cooperating in a surveillance program

of radiation damage and the effect of high temperature sodium on structural materials used within the primary tank of the EBR-II.

The materials and test specimens included in this program are as follows:

<i>Material</i>	<i>Type of Test</i>
Aluminum bronze	Tensile and Hardness
Stellite 6B	Hardness
Inconel X	Tensile, Hardness, Impact, Springs
420 stainless steel	Tensile, Hardness
18-4 high-speed steel	Tensile, Hardness
347 stainless steel	Hardness
416 stainless steel	Hardness
Berylo #25	Hardness
Borated steel	Hardness
17-4 PH stainless steel	Tensile, Hardness, Impact
304 stainless steel	Tensile, Hardness
304 stainless steel, welded	Tensile, Bend Test
Tantalum	Tensile, Hardness

All materials and specimens have been received from the vendor. In almost all cases re-marking of the specimens was necessary. Contrary to specifications, some hardness specimens had been heat treated after machining and were received with a covering of scale. In general the notches on the impact specimens also did not meet the specifications. Reworking of the specimens was done in Central Shops.

Specimens have been encapsulated in both open and closed tubes. Completion of the job of encapsulation and insertion of the capsules into subassemblies is waiting on the receipt of a few specimens from another experimenter. There will be ten subassemblies with nineteen capsules containing the above specimens per subassembly. The subassemblies will be put into the reactor at one time for irradiation in the outer blanket. The subassemblies will be withdrawn from the reactor at intervals which will probably be a compromise of operating time and reactor power.

g. Postirradiation Examination of EBR-I Mark IV Plutonium Fuel Rods (F. L. BROWN)

Eleven rods representing a complete radial section from the center to the edge of the EBR-I Mark IV core were delivered to the *alpha-gamma hot cell* for examination. The maximum fuel burnup is 0.07a/o. The Pu-1.25w/oAl alloy fuel rods were NaK-bonded in Zircaloy-2 tubes. Diameter measurements made at one-inch intervals along the length of each jacketed rod disclosed no significant dimensional changes. After decanning, the dimensions of the fuel slugs will be compared with preirradiation values for more definitive information concerning the fuel behavior. Postirradiation examination also will include density measurements of the bare fuel and metallographic examination of representative samples.

5. Development of Remote Fabrication Methods and Equipment for Metallic Fast Reactor Fuel Elements

a. The Development of Remote Controlled Methods and Equipment for Fuel Fabrication (A. B. SHUCK, R. E. OLP, AND G. POKORNY)

This program was initiated in 1956 to investigate processes, requirements and equipment for remote fabrication of irradiated reactor fuels. After preliminary investigation, the program was extended to develop processes suitable for remote fabrication of EBR-II fuel elements. By 1961, EBR-II Core I fabrication furnished a statistical basis for evaluation and refinement of the injection casting process that had been developed. Remotely - controlled fabricating equipment was designed and construction of this equipment was completed late in 1963. The last major items of the equipment were delivered to the EBR-II Fuel Cycle Facility in early 1964. Development work in 1964 resulted in two types of fuel element handling grapples, an improved welding power source and various tools for handling products and materials.

Work on this program is complete and reports are in preparation.

A blower-cooled, electrically-powered grapple is shown in Figure 29. Because grapple failure would be extremely serious, a second grapple was designed and built. This unit is pneumatically powered and contains no electrical components within the radioactive cell. This grapple is shown in Figure 30 and in an exploded view in Figure 31.

Fuel Element Welding

Remote, arc-spot welding is the method used to complete the final assembly of core and blanket fuel elements in the Fuel Cycle Facility. The hexagonal tube enclosing the upper and lower blanket sections and core section is attached to the lower adapter by six fusion spot welds. The spot welders are located on a stationary platform in the lower part of the fuel-element assembly machine. Power supply for welding is

350-671

FIG. 29. Assembled and Exploded Views of Electrically Powered, Self-Cooled Fuel Element Grapple.

350-668

FIG. 30. Pneumatically Powered and Cooled Grapple with Extension.

located in the basement and consists of a Vickers Type 51E30-2 direct-current arc welder. Mineral-insulated coaxial copper cables conduct the current from the welding power supply approximately 8 meters (27 feet) to the assembly machine inside the process cell. The

commercial welding supply was equipped for initiation of the arc by a high-voltage radiofrequency current generated by a commercial spark-gap oscillator. However, the mineral-insulated cables used in this application attenuated the radiofrequency power so that insufficient ionization was provided at the welding gap. To correct this problem by replacing the mineral-insulated cables with low-impedance cables would be very costly and would not assure the elimination of further problems.

A method was developed to start the arc by means of a direct-current high-voltage capacitor-discharge circuit. This circuit is isolated from the welder power supply by heavy-duty silicon diodes. The arc starter is shown in Figure 32, and its schematic diagram in Figure 33. In operation, the circuit functions as two power supplies, one providing high voltage to ionize the gap and start the arc and the other to stabilize the arc by discharge of large capacitors. The circuit is energized when the welder is turned on. This is done by energizing the power relay (R) from a voltage-sensitive relay (R-13). The voltage-sensitive relay also cuts off the arc starter when the weld current established. Diodes (D-2) isolate the two voltage sup-

350-666

FIG. 31. Exploded View of Pneumatically Powered Grapple.

plies and diodes (D-3) isolate the high voltage from the welder. The controls are protected from transient voltage spikes by means of resistor-capacitor networks. Rheostats (R-1 and R-2) adjust the charging rate of capacitor (C-1) to the discharge rate of the arc. The choke stabilizes the arc and insures an even flow of current. Auxiliary controls energize the relay contacts connected to the welding guns and the entire welding cycle is programmed.

Manipulator Tool

Figure 34 shows a tool designed for handling No. 6 food-pack cans with the FCF operating manipulator. This is a two-stage tong device operated by the double-hook manipulator grip. When the grip is closed part way, the tongs grip the can. The tongs are spring loaded to prevent crushing the can but hold with sufficient firmness that the loaded can may be transported in the vertical position. If the grips are closed, the tongs will rotate allowing the contents of the can to be poured.

Fuel Rod Tip Reformer

The forked tip of the fuel rod can be bent in remote handling and the bonding operations. A tip-straightening press which coined the tip between dies was developed during EBR-II Core-I fabrication. This tool was modified for master-slave manipulator operation.

350-645

FIG. 32. Impulse Arc Starter for Fuel Rod Welder.

b. Installation and Testing of Remote Controlled Fuel Fabricating Equipment for EBR-II (N. J. CARSON AND A. B. SHUCK)

This program includes the supervision of installation and operational testing of the EBR-II fuel refabrication equipment in the EBR-II Fuel Cycle Facility

350-674

Fig. 33. Arc-Initiation Circuit for Fuel Rod Welding.

(FCF). The work was done by Idaho Division and contractor personnel. The work began with the installation of electrical wiring and compressed argon pumping systems in 1962. The subcell and basement work was largely complete by the end of 1962; the argon-cell installations were complete in 1963. The air-cell installations were completed during 1964. The air-cell equipment is shown in Figure 35.

Twenty-kilogram Balance

A twenty-kilogram remote-indicating balance was installed in the Fuel Cycle Facility argon cell at the end of 1963. During 1964 the balance was tested for accuracy in the cell. Comparison weighings were made at 100-gram intervals over the range of 0 to 20 kilograms. It was obvious from these comparisons that the balance accuracy was well within the specified accuracy of ± 2 grams over its entire range.

Injection Casting Equipment

The basic operation of remote fuel fabrication is injection casting. Fuel alloy is induction melted in a leaktight furnace under reduced pressure. The melt is then raised to submerge the lower ends of tubular glass molds, pinched closed at the top, and the furnace pressure is increased. This forces the metal up into the molds producing castings nominally 0.366 mm in diameter and up to 45 cm long. The process produces castings to a diameter tolerance of 0.025 mm that need only cropping and inspection to become fuel pins.

The injection casting equipment includes two furnaces, the vacuum-pressure-cooling system, the electrical furnace controls, the pallet load and unload table, a charge table, and a heel breaker. All were in the argon cell at the end of 1963. This equipment was tested by melting and casting copper alloys and partially depleted uranium-5w/o fissium alloys in 1963. During 1964 irradiated fuel alloy was cast.

The early runs made using depleted uranium alloy showed the reference thermocouple to be in error by approximately 200°C at pouring. It was hypothesized that this error resulted from heating of the cold junction located inside the furnace. The hypothesis was verified by placing a temporary thermocouple at the cold junction. The temperature of the cold junction was found to be time dependent. This eliminated the possibility of applying a constant correction factor.

Pin Process Machine

The machine that demolds and crops the pin castings produced by injection casting and inspects the resulting fuel pins is called the pin-processing machine. It consists of a demolder, a double-cutting shear, and measuring devices that determine fuel pin length,

350-629a

FIG. 34. Manipulator Hand for Lifting and Pouring with General Purpose Manipulator.

weight, average diameter, and soundness. The pin-processing machine, which is located in the argon cell, feeds its data into a data system located in the operating annulus. The data system plots pin diameter and internal quality over the length of the pin. It also displays pin length, pin weight, calculated pin volume, and calculated pin density.

Both pin process machines were installed in the argon cell by the end of 1963. With the exception of the feeder magazines, the machines worked well.

During 1964 one machine was moved so as to be more easily reached by the master-slave manipulator. The demolder was placed on a separate stand allowing it to be fed by manipulator. Gravid molds were pushed into the demolder by manipulator and were transferred to the shear station by manipulator. This machine has worked well. A new demolder feed magazine has been constructed and tested and appears to work well; however, it has not yet operated in the argon cell.

During 1964 the data processing systems were re-

1D-103-E5976

FIG. 35. Air Cell Equipment: Leak Detectors, Bonders, Eddy Current Tester and Element Assembly Machine.

worked to improve their function. Changes in the pin processing machine functions required that corresponding changes be made in the data systems that handle inspection data. Each system was connected to an IBM card punch machine. The data systems were rewired to remove the data-storage functions and to give a prompt data display. The majority of the print-out functions were transferred to the card punch machine. Comparisons were made between laboratory measurements and remote measurements and this data is being examined. It appears to be excellent. The results of a preliminary comparison test in which a single pin was measured in the laboratory and then measured 25 times remotely is shown in Table 11.

Fuel Rod Welding

Capacitor-discharge welding is used to fuse a plug in the top of the fuel-rod jacket and to seal the fuel rod. The remote fuel-rod welding machines consist of an indexing mechanism, a rotary magazine holding 20 assembled fuel rods and an inert gas shielded welding gun. The welding machines were installed in the Fuel Cycle Facility argon cell and connected to a stored-energy power source in the basement.

The fuel-rod welding machines were operable at the end of 1963. At that time helium was used as the welding gas. Data furnished by personnel of the Chemical Engineering Division showed that small amounts of helium gas in an argon atmosphere were deleterious to electrical insulation operating in the atmosphere. Therefore, the decision was made to use argon as the welding gas.

The change to argon had two effects on welding: (1) the capacitance of the power supply became insufficient, and (2) the welds began to slump. The first problem was solved by adding two additional 17,000 microfarad electrolytic capacitors to the power supply to compensate for the decreased arc-plasma voltage drop. This returned the arc energy to above 500 watt-seconds. But there did not appear to be a simple solution to the problem of slumping.

When the arc is struck, there is a tendency for the molten metal to "stand up" in the arc. When the arc is terminated the metal settles. It first passes through a spherical shape promoted by surface-tension force and then slumps or runs down the side of the fuel rod. When helium was used, the cooling rate was rapid enough to solidify the metal before slumping. When

Argon was used the cooling was retarded sufficiently to allow slumping in some cases. This increased the apparent diameter in the weld area and prevented the rod top from being inserted in the close-fitting head of the leak detector. Thus while the weld quality might be good, the weld could not be tested. The reject rate rose to more than 50%.

It was not possible to correct slumping by means of the welding controls. Some improvement could be brought about by adjusting the electrode-fuel rod alignment; however, the alignment was already the best that could be maintained in a remote operation using the present equipment. At this point two alternate procedures were taken: (1) a small pneumatic forming device was installed at the leak detection station, and (2) the rod positioning device on the welder was redesigned. The first alternative permitted production with existing equipment while the second alternative was directed toward removing the source of the rejects.

The new rod positioning device that evolved fit in the fixture that previously held the idler wheel. It consists of a notched-shoe-and-spring assembly that can be moved in a horizontal plane by means of hand-operated cams. The notched shoe provides a positive stop near the top of the rod. The horizontal leaf spring provides a frictional hold-down for the fuel rod while it moves from under the gapping shoe to the electrode. This new positioning device appears to provide much better alignment than did the idler wheel.

Leak Detectors

The seal welds are examined for tightness with the fuel-rod leak detectors. The top end of a fuel rod is sealed into a small test chamber and a measured amount of helium gas is added. If the weld is leaktight, the resulting pressure is a predictable value determined by the volume of the test chamber and the amount of gas added. If the fuel rod leaks, the internal void volume of the fuel rod is added to that of the test chamber producing a lower but predictable value. A still lower pressure indicates a machine malfunction. Thus the fuel rod leak detectors indicate a good weld, a leaking weld, and a machine malfunction.

The fuel rod leak detector is located in the air cell. It is actuated by means of solenoid valves located in a valve cabinet in the basement. The valves are operated and the pressures are indicated at an operator's station in the operating annulus.

The leak detectors became operational during 1964. The leaking high-pressure valves were made operational by the installation of a "hold-down bushing" that prevented the unseating of the plastic valve seat. The performance of the O-ring valves was improved

TABLE 11. PIN PROCESSING DATA CALIBRATION

Pin No. 15

	Laboratory Measurements	Pin Processor Mean (25 Meas.)	Pin Processor Std. Deviation
Weight (gms)	69.0009	68.9435	0.014
Length (in.)	14.205	14.201	0.005
Volume (cc)	3.855	3.843	0.009
Density (gm/cc)	17.897	18.045	0.045

by using a high-strength manganese bronze for the spool. This material can be easily tinned on its sealing surfaces and is strong enough to withstand the sealing pressure without pinching the O-rings. An additional operator's station has been constructed that allows the individual O-rings to be flexed whenever they become sluggish because of inactivity.

Bonding

The leaktight fuel rods are bonded in the air cell. This is an operation in which heat and directional agitation are used to achieve a homogeneous sodium volume that wets both the fuel pin and the jacket. The purpose of the operation is to eliminate voids from the sodium annulus that would locally block heat transfer to the reactor coolant.

The original bonding machine consisted of a base, a top plate, a heater, a 50-rod capacity magazine, an insulating bell, and a striker head. The fuel rods are held in the magazine which fits over the heater and is supported on the top plate. The fuel rods rest on tappets in the magazine which extend down through the top plate and can be hit by an oscillating hammer that is part of the striker head. The hammer was supported on four springs. Hammer motion was initiated by energizing a solenoid that pulled the hammer down. Near the bottom of its stroke, the hammer opened a switch and de-energized the solenoid. The hammer then passed through the bottom of its stroke and started upward. As it moved it opened the switch and energized the solenoid circuit. A time delay relay in the circuit allowed the hammer to reach its uppermost position and start downward before the solenoid was again energized. When operating properly, the downward force of the solenoid was just sufficient to balance the dampening force of the tappets.

The fuel rod bonding machines were installed in 1963 and became operational in 1964. Some difficulties were experienced in achieving operation; however, none were unusual or surprising. Remote operation was achieved fairly rapidly and test runs began. The machines were tested using depleted uranium-5w/o fission alloy pins and rejected jacket preassemblies. The

jackets were loaded and welded in the usual manner and were put through the bonding cycle. The results were not encouraging. The rods contained bubbles under the restrainers and sodium trapped in the void space. Some of the rods were stripped and found to contain large nonbounded areas.

The motion of the rods during bonding was observed to be about 0.96 cm. Some of this was rebound; some was simple lifting. Only the rebound is indicative of the impact received by the rods and of the work directed toward bonding. High-speed movies were taken to estimate the rebound from the hammer. Thousand-frame-per-second movies were taken of the top of the fuel rod and the bottom of the tappets during bonding. It was estimated from these films that the rebound of the rods was about 0.51 cm. It was obvious that additional impact was needed.

Only one thing could be done with the existing machine to achieve additional impact; i.e. increase the speed of the hammer at impact. This could be done three ways: (1) by moving the equilibrium position of the hammer closer to the bottom of the tappet, (2) by making the hammer lighter, or (3) by strengthening the hammer springs. The latter change was judged to be impractical because the solenoid was already operating near its maximum current capacity. The first two changes were made. A thin, light-weight, case-hardened steel ring was attached to the top surface to raise the equilibrium position of the hammer 1.27 cm. Then the weight of the hammer was reduced from 3260 grams to 1590 grams by removing metal from the periphery. As a result of these changes, the total rise of the fuel rods was increased from 0.96 cm to 1.92 cm. As expected, the resonant frequency of the hammer also increased from 125 cycles per minute to 200 cycles per minute. This introduced problems in synchronization.

If the hammer did not oscillate at its resonant frequency, the solenoid overheated, the solenoid circuit breaker opened, and oscillation ceased. The time-delay control, which was set manually, did not have sufficient sensitivity to keep the hammer oscillating at the higher resonant frequency. It appeared that one of two changes was in order; (1) additional switches could be added to both energize and de-energize the coil without benefit of a time delay relay, or (2) distinct, unrelated impacts could be used. The second alternative was chosen since there was doubt that the 1.92 cm of rise obtainable with the existing drive mechanism was sufficient to effect bonding.

At this point the oscillating hammer drive mechanism was abandoned and a pneumatic mechanism was developed. The new unit incorporates a 10-cm diameter air cylinder. The hammer is a 26.7-cm-diameter

steel plate, 1.27-cm thick. On top is the same case hardened steel ring used on the oscillating hammer. The pneumatic unit bolts directly to the base since there is sufficient clearance in the bolt area to allow the bolts to be removed with a master-slave manipulator. The pneumatic lines pass through wall plugs at Window A2. Pressure, flow, and timing are controlled from units outside the window. Conventional quick-disconnects in the pneumatic lines allow easy disconnection by manipulator.

The pneumatically-driven hammer produces sufficient impact to raise the fuel rods 10.2 cm. All of this is rebound. The interval between impacts is more than sufficient to allow all components to come to rest. With the hammer-drive controlled to raise the fuel rods approximately 3.2 cm the bonding machine re-

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FIG. 36. EBR-II Fuel Element Assembly and Welding Machine.

...oved bubbles, trapped sodium, and voids in the annulus with better than 90 percent efficiency.

Fuel and Control Element Construction

Fuel and control elements are remotely constructed by means of the fuel element assembly machine shown in Figure 36. Presently, two sections of the fuel elements are made up by manual contact. One of these, the upper blanket section, consists of the hexagonal outer sheath containing the 18 depleted-uranium-loaded upper blanket rods and the top end fittings. The second, the lower blanket section, consists of the bottom adapter fitting, and 18 lower blanket rods held by end grids. The upper end grid is topped by 11 T-bars (9 in case of the control elements) that serve for attachment of the fuel section.

The lower blanket section is installed in the fuel-element assembly machine with the T-bar grid level with the fuel system assembly jig. The 91 (or 61) fuel-rod section is assembled by means of Model-8 manipulators assisted by the assembly jig and fixture. The sodium in the fuel rods must be kept molten during construction, but the radioactively heated fuel bundle must not reach too high temperatures. Provision is

made to electrically heat as well as to forced-air cool the fuel bundle during assembly.

The upper blanket section is suspended in a force bridge. A roller guide aligns the hexagonal sheath with the newly constructed fuel section. The force bridge is guided on two vertical-column ways and powered by means of a heavy-duty ball screw. A torque limiting clutch governs the maximum closing or tensioning force that may be developed by the machine. The hexagonal sheath passes slowly downward, thru an electrical heater and over the fuel and lower blanket assembly. The jacket tubes distort slightly to accommodate a small interference fit with restraining grooves in the sheath. The bottom of the tube slips over the top of the bottom adapter and is stopped against a shoulder. Six arc spot-weld guns are fixed to attach the hexagonal sheath to the adapter.

The fuel element assembly machine was delivered to the Fuel Cycle Facility in February, 1964. The machine was made to operate after being set up and aligned. A new screw and special ball nut with ball retainers and torque limiter were installed that allows tensile tests to be made on the assembly machine. A number of elements have been constructed that meet reactor requirements.

6. Development and Fabrication of Fast Reactor Fuel Rods and Elements

a. Fabrication of Experimental Metallic Fuel Rods for Irradiation Test (E. PILARSKI, A. G. HINS, AND A. B. SHUCK)

The primary purpose of this program is to provide fuel rods for test in EBR-II. A second purpose of the program is to evaluate uranium-plutonium alloys with respect to EBR-II fabrication processes. Careful selection of test fuel rod variants is required because of the limited numbers of rods that can be irradiated. Among the variables in fuel rod design that influence fuel rod performance are: (a) Pu concentration and isotopic analysis, (b) fission product and alloy concentration, (c) jacket materials and (d) fuel rod design.

Test rods were made up in plutonium concentrations of 10w/o, 15w/o, and 20w/o. The enrichment of the uranium was varied to compensate for plutonium concentration variation and to govern the temperature and fission rate at various positions in the reactor. The plutonium-fissionium alloys have received the most attention until recently because of their compatibility with the existing EBR-II fuel cycle.

Jacket requirements are good high-temperature

strength, adequate ductility, and resistance to penetration by the fuel alloy and corrosion resistance by reactor sodium. Limited quantities of vanadium, V-20w/oTi, Nb-1w/oZr, Nb-4w/oV and tungsten-lined Hastelloy-X tubing for making jackets became available from various sources. This tubing, being made in experimental batches, showed quality variations that must be considered in final test evaluations. The dimensions of jacket tubing, fuel pins, sodium and the jacket void volume were varied in an attempt to evaluate the fuel rod design parameters necessary to achieve increased fuel burnup.

Injection Casting

During 1964, 123 acceptable fuel rods were cast in six compositions. This, added to the 288 rods in eight compositions cast earlier, fills out the originally programmed schedule for 400 castings. The compositions were as shown in Table 12.

The alloys were made from virgin metal, and poured into an ingot mold through a perforated or strainer tundish. This was required to remove the excessive amounts of dross created in melting the finely pow-

TABLE 12. URANIUM PLUTONIUM FIZZIUM^(a) CASTINGS

Melt No.	U		Pu	Fz	No. of Castings
	Fuel	Enrichment			
R-130	75w/o	0.22%	15w/o	10w/o	6
R-186	75	55.2	15	10	25
R-174	75	90.5	15	10	23
R-185	80	15.5	10	10	20
R-181	80	59.5	10	10	25
R-150	80	93.2	10	10	24

^(a) Fizzium (Fz) is an alloy simulating fission products retained after melt refining, in this case, composed of 28.0w/oZr, 27.5w/oMo, 29.5w/oRu, 5.0w/oRh and 10.0w/oPd. Fizzium is a high-zirconium fission.

dered fizzium elements. Exceptionally clean ingots resulted that gave little difficulty in injection casting. The crucible, tundish and ingot molds were yttria-coated graphite. Standard EBR-II fuel-pin-casting techniques were employed. The metal was pressure cast into yttria-coated precision-formed Vycor-glass molds. The metal was induction heated to 1325°C–1375°C under a vacuum of less than one micron. The casting pressure was 2.7 atmospheres of helium gas.

The overall yield of acceptable castings was 84.2 per cent of the molds charged. The as-cast surfaces were good—comparable to EBR-II Core I production fuel pins. Gamma radiographs were taken and showed very little porosity; none were cause for rejection. The average casting length was 42 cm. Because precise lengths were desired for pre- and post-irradiation comparison, the castings were machined to length in place of the EBR-II shearing technique. The alloys were readily machined in helium without lubricants.

Fuel Rod Assembly, Bonding and Welding

The availability of refractory-metal has set the pace for jacketing the fuel pins described above. To date a total of 44 fuel rods have been assembled, bonded and inspected for EBR-II irradiation. The jacket tubes were of Nb-1w/oZr, Nb-4w/oV alloy and unalloyed vanadium. The fuel pins were of U(d)-10w/oPu-10w/oFz, U(7.7%U²³⁵)-15w/oPu-10w/oFz and U(15.5%U²³⁵)-10w/oPu-10w/oFz alloys. The fuel rods were assembled by techniques developed for the production of EBR-II Core I. Some modification of the process was required to load the plutonium alloy fuel pins into refractory-metal jackets.

Volumetric measurements of each fuel pin and jacket were made prior to loading. The weight of sodium required for each fuel rod was calculated from the volumes of the components. Sodium was extruded and cut to weight. It was carefully loaded into the jacket tube. The fuel pin was inserted through a plas-

tic funnel that prevented contamination of the jacket. After loading, the assembled fuel rod was heated to 150°C and vibrated at 60 cycles per second to melt the sodium and settle the components into position.

After cooling, the assembly was placed in a rotary welding fixture. A plug-restrainer, carrying an identification, was inserted in the top of the jacket and welded to the jacket by an inert-gas-shielded girth weld. The sealed fuel rod was placed in the chamber of an impact bonding machine. The chamber was evacuated, purged with welding grade helium, re-evacuated and back-filled to one atmosphere pressure. The bonding chamber was heated to 500°C for two hours. At the end of this time the bottoms of the rods were impacted at 0.5-second intervals for 16 minutes.

The completed fuel rods were inspected for α contamination, weld leaks, sodium level and the presence of voids in the sodium bond. The fuel-rod surfaces were monitored for α contamination by means of gas-proportional and scintillation counters. Loose contamination was removed by wiping with tissue while fixed contamination was reduced by polishing with abrasive paper. An attempt was made to reduce α contamination to less than 200 disintegrations per minute. The fuel rods were leak detected by means of a helium mass spectrometer leak detector. Each fuel rod was X-rayed to determine sodium level and the relative position of internal components.

The quality of the sodium bond was inspected by pulsed-eddy-current techniques and the eddy-current traces were compared with standards having voids of predetermined size. Since no reliable method was available for removing all shrinkage voids from the solidified sodium annulus, gas-filled voids were differentiated from shrinkage voids by comparative inspection at room temperature and 150°C. Rods containing sodium bonds of questionable quality were reprocessed through the bonding cycle until they could pass inspection.

b. Development of Powder-loaded Radiator-type Fuel Elements: I. Vibratory Compaction Studies (J. E. AYER AND F. E. SOPPET)

Vibratory compaction of spherical shapes was discussed in the Metallurgy Division Annual Report for 1963.⁽¹⁸⁾ With the work on spherical shapes completed, activity was directed toward the compaction of irregular shapes. Malleable steel grit, as obtained from a producer of blast-cleaning materials, was classified into fifteen size fractions from -10 +12 U. S. Sieve Size to -325 mesh. The pycnometer density of a sample from each size fraction was determined. The average density

⁽¹⁸⁾ Annual Report for 1963, Metallurgy Division, ANL 6868, Argonne National Laboratory, pp. 71-76.

The grit was 7.28 g/cc. The standard deviation of the densities of the various size fractions was 0.05 g/cc.

Over 100 separate data points have been obtained during the vibratory compaction of a single-component system of irregular shaped grit. The experimental procedure was similar to that used in the study of sphere packing. The packing efficiency of the irregular shape vs particle size was compared against the model developed upon spherical shapes. It appears that a similar packing system exists; however, in the case of the irregular-shaped particles, the influence of particle size is extended beyond the boundary condition. That is, beyond a ratio of container diameter to particle diameter of 10, where the influence of the boundary condition becomes negligible, the packing density of irregular shapes decreases with decreasing particle size.

Data for the vibratory compaction of irregular shaped particles of one size classification was submitted to the Applied Mathematics Division (AMD) for curve fitting. Before release of the work to the AMD, it was found that the packing efficiency of irregular shapes is inversely proportional to particle size "diameters" larger than 0.25 mm and is of the form $P = A + K/d_1$, where: P is the packing efficiency, A is the limiting density, d_1 is the "diameter" of the single size classification in meters, and K is a constant. The above function was found for the region where the boundary condition is negligible. The boundary condition was found, in the spherical study, to be a function Be^{-cd/d_1} where B and C are constants and D/d_1 is the ratio of diameter of container (D) to "diameter" of the single component (d_1). AMD has found the equation $P_1 = 0.635 - 0.050/d_1 - 0.072e^{-0.207D/d_1}$ to be a least squares fit

with the data submitted. The standard deviation of this equation against 105 data points is 0.0093.

The dependency of the packing efficiency upon the reciprocal of particle "diameter" has led to a speculation that surface-to-volume ratio might play a part in the relationship. To test this hypothesis, angular material was ball milled to reduce the angularity and thereby the surface-to-volume ratio. Single component packing of the ball-milled material was carried out and the packing efficiency was determined. Preliminary analysis of results indicates that the value of K , above, does indeed decrease with decreasing surface-to-volume ratio. Since, in the system of spheres, the packing efficiency was independent of absolute particle dimension ($K = 0$), the hypothesis of dependency of packing efficiency upon surface-to-volume ratio may be real. Presently data on milled grit are being analyzed to determine the value of K and the relative influence of K on packing efficiency.

In addition to the analysis of single-component packing, over ninety data points in the binary system of irregular shapes were obtained. These points were plotted and the curve of P versus d_1/d_2 was found to be of the same shape as that for a spherical system. These points were also submitted to the AMD to be fitted to a least-squares equation of the form, $P_2 = A + Be^{-cd_1/d_2}$ where: d_1/d_2 is the ratio of the first component "diameter" (d_1) to the "diameter" of the second component (d_2). The equation characterizing second component addition to a matrix of large size grit was found to be $P_2 = 0.484 + 0.192e^{-0.098d_1/d_2}$. The standard deviation of this curve against over 90 data points is 0.026. Figure 37 is a plot of packing efficiency versus D/d for

FIG. 37. Void Packing Efficiency vs. Ratio of Diameter of Container to First Fraction, First Fraction to Second Fraction, etc.

350-710

FIG. 38. Jacket Components for Metal Powder Loaded Irradiation Test Specimens.

both single-component and two-component particle packing.

It has been found that the relationship established is not readily extended to include the ternary loading, as was the case with the compaction of spherical shapes. It is felt that the very irregular nature of the void in the matrix of angular shapes is responsible for this behavior.

c. Fabrication of Particulate Fuel Test Specimens (E. PILARSKI)

A number of instrumented and noninstrumented test specimens, filled to a relatively low density with fine metallic fuel particles, were required. The purpose of these specimens is to evaluate fission gas release, thermal conductivity and fuel expansion theories. Two methods for producing U-Pu-Fz alloy powders were described previously.⁽¹⁹⁾ The shape of particles produced by micropulverizing was considered superior to that produced by atomizing. Micropulverizing was selected for producing the U(7.7%U²³⁵)-15w/oPu-10w/oFz powders used in these specimens. Both sodium- and-helium-gas-infiltrated test specimens were produced.

The Nb-1w/oZr components are shown in Figure 38. The bottom plugs were inert-gas-shielded, tungsten-electrode (TIG) welded to the tube for the noninstrumented specimens. The tantalum thermocouple well was electron-beam welded to the top plug for the helium-bonded instrumented specimens. The top plug was then TIG welded to the tube. The components for one instrumented sodium-bonded specimen are not

shown. They are similar to those for the helium-bonded specimens but incorporate a short tantalum well that was welded to the bottom end plug. A nylon or Teflon funnel was inserted into the tube. The tube was then sealed in an aluminum holder to prevent α contamination of exterior surfaces.

The tubes were individually loaded and compacted. The pulverized powder was loaded into the tube through an aluminum funnel. The tubes were vibrated with a 60-watt driver. Packing efficiencies between 53 and 62% of theoretical were obtained with the following powder fractions: -325 mesh, + 325 -200 mesh, +200 -120 mesh and -60 +120 mesh (U. S. Sieve Series).

The tubes were removed from the holder and wiped to remove loose contamination. The top plugs were inserted immediately after compaction of the helium-bonded specimens. The amount of sodium required to infiltrate the powder column was calculated. Sodium extrusions were cut and weighed. Brass funnels were used in loading the sodium to prevent weld-area contamination. The tubes were placed in a vacuum chamber and evacuated to 25 microns. They were heated to 250°C to melt the sodium. The chamber was then backfilled with helium to one atmosphere pressure. As-bonded sodium levels varied between 0.00 and 1.40 cm above the fuel column. Centrifuging was applied on tubes with levels greater than 0.16 cm above the fuel column until no further decrease in level was obtained.

Loose contamination was removed by abrasion and wiping before inserting the top plug. All tubes were decontaminated to a maximum of 1000 disintegrations per minute before welding. Closure welds were made with a helium-argon shielding gas.

⁽¹⁹⁾ Annual Report for 1963, Metallurgy Division, ANL 6868, Argonne National Laboratory, pp. 72-76.

Helium mass-spectrometer leak detection disclosed no faulty welds. X-radiographs were taken to show fuel column, sodium level and restrainer positions. Eleven helium-bonded specimens, two with thermocouples, and ten sodium-bonded specimens, one with a thermocouple, were submitted for irradiation testing.

d. Assembly Welding and Testing of EBR-II Alpha Determination Elements (H. F. JELINEK)

A determination of breeding ratios for fast reactors was proposed for EBR-II. The isotopes, U^{233} , U^{235} , U^{238} and Pu^{239} , Pu^{240} , and Pu^{242} will be used for determining the ratio of capture to fission cross sections as a function of reactor position.

This work consisted of fabricating seven EBR-II-type fuel rods containing a total of 33 test capsules and nine blanket rods containing 32 test capsules. The test capsules were supplied by the Chemical Engineering Division. The seven core rods have been completed. They were loaded, bonded and inspected in Building 350. The results of bond inspection were satisfactory and X-rays showed all capsules, inner components and sodium levels in the proper position. The upper and outer blanket rods were assembled, bonded and inspected to EBR-II standards by Foundry and Fabrication Group personnel. All hardware is on hand for the assembly of the fuel and blanket elements. These specimen rods are being assembled into three core fuel elements, one inner blanket element and four outer blanket elements. The distribution of specimen capsules between the various types of EBR-II fuel elements is shown in Table 13.

e. Development of FARET Test Elements (J. H. HANDWERK, A. J. CARREA, AND D. E. WHITE)

The initial design of the fuel elements for FARET required a fuel that had a known gas annulus between the fuel pellet and the cladding. In order to maintain this annulus the fuel pellets had to remain intact under the thermal flux and stress imposed by the reactor.

Out-of-pile tests were made with a uranium oxide pellet. In these tests, the oxide fragmented under a thermal flux of approximately 30 w/cm. Since uranium carbide has a higher thermal conductivity than uranium oxide, a series of tests were made with uranium carbide pellets. These pellets were fabricated from fused uranium carbide. The fused carbide was crushed to a fine powder (-200 mesh) by pebble milling in alcohol. The alcohol was evaporated and 0.5w/o stearic acid was added to the uranium carbide powder.

The mixture was pressed at 9600 kg/cm² and vacuum sintered at 1850°C. The pellets formed were machined to 1.33 cm in diameter, and 1.27 cm in length. An 0.18 cm axial hole was machined in each pellet. In addition

TABLE 13. DISTRIBUTION OF CAPSULES IN EBR-II ELEMENTS

Isotope	Core Elements	Blanket Elements			Total
		Inner	Outer	Upper	
Pu-239	8	1	4	3	16
Pu-240	4	1	2	3	10
Pu-242	6	1	4	3	14
U-233	6	0	2	1	9
U-235	6	1	2	2	11
U-238	3	0	2	0	5
Total	33	4	16	12	65

to this central hole, two additional holes were machined in some pellets to serve as thermocouple holes in an effort to obtain an approximate thermal conductivity of the uranium carbide. These holes were 0.18 cm in diameter and were machined on a 0.79 cm B. C., 180° from one another.

The tests with uranium carbide indicated that UC would withstand the thermal flux of the reactor without fragmenting; however, the geometry of the pellet required would be difficult to fabricate. An alternate design required a slip-fit pellet that did not have to remain intact during the reactor operation. For this design a fuel consisting of mixed UO_2 - PuO_2 was selected. In-pile performance tests were planned, and for the first series of tests a 3% enriched UO_2 fuel was used. This material was pressed and sintered by conventional means to 95.4% of theoretical density (10.46 g/cc), and a test element having a column of pellets 15.24 cm long and 1.33 cm in diameter was made. Additional test fuels are UO_2 -3.5w/o PuO_2 and UO_2 -12.5w/o PuO_2 . These pellets are now being fabricated.

f. Development of Methods for Producing PuC and (U-Pu)C Fuels (W. G. TOPE AND G. TALABER)

This program was divided into three parts; (1) the preparation of plutonium monocarbide, (2) the preparation of uranium-plutonium monocarbide, and (3) the fabrication of irradiation test specimens for the Engineering Irradiation Group.

The experimental work to synthesize and cast plutonium monocarbide has been completed and a report⁽²⁰⁾ is in preparation.

Experimental Production of (U-Pu)C

The experimental work during 1964 has been directed toward developing a production method to form the solid-solution carbide. Several synthesis pro-

⁽²⁰⁾ W. G. Tope, *Production of Plutonium Monocarbide by Reaction of Elemental Plutonium and Carbon*, ANL-6969 (to be published).

esses appear feasible for making (U-Pu)C. Raw materials were procured and the three following reactions were selected for investigation:

The compositions of interest range from $(U_{0.9} \cdot Pu_{0.1})C$ to $(U_{0.5} \cdot Pu_{0.5})C$. Emphasis has been placed upon a composition of $(U_{0.8} \cdot Pu_{0.2})C$ for irradiation testing.

The solid-solution carbide will be fabricated into irradiation test specimens by vibratory compaction. Currently 5 specimens, each 36 cm in length by either 0.653 cm or 0.674 cm in diameter, are required. Additional specimens will be required as new cladding materials become available and preliminary irradiation results are evaluated. The present estimate calls for a minimum of 18 specimens, each 36 cm long and 24 specimens each 5 cm long. These quantities probably will be increased.

Ayer and Soppet⁽²¹⁾ have found that the optimum particle for vibratory compaction is a 100% dense sphere. Further application of their data indicates that a two-component system will give satisfactory results for this application. The larger particles should be 25/30 mesh (U. S. Standard) and the smaller particles should be minus 325 mesh (U. S. Standard).

Reaction (1) was investigated by using the same method as for reacting plutonium. A U-20w/oPu alloy was prepared and vacuum melted in a graphite crucible liner. The results were not encouraging. The reaction rate for the alloy was much slower than for pure plutonium. The maximum carburization attained in these experiments was 3.8w/oC for material reacted at 2000°C. The U-20w/oPu alloy was very susceptible to oxidation even in a protective atmosphere containing less than 500 ppm O₂ and 50 ppm H₂O. Although additional experimentation is necessary to properly evaluate this method, the work was curtailed in order to investigate more promising methods.

Reaction (2) was investigated with fused uranium carbide purchased from Kerr-McGee Oil Industries Corporation and plutonium carbide formed by direct reaction of plutonium and carbon.

The first approach was to diffuse the plutonium carbide into uranium carbide particles. Experiments were run with various sizes of particles. The largest size particle was 177 microns or minus-80 mesh (U. S.

Standard). Each charge was physically mixed and vacuum heated in a tantalum crucible above the PuC peritectic decomposition temperature (1654°C). The temperature range explored was from 1850°C to 2100°C. At increments of time the product was sampled, metallographically examined and analyzed for carbon. The product was crushed and resized before refiring to determine the effect of fresh surfaces on the diffusion rate.

Metallographic examination was used to determine the rate of diffusion by comparing the UC, PuC and (U·Pu)C phases in the various specimens. For an 80w/oUC-20w/oPuC mixture that had a maximum particle diameter of 177 microns, essentially all the PuC had diffused into the UC after 40 minutes at 2100°C. For particles that had a maximum diameter of 44 microns, 30 minutes at 1850°C was sufficient. In all cases a small amount of intergranular material remained as a second phase. This phase was assumed to be PuC, but it may be free metal or an insoluble oxide. Chemical analyses showed a depletion of carbon and most of the products became hypostoichiometric. Metallography also showed some areas of unreacted UC when the initial UC particle size was near 177 microns. These areas were not observed when the UC particle size was minus-44 microns.

Chemical analyses showed a depletion of plutonium. The minimum loss occurred when the minus-44 micron particles were used. The tantalum was attacked and is not considered a suitable crucible material at the conditions investigated. Since diffusion into large dense particles was not successful, another approach was taken.

Pressing and sintering with a liquid phase was investigated. Weighed quantities of UC and PuC were physically mixed and pulverized in a bantam micro-pulverizer. The minus-44 micron fraction was pressed into pellets using a 3.18-cm diameter die. It was necessary to add a binder to give green strength to the pellets. Carbowax 5000, dissolved in absolute ethyl alcohol, was used. The amount of binder was kept to a minimum, and 0.5w/o was found to be sufficient. Wafers pressed at 10 tonne/cm² can be gently crushed to give granules of the desired size. The off-size material was recycled through the pressing and sizing operations. Sintering of both wafers and granules was encouraging.

A 600-gram batch of 20/30 mesh (U. S. Standard) granules was prepared. The batch was charged into a molybdenum crucible and sintered in a helium atmosphere at 1800°C for one hour. The sintered product was easily granulated. Duplicate samples gave very consistent results. The carbon content decreased from

⁽²¹⁾ J. E. Ayer and F. E. Soppet, *Vibratory Compaction—Part I, The Compaction of Spherical Shapes*, accepted for publication—Journal of the American Ceramic Society.

4.18w/o (charge calculated value) to 4.62w/o. Oxygen content increased from about 0.3w/o to 0.75w/o. Incomplete data prevented an accurate calculation of oxygen in the charge material. Nitrogen content was 0.11w/o. Density measurements, made by immersion in bromobenzene, gave 11.9 gm/cc which is about 88% of theoretical. Metallography showed some very porous particles and some dense particles. A minimum of two phases was present.

Reactor crucible problems have curtailed a systematic investigation of resintering of the granules to increase their density. The molybdenum crucible, which performed very well at 1800°C, failed during 2100°C tests. Tungsten crucibles were recently obtained. One of these was tried and it performed satisfactorily. Additional sintering occurred during these tests, but the products have not been evaluated.

The two remaining problems associated with pressing followed by sintering are low density and high oxygen content. It is felt that a sintering cycle can be developed that will increase the product density. The increase in oxygen may be due to partial oxidation of the minus 44-micron size particles during the pressing and sizing operations prior to sintering. Oxygen, adsorbed on the surface of the particles, may react during sintering. Additional oxygen may derive from thermal cracking of the binder and alcohol carrier during sintering.

The UC stock contained about 0.3w/o oxygen. Sintered, mixed carbides that contained no binder also analyzed near 0.3w/o oxygen. Sintered carbides that contained a binder analyzed 0.9 ± 0.15 w/o oxygen. The difference is significant. If oxidation of the particles is the problem, then a higher purity glovebox atmosphere is necessary. Glovebox exposure of the green material has been kept to a minimum.

Reaction (3) is presently being investigated. Its major advantage is a lower reaction temperature. Uranium monocarbide and uranium dicarbide have been purchased from Vitro Laboratory. The UC contains 226 ppm oxygen. The particle shape is spheroidal. The UC is 10/50 mesh (U. S. Standard) and the UC₂ is 10/30 mesh (U. S. Standard).

It is necessary that the work on reaction (2) be continued to determine sintering-cycle parameters, and that reaction (3) be further investigated as a means to produce a high-quality single-phase product.

The recommended sintering cycle for reaction (2) is: (a) vacuum degas the granules in a molybdenum crucible while slowly raising the temperature to 1000°C; (b) add a helium atmosphere; (c) raise the temperature to 1800°C and sinter for one hour; (d) cool and remove from the furnace; (e) regranulate to

size; and (f) resinter in a tungsten crucible at 1900°C for one hour in a helium atmosphere.

Vibratory-Compacted Irradiation Specimens

Twenty-four vibratorily compacted irradiation specimens were prepared in Nb-1w/oZr cladding. In twelve of these specimens the fuel is particulate carbide compacted in 0.664 cm I.D. tubing to 5 cm depth. Six specimens contain PuC and the remaining six specimens contain physically mixed UC-20w/oPuC.

In the other twelve specimens the fuel is physically mixed UC-20w/oPuC and UC-40w/oPuC compacted in 0.364 cm I.D. tubing to a depth of 5 cm.

Fuel Preparation and Data

The plutonium carbide was from four different batches of material prepared by direct reaction of plutonium with a graphite crucible. Each batch was sampled for carbon and minor element evaluation. Nitrogen content was near 25 ppm and oxygen content, less than 750 ppm. Freshly prepared material contains about 300 ppm oxygen, but glovebox exposure and handling increased this value.

The depleted-uranium carbide was procured from Kerr-McGee Oil Industries. The material was made by arc melting. Two samples on this material were analyzed at 0.19w/o and 0.43w/o oxygen. Two carbon samples averaged 4.76w/o. Bright pieces were selected for crushing and screening to obtain sized material.

The empty tubes were leak checked and degreased. Each tube was fitted with a protective sleeve made of Teflon or nylon. Loading and compaction was done with the tube encased within a tube holder. The holder prevents contamination of the outside surface of the jacket. Most of the tubes were also coated with collodion to provide a secondary barrier, while some were wrapped with aluminum foil.

The vibratory-compaction apparatus consisted of an audio oscillator, a 200-watt amplifier and a 60-watt speaker driver. The phenolic diaphragm of the speaker driver was reinforced with an aluminum disc. The tube holder was mechanically attached to the diaphragm during compaction. A tamper rod and weight were used.

The tube and holder assembly was weighed before loading and after compaction. The final fuel height was measured using a standard rod and dial indicator. The protective sleeve was then removed and the top plug was inserted. At this point the specimens were transferred to an uncontaminated glovebox for decontamination and welding.

The collodion or aluminum foil was removed and the specimens were surveyed. In some cases a fiberglass

eraser was used to remove local contamination. The closure welds were made by inert-gas-shielded welding.

Decontamination and Final Inspection

After closure welding all specimens were surveyed both by smears and by direct counting. Nine showed no detectable alpha contamination and the remainder were contaminated primarily in the weld zone. Weld

contamination was reduced by pickling in HNO_3 and KMnO_4 solutions. No loose contamination remained on the specimens.

The specimens were leak checked by pressurizing in a helium-filled chamber and then evacuating with the effluent gas passing through a mass spectrometer. The specimens were X-rayed to examine the welds and fuel levels. A final survey was made just prior to shipment.

7. Development of Fabrication for Zero Power Reactor Fuel Elements

a. Zero Power Reactor Fuel Elements (A. B. SHUCK, E. M. PILARSKI, A. G. HINS, G. BURTON, JR.)*

A program to develop a process for fabricating and jacketing U-20w/oPu-2.5w/oMo plates was completed during this reporting period. A report covering this process is in preparation.⁽²²⁾

The physical design calculations for a new reactor are generally tested on a critical assembly or zero-power reactor. The effects of fuel composition, core size and shape, moderators, reflectors, coolants and structural materials are tested and optimized. This is done by simulating the reactor structures with small "building blocks" of the various materials being tested. Final assembly of the zero-power reactor is by remote control. Neutron sources are introduced and neutron multiplication is measured as the reactor approaches nuclear criticality.

Large numbers of stainless steel jacketed uranium-plutonium fuel plates are required for experimental verification of the Southwest Experimental Fast Oxide Reactor (SEFOR) designs in the Zero Power Reactor III (ZPR-III). These elements will eventually be used in the Zero-Power Plutonium Reactor (ZPPR). The plates will be fabricated from uranium-base alloy containing 17.9w/o ($\text{Pu}^{239} + \text{Pu}^{241}$). For safe operation, the critical assembly should have a negative temperature coefficient of reactivity. This requires that the jacketed fuel plates show a large positive thermal expansion. The jackets must remain leak-tight over several years of handling. The fuel alloy should be oxidation resistant and it must not present a significant fire hazard if a jacket is accidentally ruptured in air.

Because the plates for the SEFOR experiment in

ZPR-III are to be commercially fabricated and early delivery is required, the process developed to fabricate the fuel elements must be adaptable to conventional equipment. A minimum of special tooling should be required. Jacket clearances were reduced over the previous zero-power plutonium loadings to meet the thermal expansion requirements. Assembly of the tight-fitting components without plutonium contamination of the welds required a new jacket design.

The development and properties of U-20w/oPu-2.5w/oMo alloy was described previously (pg. 12 this report). This alloy has satisfactory casting properties. It is essentially unworkable at room temperature although it shows some plasticity above 400°C. A protective picture-frame jacket was necessary to prevent surface chilling and cracking of the alloy during hot-rolling tests. Because of the rolling difficulties, precision casting was chosen as the method for making the fuel plates.

Both copper chill molds and graphite "warm" molds were tried in casting the alloy. An yttria wash was used to protect the surfaces of both mold materials and the metal was melted in yttria-washed carbon crucibles by vacuum-induction heating. Best results were obtained when the alloys were poured at 1275°C into a carbon mold at 545°C. The cast plate sizes ranged from 4.493 cm x 6.767 cm x 0.218 cm to 4.514 cm x 14.681 cm x 0.566 cm. The average thickness shrinkage factor was 2.25 per cent. The shrinkage factor for length and width was 1.75 per cent. Mold replication was excellent. The thickness variations were about 0.4 per cent from a given mold. The length and width variations were within 0.1 per cent. Corner radii were consistent. Recoating and reuse of the graphite molds were found to be practical. A seven-cavity mold was satisfactory used to test multiple mold castings. Figure 39 shows mold construction and Figure 40 shows castings made in these molds.

The sleeve-and-end-plug jacket design was previ-

* Now with Nuclear Materials and Equipment Corporation, Apollo, Pa.

⁽²²⁾ Shuck, A. B., Pilarski, E. M., Hins, A. G., and Burton, G., Jr., *Development of a Process for Manufacturing ZPR-III U-Mo-Pu Test Fuel Elements*, ANL-6955 (Mar. 1965).

ously used for ZPR-III plates. Sufficient clearance was allowed between the core and jacket so that the plutonium core could be inserted in a guard sheath that prevented contamination of the jacket. The guard sheath was removed and a spring was inserted to hold the plate against one side of the jacket. In this design, the large clearances prevented the prompt thermal expansion of the element.

A new close-fitting jacket was designed for the SEFOR critical experiment. It consists of two 0.03-mm-thick stainless steel panels. Each panel has a formed cavity that is about 0.05 per cent longer and wider than the dimensions of the core plate. The depth of the cavity in each panel is one-half the core plate thickness. Each plate has a turned-out rim that provides metal for seal welding.

The fuel element is assembled by placing the core plate in the cavity of one panel and then positioning the second jacket panel over the core plate. Care is required to prevent plutonium from contaminating the exterior surfaces or the welding rims of the jacket panel. The assembly is sealed by the nonconsumable-electrode, inert-gas-shielded arc-weld method. A special welding machine in a vacuum chamber was constructed for making the welds. This allows the final weld to be made at a pressure of about 400 millibars. The side welds are made first; the assembly is then clamped between two copper chills which expose only the edges of the side rims. The rims are fused together by a direct-current arc of about 12 amperes with an electrode traverse rate of about 20 cm per minute.

A reinforced bearing shoe was required on each end of the element. These serve as bumpers to transmit motion from one element to the next. Fuel elements were made with various designs of bearing shoes, all of which were objectionable because of cost, decontamination difficulties, or complexities. A weld-cast shoe was developed that overcame these objections. The ends of the fuel elements were closed by means of two five-millimeter-diameter cylindrical weld beads. These beads were subsequently milled flat and parallel to provide the bearing surfaces that transmit the thermal expansion of one element to adjacent elements.

The weld-cast shoes are made from filler strips that are spot welded to either end of the jacket panels. The assembly is clamped between chill molds that support the large weld. Cylindrical five-millimeter-diameter stainless steel arc-start and runout bars are provided at each end of the weld joint. The first weld is made at one atmosphere pressure with an arc current of 120 amperes and an electrode traverse rate of 7.6 cm per minute. The second shoe weld is made at a helium pressure of 350 to 400 millibars, sealing the fuel element with this internal pressure. The arc current is 135 amperes. When removed from the welding chamber, baro-

metric pressure forces the jacket panels into contact with the core plate. It should be noted that the minimum station pressure recorded at the National Reactor Test Site is about 850 millibars, over twice the

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FIG. 39. Mold Sections for Casting of 5 cm by 15 cm SEFOR-ZPR-III Plates.

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FIG. 40. 5 cm by 15 cm SEFOR-ZPR-III Plate Castings.

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FIG. 41. Stages of Welding and Shoe Casting on 5 cm by 15 cm SEFOR-ZPR-III Plates.

internal pressure of the fuel element. After inspection, the welds are machined. Figure 41 shows 5 cm x 15 cm fuel elements in various stages of welding.

The fuel element is leak detected, gaged and inspected for acceptability. A total of 241 fuel plates were cast and 450 jacket panels were made in the development of these methods. Natural uranium plates were also cast and jacketed for transient excursion dilatometry tests in TREAT.

Six 5 cm x 15 cm x 0.63 cm stainless steel jacketed zero-power reactor plates were made up for excursion test in TREAT. Leak detection revealed that five of these plates had defective jackets. Examination showed cracks appearing just below the weld in the region contacted by the copper chills. The cracks were of a grain-boundary nature, but no evidence of grain-boundary constituent could be microscopically detected. However, the presence of copper was detected by means of a microprobe analyzer in quantities several times higher than background. It was found that particles of copper were gouged from the chill bars during the assembly of the welding fixture and deposited on the surface of the jackets. This copper attacked the grain boundaries in the stainless steel under the influence of welding heat producing hot shortness. The assembly technique was therefore changed to prevent copper contamination.

Specifications were worked out with the General Electric Atomic Power and Equipment Division, the ANL Idaho Division, and the AEC San Francisco office.

A contract was awarded by the AEC San Francisco office to the Nuclear Materials and Equipment Company in mid-December for the production of the SEFOR fuel elements.

Argonne National Laboratory will inspect a number of SEFOR critical test fuel elements that will be used in Zero Power Reactor III. The quality assurance monitoring program is divided into two phases: pre-production qualification and production evaluation. The qualification program is to insure that the fabricator selects adequate manufacturing equipment, institutes suitable fabrication processes and can produce ZPR-III fuel elements in compliance with specifications and design drawing requirements. A limited number of sample fuel elements and components produced by approved processes will be subjected to destructive evaluation by the Laboratory. Production evaluation will consist of the fabricator's in-process inspection and ANL evaluation of approximately one of every one hundred fuel elements and components produced. The ANL evaluation will include isotopic and chemical analysis, inspection of jacket components, weld inspection, leak detection and metallography, and radiography of the assembled fuel elements.

b. The Manufacture of Plutonium-bearing Glass-bonded Fuels for Doppler Coefficient Measurement (J. E. AYER, A. G. HINS, D. E. WHITE, D. C. CARPENTER, AND C. F. KONICEK)

One of the criteria to assure safety in the operation

of fast breeder reactors is a prompt negative power coefficient of sufficient magnitude to, at least, limit the effects of excursion. In metallic fuel systems this is achieved through the expansion and the resulting decrease in fuel density with increasing temperature. Nonmetallic fuel systems that exhibit small changes in density with temperature may rely on the Doppler effect to provide a decrease in reactivity with increasing temperature. For reactors the Doppler effect, in its simplest terms, is the change in reactivity resulting from temperature-induced variations of the effective capture and fission cross sections of the material of the reactor. The determination of the magnitude of the Doppler effect is by definition relevant to the study of reactor systems and such investigations are under way at ANL. The fabrication of fuel specimens upon which measurement of the Doppler effect would be made is the subject of this section.

Specimen Specification

The Doppler element consisted of two fuel rods, each containing fuel pellets, and assembled end-to-end. Two lots of such elements were to be manufactured. One lot was to contain pellets made up of depleted $\text{UO}_2\text{-12.5w/oPuO}_2$; the second lot to contain PuO_2 pellets.* Two of the requirements for the Doppler pellets were relatively low fuel density and essentially zero expansion from room temperature to 1000°C . The fuel body was formed by a stack of twelve right-circular cylindrical pellets held in contact by quartz spacers and the ends of the fuel rod. The requirements of low density and low change in density with temperature were met through the use of glass-bonded fuel bodies.

The fuel pellets were required to have an OD of 1.247 ± 0.013 cm and a length of 1.232 ± 0.003 cm. An axial hole, through which a thermocouple protection tube was inserted, was specified at a nominal 3.7 mm diameter. Each pellet was required to weigh 11.000 ± 0.065 grams.

The capsules for containing the fuel pellets were supplied by the Reactor Physics Division of ANL. The outer diameter of a capsule has a mineral-insulated, Inconel-sheathed, heating element wound spirally and brazed along its length. The heating element is used to control the temperature of the fuel body during experiment. Temperature of the fuel body is sensed through a coaxial thermocouple protection tube extending from one end of the capsule to within 2.5 cm of the opposite end. After being loaded with pellets and quartz spacers, the container was pressurized to about 2 kg/dm^2 with helium and sealed.

* In addition uranium fuels were required. Their preparation is described on pages 47 and 48.

The capsules were ready for leak testing if, after assembly and welding, they were free of alpha-active materials. A capsule was considered clean when it showed less than 400 dpm direct count and zero wipe count. An acceptable capsule was one that showed a leak rate less than 2×10^{-6} standard cc/sec after helium mass spectrometer leak detection at 1000°C , with a pressure less than 0.1 mm Hg on the capsule exterior.

Fabrication of Mixed Oxide Specimens

The manufacture of pellets and the jacketing, welding, and decontamination of the Doppler specimens was carried out in the gloveboxes of the ANL Plutonium Fabrication Facility.

Ball milling was required to provide a uniform starting substance, free of agglomerated material or chunks. The product from milling was divided into ten gram lots and compacted in a die. The resultant wafers were granulated. Granules were made to achieve low density in the final fuel pellets. The mixed oxide grains were raised to 1200°C and held at that temperature for one hour in a helium atmosphere of about three kg/cm^2 pressure.

Charges of 11 grams of fired oxide granules were mixed with 40% Na_2SiO_3 -60% H_2O water glass. The mixture was packed into a die and pressed into an annular shape of controlled length. The pressing of a fixed weight of oxide granules to a controlled length in a die resulted in pellets of 70% theoretical density.

Each "green" pellet was allowed to dry for about 16 hours and was then heated to 1200°C for one hour in helium. The purpose of this firing was to drive the water from the Na_2SiO_3 and to disperse the oxides of uranium and plutonium into the silicate. The resulting dispersion causes the oxide granules to bond to each other through the silicate-oxide layer.

Each pellet, after firing, was measured for length and diameter to the nearest 0.03 millimeter. The weight of every pellet was taken to the nearest milligram.

Chemical analyses were made on process materials as follows: sintered granules were analyzed by X-ray diffraction for uranium and plutonium content, and by gas-analysis techniques for oxygen. The finished oxide pellets were sampled and analyzed for silicon by X-ray diffraction and by spectrochemical methods for elements not absorbed from hydrochloric acid media by an anion exchange resin.

Fabrication of Plutonium Oxide Specimens

The procedure for making plutonium oxide pellets was modified slightly over that used for the mixed

oxide specimen manufacture. During the sintering operation of PuO_2 , an alumina crucible containing a charge of granules was "fired" at 1200°C for about one hour. Upon opening the furnace we found that a small area of the crucible had been dissolved by the charge. A sample of the granules had been submitted for spectrochemical analysis. This showed about 0.2 weight per cent sodium. We feel that, at 1200°C , the sodium, which no doubt occurred as an oxide, dissolved the alumina to form a glassy liquid phase which flowed outward from the area of attack. The presence of sodium in such concentrations was not objectionable from a practical standpoint, so all future heating of PuO_2 was carried on in a tungsten crucible which resisted the attack.

Pellet forming was carried on in the same manner for both pellet compositions. However, it was found that a thin coating of Na_2SiO_3 on the outside of a PuO_2 pellet was extremely helpful in minimizing contamination of the capsule hardware. The pellets were air dried after coating and refired to insure evaporation of all constituents volatile at testing temperature.

Capsule Assembly

Capsule assembling techniques previously developed in the Plutonium Fabrication Facility were modified

to meet the requirements of the Doppler-capsule production. Leaktight, α -contamination-free capsules with a minimal clearance, (0.025 cm axial and 0.025 cm radial clearance), between fuel and capsule wall were desired.

The Inconel capsules were inspected visually and with a helium mass spectrometer leak detector for soundness. Some capsules were rejected because of leaks or other defects.

Hardware, pellet, and quartz spacer components were selected for each assembly to provide the desired axial clearance between the core stack and the capsule end caps. In some cases it was necessary to add a stainless steel shim disk to the column to obtain the required length. Figure 42 shows an assembled Doppler capsule and the components from which the Doppler-test specimens were made.

Loading the Doppler capsules without contaminating the exterior of the capsules presented difficulties. The oxide pellets tend to form dust and are highly contaminating. The exterior of the capsule is roughened by the spiral heater element and does not present a satisfactory surface for sealing or for decontaminating. Loading was successfully accomplished by attaching the capsule through the hood wall by means of a soft plastic fitting. The plastic was compressed into the

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FIG. 42. Doppler Capsule and Components.

heater helices to form a protective seal. The pellets were loaded into the capsules through a 0.1-mm thick loading funnel which was cemented at the upper edge to the fitting. In spite of these precautions, nearly all of the capsules loaded showed a surface α count of several thousand dpm.

Capsule decontamination was necessary before closure welding to prevent plutonium from alloying into the molten weldbead. Such contamination results in a permanently contaminated surface. After loading the ends of most of the mixed oxide capsules were α -contaminated to 5,000 to 10,000 dpm. Decontamination was carried out until a total count of less than 400 dpm was achieved on the capsule surfaces.

Decontamination of capsules loaded with uncoated PuO_2 pellets proved to be very difficult. The capsules were contaminated beyond the measuring capability of our monitoring instruments. In addition, the general glovebox area became contaminated to a level above 1,000,000 dpm. Use of a silicate coating on the pellets, as previously mentioned, reduced the contamination to levels comparable to those found on the mixed-oxide capsules. It was found that the brushing of the pellets before loading reduced the overall contamination problem.

Two welds were made to seal the capsule. The end cap was joined to the capsule by a TIG girth weld. The final seal was made by a capacitor-discharge weld on the tip of a $\frac{1}{16}$ " diameter evacuation tube attached to the end cap. In preparation for sealing, the evacuation tube was attached to a vacuum-pressure line. The capsule was evacuated then pressurized with tank helium to 22 kg/dm².

A pinch-off clamp was attached to the evacuation tube, the tube was cut above the pinch-off, and the weld was made.

Capsule Inspection

The following procedures were used to test the assembled capsules:

1. Completed capsules were transferred to an air glovebox where they were surveyed for alpha contamination with a gas-proportional counter. After the loose contamination was removed by tissue wipes, the fixed contamination level was below 400 dpm on all capsules.

2. A room-temperature helium mass spectrometer leak test was made on all capsules. The test was inconclusive in most cases because helium had been absorbed by the porous heater wire braze while in the helium glovebox atmosphere.

3. The capsules were radiographed to show the position and condition of the pellets and to inspect the welds for soundness. All girth welds and seal welds were of satisfactory soundness.

4. Each capsule was leak detected at 1000°C before acceptance. The capsule was leak detected in a chamber that was evacuated to about 0.1 mm pressure. The capsule was heated to 1000°C using its helical heater. During heating the line between the chamber and the evacuating pump was continually sampled by a helium mass-spectrometer leak detector. All accepted capsules showed leak rates less than 2×10^{-6} std cc/sec.

Nine acceptable capsules containing UO_2 -12.5w/o PuO_2 pellets and eight capsules containing PuO_2 pellets were made by the methods described above. Upon completion of each lot of capsules the batch was shipped to the ANL Idaho Facilities for experimental determination of Doppler effects.

c. The Manufacture of Glass-bonded Urania Fuels for Doppler Coefficient Measurement (J. H. HANDWERK, J. E. AYER, A. G. HINS, AND D. E. WHITE)

A quantity of normal-urania and enriched-urania specimens were prepared to continue the Doppler experiments in ZPR-III. Like the plutonium-bearing specimens, discussed on pages 44 to 47, these specimens were formed by bonding, with glass, sintered granules of the desired type of oxide. A theoretical density of only 70% was specified for these fuels.

The normal urania specimens were produced by using spherical material prepared by the Chemical Engineering Division's fluidized bed technique. The material as produced, was 70 to 80% of theoretical density, and was sintered in vacuum at 1750°C to increase the particle density to 90% of theoretical. The dense spheres were mixed with 1w/o of sodium metasilicate and were then cold-pressed into pellets. The specimens were air dried and then sintered in hydrogen at 1200°C. In all, thirty-seven (37) pellets, 2.64 cm in diameter, twenty-five (25) pellets 1.85 cm in diameter and one-hundred fifty (150) pellets, 1.27 cm in diameter, each 2.54 cm in length with a 0.36 cm diameter axial hole were fabricated.

Two hundred (200) 97% enriched urania pellets, 1.27 cm in diameter, 1.27 cm in length with a 0.36 cm diameter axial hole, were also produced. The granular material used for these specimens was prepared by isostatically compressing the enriched oxide powder into cakes. The resulting cakes were crushed and the material screened to recover grains 250 to 150 μ in size. Material below this grain size was recompressed and recycled. These granules were then vacuum sintered at 1750°C to densify the particles to 90 to 95% of theoretical. The particles were mixed with 1w/o of sodium metasilicate and were pressed and sintered in hydrogen at 1200°C.

Two hundred (200) pellets of the mixed oxide, and two hundred (200) pellets of plutonium oxide were fabricated. These pellets were 1.27 cm in diameter and 1.27 cm long with a 0.36 cm axial hole. The mixed oxides were ball milled in alcohol to achieve a uniform mixture. The alcohol was evaporated, and the oxide mixture was compressed into slugs without binder. These slugs were crushed, and the crushed material was screened to separate the 250 to 150 μ particles.

The fines generated were recompressed, and recycled.

The plutonium oxide, as-received, was a fine powder. This material was compressed without binder, and the resulting slugs crushed, and screened to produce 250 to 150 μ particles.

Pellets were fabricated by mixing each material with 1w/o sodium metasilicate and pressing in a steel die. The pellets formed were dried, and sintered in helium at 1200°C.

8. Fast Reactor Jacket and Component Development

a. Vanadium-20w/o Titanium Fabrication (W. R. BURT, JR., W. C. KRAMER, R. D. MCGOWAN, F. J. KARASEK, AND R. M. MAYFIELD)

During the year, the Foundry and Fabrication Group was involved in a major effort culminating in delivery of V-20w/oTi (TV-20) bar, rod, sheet and tubing to other groups for further testing for reactor service applicability. Major emphasis was placed on tubing fabrication with approximately 61 meters (200 feet) of tubing with a 0.4 mm (0.015 in.) wall thickness and ranging in outside diameter (OD) from 4.3 mm to 5.3 mm (0.168 in. to 0.208 in.) being delivered for irradiation testing of prototype fuel elements.

Fabrication of bar, rod, and sheet was relatively easy and employed conventional methods. Fabrication of tubing employed both conventional and developmental techniques. The fully integrated consolidation and fabrication program that was developed has been detailed in a forthcoming topical report.⁽²³⁾ A brief summary of this work is given herein.

Preliminary Studies

In order to evaluate fabricability of vanadium-titanium alloys and to provide sheet stock for sodium corrosion testing, a series of alloy buttons were arc-cast with titanium contents of 0, 3, and 5w/o and from 5 to 30w/o in 5w/o increments. Two alloy series were made to determine the effect of oxygen content on fabricability. One series of alloys contained ~200 ppm oxygen while the second contained ~1300 ppm oxygen. Carbon, nitrogen, and hydrogen contents were the same for both series (~400, ~250, and ~20 ppm, respectively). Charge materials were arc-melted into buttons which were canned in Type 304 stainless steel (304 SS) and hot-rolled to 0.32 cm (0.125 in.) sheet. After dejacketing, the sheets were cold rolled to a

thickness of 0.16 cm (0.063 in.), vacuum annealed for one hour at 900°C, and cold rolled to the final 0.08 cm (0.031 in.) thickness. Corrosion samples were cut from sheet material.

Hardness data as a function of titanium content are shown in Figure 43. The data represents two structural conditions—as rolled and as-annealed—and two levels of oxygen content. All of the alloys were fabricated into high-quality sheet with the alloys containing 25 and 30w/o titanium being the most difficult to fabricate. These latter two alloys might prove difficult to fabricate into high-quality, small-diameter tubing. The higher oxygen content did not affect fabricability measurably although again the higher the titanium content the more difficult the fabrication. For vanadium alloys containing 10w/o or more of titanium, an increase in oxygen content of 1000 ppm appears to be equivalent in its effect on fabricability to about a 5w/o increase in titanium content.

106-8354

Fig. 43. Hardness Data for Rolled and Annealed V-Ti Sheet as a Function of Titanium and Oxygen Content.

⁽²³⁾ Burt, W. R., Jr., et al., *Consolidation and Fabrication Techniques for Vanadium-20w/o Titanium (TV-20)*, ANL-6928, (Feb. 1965).

Preliminary sodium corrosion testing of the alloys indicated increasing corrosion resistance with increasing titanium content with 10w/o being the lowest alloy of interest. The vanadium-20w/o titanium alloy was selected to obtain better corrosion resistance and mechanical properties (relative to V-10w/oTi) consistent with sufficient fabricability to ensure production of high-quality, small-diameter, thin-wall tubing.

Consolidation

For large-scale consolidation and fabrication, vanadium in the form of chips was used as starting material. These chips were procured from the Union Carbide Corp. as the interstitial element content of 400 to 450 ppm carbon, 200 to 500 ppm oxygen, 100 to 500 ppm nitrogen and 0 to 10 ppm hydrogen represented the purest material available in large quantities. Titanium sponge from the DuPont Company was used for the alloying addition. The interstitial level of the sponge was 30 to 300 ppm carbon, 60 to 400 ppm oxygen, 20 to 45 ppm nitrogen, and 5 to 45 ppm hydrogen.

Electron-beam melting was selected as the initial alloying and consolidation technique as the high vacuum ($\sim 10^{-5}$ torr) prevented contamination during melting. Neither vibratory particulate feeding nor titanium sheet tack-welded to a pre-consolidated vanadium bar resulted in ingots with adequate homogeneity. However, cold pressing the vanadium chips and titanium sponge charge materials into briquets, which were tack-welded together to form "drip rods," did result in adequate homogeneity on EB melting. Two problems accompanied EB melting. First slow melt rates to ensure homogeneity resulted in significant metal loss due to vaporization, and second, porosity in the EB ingots was always observed even after remelting.

Accordingly, a re-melt operation was performed by using the EB ingots as a consumable electrode for arc melting. This melting technique limited porosity in the cast ingot to a small annular band just under the ingot sidewall. This porosity normally was removed in conditioning the ingot for extrusion. Arc melting also improved ingot sidewall quality, produced a finer ingot grain size, and eliminated metal loss through vaporization. Higher melt rates were achieved in arc melting and minimal contamination was observed.

This consolidation technique was used to produce three 9.7 cm (3.8 in.) diameter arc-cast ingots. After cropping the top and bottom, the ingots were 27 to 33 cm long and weighed 12 to 14 kg (26 to 31 lbs.). A typical arc cast ingot is shown in Figure 44 as are the macro- and microstructures. Analytical results on the three arc-cast ingots are shown in Table 14. In general, the target alloy content ($20.0 \pm 1.0\text{w/oTi}$) was

achieved in each of the ingots. Total interstitial contents are only slightly above the desired maximum of 1000 ppm.

Primary Fabrication (Extrusion)

The TV-20 alloy proved amenable to hot working by extrusion. Hot forging or rolling was not attempted as suitable equipment was not available. The optimum extrusion temperature was 1100°C, although 1000°C was feasible by reducing the reduction ratio to compensate for the increased stiffness of the alloy. Higher temperatures generally resulted in a poorer extruded surface quality.

TABLE 14. ALLOY AND INTERSTITIAL ELEMENT ANALYSES FROM THREE-TV-20 ARC CAST INGOTS

Ingot Number and Position	Element Analyses					
	Titanium (w/o)	Carbon (ppm)	Oxygen (ppm)	Nitrogen (ppm)	Hydrogen (ppm)	Total (ppm)
AM21 ⁽¹⁾						
Top	20.2 ⁽³⁾	387	360	270	1	1018
Middle	18.7					
Bottom	19.2					
AM25 ⁽²⁾						
Top	20.0	342	395	379	20	1136
Middle	19.9					
Bottom	19.4					
AM28 ⁽²⁾						
Top	20.8	289	420	291	50	1050
Middle	21.1					
Bottom	20.1					

⁽¹⁾ 20w/oTi in EB melt charge briquets.

⁽²⁾ 21w/oTi in EB melt charge briquets.

⁽³⁾ A hardness traverse taken at 1.3 cm (0.5 in.) intervals along the ingot length gave DPH readings ranging from 198 to 215 with the mean value being 208.

To prevent contamination during billet heating and extrusion, all TV-20 billets were "canned" in 304 SS. This also allowed the billets to be heated in an air atmosphere. Initial extrusions of cast ingots indicated that the alloy formed severe longitudinal striations as shown in Figure 45a. If this surface was removed by conditioning and the material re-extruded, the resulting surface quality was vastly improved and required little if any conditioning prior to secondary fabrication. The re-extruded surface quality is shown in Figure 45b.

To extrude TV-20 tube blanks requiring minimal conditioning, a double extrusion technique was employed. The initial arc-cast ingots were canned in 304 SS and extruded at 1100°C and a 3.6:1 reduction ratio, which was sufficient to break up the cast structure and yield fine-grained, recrystallized bar. The 304 SS jackets were removed by machining and the characteristic

(a) 38425

0.4X

(b) 38446

0.9X

Etchant: 5% AgNO_3 , 2% HF (swab)

(c) 38584

100X

Etchant: 10% KOH , 10% $\text{K}_3\text{Fe}(\text{CN})_6$

FIG. 44. Photograph of Typical Arc-cast Ingot of TV-20 with its Associated Macrostructure and Microstructure.

longitudinal striations removed by conditioning the extruded TV-20 bars to the 4.4 cm (1.74 in.) diameter required for re-extrusion. The TV-20 billets were again canned in 304 SS for re-extrusion. Billets for tube blank extrusion were drilled with a 1.6 cm (0.63 in.) diameter hole and a 304 SS ID liner tube incorporated in the billet assembly. Re-extrusions were made at 1100°C with reduction ratios ranging from 8 to 13:1. Sheet bars were extruded to a 0.62 cm x 2.54 cm (0.25

in. x 1.00 in.) size while extruded tube blanks were approximately 1.96 cm OD x 1.27 cm ID (0.77 in. OD x 0.50 in. ID) before removal of the protective 304 SS. Tube blanks were conventionally extruded over a tool steel mandrel having a light coating of Corning 7052 glass to improve the extruded surface quality of the ID.

After re-extrusion, the 304 SS jacket was removed from extruded sheet-bar and tube blank outer surfaces

by mechanical stripping. The jacket was removed from the inner diameter of the tube blank by pickling in hot HCl.

The typical longitudinal microstructure of a tube blank extruded at 1100°C and a 13:1 reduction ratio is shown in Figure 46. The structure is fine-grained and recrystallized. A minor amount of particles aligned in the extrusion direction as "stringers" can be seen. Stringers of this type were also present in extruded sheet bar. Tests on rolled sheet indicated that these "stringers" did not impart directionality to mechanical properties of the material. Hardness of re-extruded TV-20 was approximately 206 DPH (93 R_B) compared with 208 DPH (94 R_B) for arc-cast ingots.

Secondary Fabrication

The fabrication of bar, rod, and sheet proceeded in a fairly conventional manner by cold rolling extruded bar or sheet-bar products. No difficulties were encountered in rolling the material to the required thicknesses or diameters needed for test specimens. In general, reductions in area of about 70 to 75 percent could be achieved before inprocess annealing was required. Finished materials were delivered to requesting groups in a stress-relieved (one hour at 700°C in vacuum) or full-recrystallization annealed (one hour at 900°C in vacuum) condition. All materials were nondestructively tested prior to delivery.

Conversion of extruded tube-blanks to the desired final tube sizes was accomplished by swaging and drawing. The latter operation was by ductile-core drawing* for the most part with plug drawing being used periodically to size the tube and as a last drawing operation to ensure dimensional control and surface finish. An overall flow sheet for secondary fabrication of TV-20 tubing is shown in Table 15.

The initial swaging operation was necessary in order to true up the tube-blank wall, improve the surface finish, and obtain the proper D/t (outside diameter/wall thickness) ratio prior to ductile-core drawing. A tube reducer can be used for the same purpose, but such equipment was not available at ANL. Initially, as-extruded tube-blanks were swaged over a hard tool-steel mandrel through three passes resulting in a total reduction in area of approximately 35 to 40 percent. Although dimensional control and surface finish were excellent, ultrasonic examination revealed that the swaged tubes contained serious longitudinal cracks (and radial cracks in some cases) originating on the internal surface. An evaluation of swaging revealed that the alloy was highly susceptible to crack-

ing when attempting heavy reductions by swaging over a hard mandrel. To prevent cracking, in-process annealing should be employed after an approximate 15 percent reduction by this technique. Similarly, improving the surface quality of the as-extruded tube blank prior to swaging minimized crack initiation and/or propagation. Accordingly, extruded tube blanks were acid-etched on the ID and vacuum annealed (one hour at 900°C) after each of three swage passes. The final swaged and annealed tubes measured approximately 1.55 cm OD x 1.14 cm ID (0.61 in. OD x 0.45 in. ID).

(a) Surface quality after initial extrusion

38929

1×

(b) Surface quality after re-extrusion

FIG. 45. Typical Surface Quality of V-20w/oTi Extrusions.

38746

150×

Etchant: 10% KOH, 10% $K_3Fe(CN)_6$

FIG. 46. Longitudinal Microstructure of a V-20w/oTi Tube Blank Extruded at 1100°C and a 13:1 Reduction Ratio.

* Simultaneous co-reduction of a tube and a deformable core of a material such as steel or copper. The core serves to support the tube ID and prevent laps or folds from forming.

TABLE 15

FLOW SHEET FOR SECONDARY FABRICATION OF V-20w/oTi (TV-20) TUBING

Note: Starting tube blank size: 1.8 cm OD x 1.24 cm ID x 30 cm long (0.710 in. OD x 0.490 in. ID x 12 in. long).

Although the alloy was found to draw readily with 60 to 70 percent reductions feasible before annealing was necessary, surface quality was poor as the alloy galled severely when carbide dies and conventional lubricants were used. The use of aluminum-bronze dies and a chlorinated-wax lubricant (Aldraw J-1) eliminated this problem. For plug drawing, hardened beryllium-copper plugs were used in conjunction with aluminum-bronze dies and the chlorinated-wax lubricant.

The tubes were initially drawn with cold-rolled steel cores in order to increase the D/t ratio from the 7.6:1 of the swaged tubes to 11.7:1. The steel cores were removed by reeling and the tubes cleaned and vacuum annealed. Two additional ductile core draw schedules with an intermediate anneal were used incorporating hard-drawn copper cores. Copper cores were used so that the D/t ratio essentially remained constant. A

plug draw was used after the first schedule to improve the inner tube surface and to further control the D/t ratio. In the final ductile-core draw, the core was removed when the tubes were slightly above the finished size. Two plug draws normally were used in the final sizing operation. Figure 47 shows TV-20 tubes of various sizes produced at ANL.

After the final draw, the tubes were cleaned, hand straightened, and dimensionally inspected. An eddy-current technique was used to determine tubing integrity with the reject level set for a defect depth in excess of 10 percent of the wall thickness. X-ray radiography was used to locate pits on the inner surface. In general, the tubing quality far exceeded the minimum defect level of 10 percent. Less than 5 percent of fabricated tubing was rejected in nondestructive testing.

FIG. 47. Photograph of Variety of V-20w/oTi (TV-20) Tube Sizes Produced at Argonne National Laboratory.

Following the nondestructive testing, the tubing was vacuum annealed for one hour at 900°C. This heat treatment resulted in a completely recrystallized fine-grained structure as shown in Figure 48b. The typical as-drawn structure is shown in Figure 48a. The hardness dropped from approximately 238 DPH (98 R_B) for as-drawn tubing to 194 DPH (90 R_B) for the annealed tubing.

Commercial Participation

Industrial participation in the TV-20 fabrication program has been encouraged so that increased de-

(a) As-drawn tubing (~67% reduction from last in-process anneal).
Etchant: 10% KOH, 10% $K_3Fe(CN)_6$

(b) Drawn tubing after vacuum annealing for one hour at 900°C.
Etchant: 5% HF, 2% $AgNO_3$

FIG. 48. Longitudinal Microstructure of 4.8 mm OD x 0.4 mm Wall (0.192 in. OD x 0.016 in. wall) V-20w/oTi tubing As-drawn and As-annealed after Drawing.

mands for tubing may be met by commercial procurement. Large 10.2 cm (4 in.) diameter ingots have been produced by the Haynes Stellite Division of the Union Carbide Corporation, Kokomo, Indiana. These ingots were produced in a manner similar to that used at ANL and the resultant ingots met ANL specifications. (Some of this material has been processed at ANL into high-quality finished tubing.) The Stellite Division also has produced 15.2 cm (6 in.) diameter ingots that have been extruded to about 5.1 cm (2 in.) diameter bar stock by the Canton Drop Forge Company, Canton, Ohio. The ingots were canned in mild steel and extruded at 1105°C (2025°F) and a 7.3:1 reduction ratio.

Extruded tube-blanks measuring 1.90 cm OD x 1.27 cm ID (0.75 in. OD x 0.50 in. ID) were supplied to three commercial tube fabricators—the Superior Tube Company, Norristown, Pa., Fansteel Metallurgical Corporation, North Chicago, Ill., and the Wolverine Tube Division of Calumet & Hecla, Inc., Allen Park, Michigan. While all evaluations are not complete as yet, the fabricators have indicated that the material works easily with no difficulties encountered to date. A total of 10 meters (33 feet) of as-drawn tubing measuring 5.3 mm OD x 0.38 mm wall thickness (0.208 in. OD x 0.015 in. wall thickness) has been received from the Superior Tube Company. Nondestructive testing by eddy-current and X-ray radiography indicated that the tubing was of high quality with only two very small areas indicating defects greater than 10 percent of the wall thickness.

No attempt has been made, as yet, to develop commercial capabilities for TV-20 tube-blank extrusion. Such capabilities will be necessary if finished tubing is to be procured totally from a commercial source.

b. Alloy Development—Ternary Additions to Vanadium-Titanium Alloys (F. J. KARASEK, W. C. KRAMER, AND R. M. MAYFIELD)

A limited effort was expended during the year, in the preparation and fabrication of several vanadium-titanium alloys with ternary additions of chromium, molybdenum, tantalum, or niobium. Major emphasis was placed on chromium additions. The purpose of the study was to evaluate alloy fabricability via rolling and to obtain sheet for sodium corrosion test specimens. While the alloy button melts were small, sufficient 0.08 cm (0.031 in.) thick sheet usually resulted to also provide one or two samples for creep tests.

The alloys were fabricated in the same manner as the vanadium-titanium alloys described in the previous section; i.e. button arc-melting, hot rolling in a stainless-steel can, and cold rolling to sheet. Low oxygen (~300 ppm) vanadium and titanium melt

stock, used in the preparation of these ternary alloys were from the same lots used to prepare the vanadium-titanium binary alloys.

The ternary alloys produced and resultant fabricability comparisons with the V-20w/oTi binary alloy are as in Table 16.

TABLE 16. EFFECT OF TERNARY ADDITIONS ON SHEET FABRICABILITY OF V-20w/oTi BASE ALLOY

Alloy (w/o)	Sheet Fabricability (as compared to V-20w/oTi)
V-5Ti-15Cr	Difficult
V-15Ti-5Cr	Similar
V-15Ti-7.5Cr	Similar
V-20Ti-5Cr	Slightly more difficult
V-30Ti-5Cr	Considerably more difficult
V-30Ti-10Cr	Considerably more difficult
V-20Ti-2Mo	Similar
V-20Ti-2Ta	Similar
V-20Ti-2Nb	Similar

All the alloys with the exception of the V-5w/oTi-15w/oCr alloy were amenable to cold (room temperature) rolling after hot breakdown of the arc-cast button. It was necessary to "warm" (450°C) roll the V-5w/oTi-15w/oCr alloy to an approximate 60 percent reduction in thickness to 1.3 mm (0.052 in.) sheet before any reasonable amount of cold rolling could be accomplished without excessive cracking. Hardness data for the ternary alloys, obtained at various stages of fabrication, are given in Table 17.

TABLE 17. HARDNESS DATA FOR SELECTED VANADIUM-BASE TERNARY ALLOYS AT VARIOUS STAGES OF FABRICATION

Alloy Composition w/o	Average ^(a) As-Cast Hardness, DPH	Hot Rolling Temp. °C	Average ^(a) Hardness after Hot Rolling, DPH	Average Hardness after 50% Cold Reduction, DPH	Average ^(a) Hardness after 1 hr. 900°C Vac. Anneal, DPH
V-5Ti-15Cr	219	850	213	298	—
V-15Ti-5Cr	234	1000	211	274	211
V-15Ti-7.5Cr	258	1050	219	287	228
V-20Ti-5Cr	250	1050	226	283	230
V-30Ti-5Cr	239	1000	245	303	257
V-30Ti-10Cr	285	1000	268	326	284
V-20Ti-2Mo	240	1000	215	257	211
V-20Ti-2Ta	206	1000	223	252	206
V-20Ti-2Nb	228	1000	234	245	211

^(a) Hardness data converted from R_A hardness measurements.

If the hardness values of Table 17 are compared with those shown in Figure 43 for the V-Ti binary alloys, one will note that the V-Ti-Cr alloys are all harder than the base V-Ti alloy in either the as-worked or annealed condition. The 2w/oMo, Ta and Nb ternary alloys show less hardness variation from the V-20w/oTi reference binary alloy, as would be expected. The sheet fabricability rating for all the ternary alloys shown above reflects the above changes in hardness.

c. Annealing Studies of Refractory Metals (J. E. FLINN)

An annealing study of four Nb-base alloys; Nb-1w/oZr, Nb-5w/oZr, Nb-10w/oTi-5w/oZr, and Nb-39w/oV-1w/oTi, was completed during the year. Each alloys' annealing behavior was examined by means of metallography and hardness measurements. Care was exerted during evaluation to distinguish between

106-8311

FIG. 49. Annealing Curves for Nb-39w/oV-1w/oTi, 2 Hours at Temperature.

true (base metal) and pseudostructural and hardness effects which can arise during the annealing cycle and sample preparation.⁽²⁴⁾

⁽²⁴⁾ Annual Report for 1963, ANL-6868, pp. 89-91.

Annealing curves for Nb-39w/oV-1w/oTi and Nb-5w/oZr, respectively, are shown in Figures 49 and 50. Metallographic examination of the specimens, for all reductions, showed little or no apparent change in structure with annealing temperatures sufficiently high to produce minimum hardness. This suggested that nearly the entire reduction in hardness was one of recovery, as observed by optical microscopy. Several photomicrographs of Nb-39w/oV-1w/oTi and Nb-5w/oZr are shown in Figures 51 and 52 that may be used in conjunction with Figures 49 and 50 to illustrate this point. As a consequence, the lowest temperature at which the minimum hardness was observed was not high enough to yield a fully recrystallized structure, i.e., the temperature at which the grains of a crystal

106-8337

FIG. 50. Annealing Curves for Nb-5w/oZr, 2 Hours at Temperature.

were restored from a deformed structure to a strain-free uniform geometrical structure.

The annealing curves for Nb-1w/oZr and Nb-10w/oTi-5w/oZr were similar in profile to those for Nb-39w/oV-1w/oTi and Nb-5w/oZr. A summary of the observed microstructures at the various annealing temperatures are shown in Table 18 for the four Nb alloys.

Once a fully recrystallized structure (strain-free uniform geometrical structure) had occurred, the grains began to grow with increasing annealing temperatures. Figure 53 shows the change in the mean linear intercept (mean grain diameter) as a function of temperature at constant reductions for Nb-39w/oV-1w/oTi. It appears that the grain growth of this alloy is independent of reduction, thus suggesting that any difference in structure due to the degree of working had been

eliminated during the early stages of the annealing cycle, i.e. prior to grain growth.

The grain growth behaviors for the other three Nb alloys were similar to Nb-39w/oV-1w/oTi, showing little dependency of the post-recrystallization grain size on prior deformation. However, all three of these alloys exhibited nearly a constant grain size at 1500°C

and 1600°C as contrasted with the Nb-39w/oV-1w/o grain growth over the same temperature range as indicated in Figure 53. This behavior could be the result of a microstructural phase change occurring in this temperature range; probably involving Zr, since this element was common to all three alloys.

FIG. 51. Longitudinal Microstructures of Cold Worked and Annealed Nb-39w/oV-1w/oTi Alloy. (The alloy was cold-worked 50 and annealed for 2 hours at the temperatures indicated.)

40143

(a) As-worked

250X

40144

(b) 1100°C

250X

40145

(c) 1250°C

250X

Etchant: 3 parts H₂O; 2 parts HF; 4 parts HNO₃

FIG. 52. Longitudinal Microstructures of Cold-worked and Annealed Nb-5w/oZr Alloy. (The alloy was cold-worked 38% and annealed for 6 hours at the temperatures indicated.)

106-8324

FIG. 53. Isochronal Grain Growth of Nb-39w/oV-1w/oTi, 2 Hours at Temperature.

TABLE 18
SUMMARY OF THE RESULTING MICROSTRUCTURES OF ANNEALED, NIOBIUM BASE ALLOYS

Alloy	% Reduction	Annealing Temperature, °C (Time—2 hours)										
		Rm.	600	800	950	1100	1250	1400	1500	1600	1700	1800
Nb-39V-1Ti	25	W	W	W	W*	CR	G	G	G	G	—	—
	50	W	W	W	PR*	CR	G	G	G	G	—	—
	81	W	W	W	PR*	CR	G	G	G	G	—	—
Nb-1Zr	21	W	W	W	W	CR*	G	G	GS	GS	G	G
	44	W	W	W	W	CR*	G	G	GS	GS	G	G
	64	W	W	W	W	CR*	G	G	GS	GS	G	G
Nb-5Zr	82	W	W	W	W	CR*	G	G	GS	GS	G	G
	12	W	W	W	W	W*	CR	G	GS	GS	G	G
	38	W	W	W	W	W*	CR	G	GS	GS	G	G
Nb-10Ti-5Zr	60	W	W	W	W	W*	CR	G	GS	GS	G	G
	80	W	W	W	W	W*	CR	G	GS	GS	G	G
	8	W	W	W	W*	W	CR	G	GS	GS	G	G
	35	W	W	W	W*	PR	CR	G	GS	GS	G	G
	58	W	W	W	W*	PR	CR	G	GS	GS	G	G
	80	W	W	W	W*	PR	CR	G	GS	GS	G	G

W—As-worked structure

PR—Partial recrystallization first observed

CR—Recrystallized structure

G—Grain growth

GS—Grain size appears to be stable

*—Temperature first minimum hardness observed

9. Nondestructive Tests of Experimental Fast Reactor Components

a. Electromagnetic Testing of Tubing by Using Pulsed Fields (C. J. RENKEN)

Pulsed electromagnetic test equipment has been used exclusively for those applications requiring the use of an electromagnetic method for about two years. During this time sufficient experience has been acquired to evaluate the advantages and disadvantages of this equipment compared to commercial eddy current equipment, and also the ultrasonic methods.⁽²⁵⁾ At the same time, improvements have been made that have in some measure reduced or eliminated some of the disadvantages as they became evident.

One of the most successful applications of pulsed electromagnetic test equipment has been in the inspection of Type 304 stainless steel jacket tubing, 3.96 mm ID x 0.229 mm wall, which is to be used for jacketing the fuel elements produced in the EBR-II Fuel Cycle Facility when it begins operation. Over 18,600 meters of this tubing have been inspected with this equipment to a 10% defect level, that is, any

localized reduction in wall thickness of over 10% for any reason is cause for rejection. Only a relatively small amount of this tubing is now on hand ready for fabrication owing to a series of problems in obtaining quality tubing, but hundreds of defects have been detected and scores of these sectioned to check the correlation of the instrument output signal with defect depth. Correlation has been generally excellent considering the variety of defect types that have been encountered, especially since installation of new pulsed equipment using an encircling mask-aperture assembly in mid-1963.

A considerable amount of this tubing had been checked by the fabricator with commercial eddy current test equipment before shipping, but numerous serious defects continued to be detected during the testing at ANL. No problems have been encountered with spurious signals that indicate the presence of a defect where none existed. Numerous defects have been detected, however, which did not fall within the "10% localized reduction in wall thickness" defect criterion, including mill scale and projections of metal on the inner surface caused by a pitted mandrel. A

⁽²⁵⁾ Renken, C. J., *A Pulsed Electromagnetic Test System Applied to the Inspection of Thin-Walled Tubing*, ANL-6728 (Mar. 1964).

39085

FIG. 54. A Crack Detected in Type 304 Stainless Steel Jacket Tubing Intended for EBR-II Fuel Rods.

crack encountered in one of these tubes is shown in Figure 54.

In this application the operation of this pulsed electromagnetic test equipment has produced results which are probably at least equal in sensitivity and reliability to results attainable with any other method. The inspection speed of 3.66 meters/min was considerably higher than could have been obtained by an ultrasonic method of equivalent capability and this inspection speed could easily have been increased by a factor of two or even four if the time required for handling and marking the tubes would have justified such an increase.

Pulsed electromagnetic test equipment with point-type mask-aperture assemblies has been used for numerous tubing test applications on a very wide range of materials of up to 0.69 mm wall thickness. With materials of relatively good conductivity, or thicker walls, however, it operates at an increasing disadvantage compared to ultrasonic methods. It has been used to successfully test 304 stainless steel tubing of 0.508 mm wall thickness and D-43 of 0.483 mm wall thickness. In these applications a 0.508 mm long 10% Elox notch on the ID served as a standard, and the noise and interference generated by the tube was less than 20% of the standard signal. In some applications, though, interference has been a very serious problem. Zircaloy-2 tubing has been particularly troublesome usually because of localized concentration of hydrides. This interference can often be eliminated by longitudinal scanning instead of spiral scanning, but a new interference problem may arise with tubing containing heavy tube reducer marks. The recent development of two aperture, point-type mask-aperture assemblies has reduced interference problems in general. These devices are provided with two apertures about 1.5 mm apart instead of the single aperture of earlier assem-

blies. Fields of identical amplitude but opposite polarity exist in each of the apertures so that those conditions which occur under each aperture simultaneously do not appear in the pulse generated across the pickup. Pulse sampling in the time domain is used as with the older mask-aperture assemblies. Other improvements have already suggested themselves.

The dual aperture mask-aperture assemblies have shown their usefulness in the vanadium-titanium alloy tubing development program. Noise in recently produced tubing of this type rarely exceeds 10% of the signal produced by a 10% x 0.787 mm long Elox notch on the inner circumference. This tubing is tested by the electromagnetic test equipment after it has been reduced to a wall thickness of less than 0.508 mm.

b. Radiography of Tubing (N. P. LAPINSKI)

Radiography is not generally regarded as a suitable inspection method for small diameter tubing. This is primarily due to the fact that a double wall technique is employed and the image appearing on the film is degraded by scatter and filtering. However, the value of radiography as a complementary inspection to aid ultrasonic and eddy current techniques is essential. The radiographic techniques employed are such that sensitivity is always better than two per cent. Very fine grain film and when applicable, lead screens are employed to attain the radiographic sensitivity.

Two types of tubing in which products of surprisingly poor quality were encountered are 0.508 mm wall niobium-1w/o zirconium and welded 304 stainless steel. Radiographs of the Nb-1w/oZr tubing revealed numerous areas of higher transmission which indicates an absence of metal. These were assumed to be sur-

22E

100X

FIG. 55. A Weld Imperfection in Type 304 Stainless Steel Tube Detected by Radiography.

face imperfections on the inner wall of the tube. Sectioned samples of some of the questionable areas were visually inspected to ascertain the presence of surface imperfections. Careful examination revealed no voids were present. Metallographic examination followed, and it was then discovered that the defective areas were small laps located near the surface.

Radiographs of the 304 stainless steel welded tubing revealed both surface and internal defects. The surface defects were of the usual type but an odd type of

defect occurred in the welded area of numerous tubes. Its appearance on the radiograph gave reason to assume a lack of penetration at the root of the weld, or cracks in the weld. Metallographic examination verified existence of defects in the welded portion of the tubing, but not of the type originally believed to be present. These defects were voids in the welds. Figure 55 is a microphotograph of the type of weld voids present in the tubing. This type of defect was also detected by electromagnetic tests on this tubing.

10. Study of the Materials Used in the Liquid Metal Seal of EBR-II

(B. BLUMENTHAL, L. R. KELMAN AND H. V. RHUDE)

The top seal of EBR-II is a liquid metal seal. Its design and operation raised a number of questions pertaining to the oxidation of the liquid metal, its compatibility with the container material, and segregation during thermal cycling. An apparatus was built simulating a rotary seal that allowed observation of the behavior of the liquid metal over a period of 70 days, its crossing characteristics, and compatibility

with Type 304 stainless steel under the experimental conditions of rotation and temperature. Repeated thermal analyses caused the alloy to segregate substantially. The influence of sodium on the segregation was determined. Specific recommendations were made regarding the design and operation of liquid metal seals. The results of this investigation have been published.^(26,27)

11. Selection of the Structural Material for the FARET Liquid-Metal System

(L. R. KELMAN AND R. J. DUNWORTH)

Type 304 stainless steel was selected as the material for the components of FARET's liquid metal systems (especially the pressure vessel and piping). A report has been prepared on the metallurgical considerations that went into this selection.⁽²⁸⁾ Following is a summary of this study:

1. The FARET conditions of 650°C sodium in an intense neutron environment are an extrapolation from our current knowledge necessitating some element of risk and speculation in our selection of a material.
2. AISI Type 304 stainless steel comes closest to meeting FARET conditions and material selection requirements.

⁽²⁶⁾ Blumenthal, B., Kelman, L. R., and Rhude, H. V., *Some Metallurgical Considerations in the Design and Operation of the Top Seal of EBR-II*, ANL-6737 (1964).

⁽²⁷⁾ Blumenthal, B., Kelman, L. R., and Rhude, H. V., *Some Metallurgical Considerations in the Design and Operation of Liquid Metal Seals*, Trans. ANS, Vol. 7, No. 1, 190 (1964).

⁽²⁸⁾ Kelman, L. R., and Dunworth, R. J., *Selection of the Structural Material for the FARET Liquid-Metal Systems*, ANL-6939, (Dec. 1964).

- (a) It has been used extensively in liquid sodium systems to 540°C, and there is some experience to 650°C. It has been used extensively in the petrochemical and the chemical processing industries to 650°C but with a different environment (usually extremely corrosive and for shorter times) than anticipated in FARET.
- (b) Type 304 stainless steel has been selected by other organizations for proposed applications similar to those in FARET.
- (c) Allowable stresses and the basis for establishing allowable stress values for service temperatures of 650°C are available in the ASME Boiler and Pressure Vessel Code.
- (d) Long-time data based on currently commercial Type 304 stainless steel shows that the Code values may be too low. The Code values are based on unwarranted extrapolations from a relatively limited amount of short-time data. The 650°C creep strength of Type 304 stainless steel is similar to that of

Type 316 stainless steel if the optimum composition of Type 304 is specified and verified.

- (e) Retention of some ductility and impact resistance over a long time under FARET conditions is necessary to avoid catastrophic brittle failure. The excellent low-temperature ductility of Type 304 stainless steel is somewhat degraded at FARET temperatures by carbide precipitation. Type 304 stainless steel gives no sigma problem if its composition is controlled. It retains a greater degree of ductility under these temperature conditions than do most other candidate materials.
- (f) There exists no service experience or convincing experimental data on the effect of long exposure to neutron radiation of Type 304 stainless steel (or of any other candidate material) under FARET's conditions of stress and temperature. This is the area of greatest extrapolation in the selection of a structural material for FARET.
- (g) The selection of Type 304 stainless steel for FARET is based on a reasonable extrapolation from our existing knowledge of sodium compatibility and the effect of sodium on mechanical properties.
- (h) Type 304 stainless steel has a very well-developed technology. It can be obtained

readily through normal channels in a wide variety of shapes and sizes with reasonable assurance that specifications and delivery schedules will be met.

- (i) There is a wealth of experience that indicates that Type 304 stainless steel is one of the most readily welded of the austenitic stainless steels.
3. Type 316 stainless steel was the second choice for the FARET application. It was considered less desirable than Type 304 stainless steel only because of its tendency to develop sigma phase on long time exposure at FARET temperatures with resulting embrittlement. It is possible that neutron irradiation will accelerate sigma formation especially if the material is under stress. Except for this, it comes as close as Type 304 stainless steel to satisfying FARET conditions and materials selection requirements.
 4. Types 347, 321 stainless steel and the high chromium austenitic stainless steels were eliminated from consideration because of welding problems and because they are subject to embrittlement from sigma formation.
 5. The superalloys were eliminated from consideration because none of them have an adequately developed technology and they have very limited service history.

12. Economic Studies of Plutonium Fabrication Systems

(J. E. AYER AND A. B. SHUCK)

This program was initiated to cover cost analyses and economic studies of reactor fuel systems. During the month of July, three students from the AMU-ANL Summer Engineering Practice School were assigned to an engineering cost study. The task undertaken was to project a fuel cost based upon EBR-II remote fuel fabrication techniques. The task culminated in a report entitled "Engineering-Cost Study of Fast Reactor Fuel Refabrication Process" published by the AMU-ANL Summer Engineering School.⁽²⁹⁾ The report was developed from a FORTRAN computer program. The results of the report are expressed as refabrication costs versus throughput, fuel pin diameter and length. The work of the AMU-ANL study group confirmed

the value of computer techniques for studying the economic parameters of fuel fabrication.

A new metal fuel manufacturing flow diagram was developed for a reference 1000 Mwe fuel element designed by Weills and Hub of the ANL Reactor Engineering Division. The fuel element was designed for ease of fabricating. Sufficient void volume was allowed for fuel expansion at 5% burnup. The fissile isotopes were $15w/oPu^{239}$ and Pu^{241} . The alloy was assumed to be $U-25w/oPu-4w/oFz$. Vanadium- $20w/o$ titanium alloy jackets were specified for resistance to plutonium alloy penetration. Stainless steel interacts with plutonium-bearing metal and is not satisfactory for this fuel alloy. Two cases are under study. Case II, termed the "integrated" element, employs full-length jackets with uranium upper and lower blanket pins and fuel pins in the same $V-20w/oTi$ tube. The economic evaluation of this case has been completed. Case I, the segregated element, provided separate

⁽²⁹⁾ Ebert, D. D., Buczwinski, T. A., and Sana, J. V., *Engineering Cost Study of Fast Reactor Fuel Fabrication Process*, AMU-ANL Summer Engineering Practice School (July 27, 1964).

106-8356T

FIG. 56. Flow Diagram for Fabrication of Metal Fuel.

ainless steel jackets for the upper and lower blanket pins. The costly V-20w/oTi alloy is used for jacketing the fuel section only. Remote assembly of the segregated element is more complicated. Evaluation of the computer program for Case I is presently in progress.

The proposed flow diagram for manufacturing the fuel is shown in Figure 56. The fuel fabrication process is similar to the present injection casting process used for EBR-II, but nonproductive inspection and evaluation steps have been greatly simplified.

The analysis of Case II has been given first consideration in order to fulfill requirements for a metal fuel fast reactor design study. Preliminary runs on the CDC 3600 computer have been especially valuable in pointing out areas that warrant unusual attention. The study of refabrication cost for Case II revealed that cost is greatly influenced by the cost of the jacket alloy and the diameter of the fuel pin. A summary of costs generated in a preliminary run is given in Table 19.

Table 19 is based upon the requirements of a metal-fuel fast-reactor design study and is calculated upon a plant throughput of 100 kg/day of fuel, axial blanket and inner radial blanket. The plant is assumed to operate two shifts per day, five days per week. The throughput in this instance is sufficient to satisfy the needs of a single 1000 Mwe reactor. The outer radial blanket is processed at the rate of 62 kg/day. This rate is equivalent to the outer radial blanket discharge rate.

The highest single cost in Table 19 is the product material cost. Product materials for the refabrication of metal fuels are crucibles, molds, end fittings, jacket tubing, etc. Table 20 is a breakdown of product material costs for the reference fuel refabrication at a throughput of 94.2 kg per day of fuel and axial blanket.

In the above tables it is assumed that operating and maintenance costs are twenty per cent of the total annual charge for equipment, buildings and labor. The annual charges for general and administrative expenses and working capital—research and development—profit charges are respectively fifteen and fifty per cent of appropriate subtotals reported by Collins.⁽³⁰⁾

⁽³⁰⁾ Collins, G. D., *Fabrication Cost Estimate for UO₂ and Mixed PuO₂-UO₂ Fuel*, GEAP-3824 (January, 1964).

TABLE 19. FUEL REFABRICATION COST ESTIMATE PLANT THROUGHPUT = 99.4 KG/DAY FUEL AND AXIAL BLANKET

Item	Core and Axial Blanket and Inner Radial Blanket	Outer Radial Blanket
Equipment Capital Charge	\$ 441,300	\$ 370,900
Building Cost	203,500	62,700
Direct & Indirect Labor	611,500	114,800
Operating and Maintenance Cost	251,200	109,700
Subtotal	1,507,500	658,100
General & Administrative Expense	226,100	98,700
Product Materials Cost	2,035,500	504,500
Shop Cost Subtotal	3,769,100	1,261,300
Working Cap., R & D, Profit	1,884,500	630,700
Total Annual Cost	\$5,653,600	\$1,892,000
Unit Price in \$/kg U-Pu	\$218	\$117

TABLE 20. PRODUCT MATERIAL COST BREAKDOWN

Item	\$/Day	% of Total
1. Cost of Crucibles	\$ 114.73	1.60
2. Cost of Molds	1,253.37	17.45
3. Cost of Pallets	69.12	0.96
4. Cost of Jacket End Fittings	316.29	4.40
5. Cost of Refractory Metal Jacket Tubing	4,535.52	63.14
6. Cost of Sodium	0.93	0.01
7. Cost of Bundle Hardware	893.80	12.44
TOTAL	\$7,183.76	100.00

Equipment capital charge is taken as twenty-five per cent of the cost of purchased and installed processing equipment.

The findings in the initial trials of the computer program are being analyzed to determine areas of excessive cost, program errors, etc. The program is being modified and corrected and when edited will be reported.⁽³¹⁾

⁽³¹⁾ Ayer, J. E., Jones, D. A., Ebert, D. D., Buczwinski, T. A., and Sana, J. V., *A Cost Estimate for Remote Fabrication of Metallic Fuels*, ANL-6950 (to be published).

B. PLUTONIUM RECYCLE DEMONSTRATION EXPERIMENT IN EBWR

1. Fuel Element Fabrication for the Plutonium Recycle Demonstration Experiment in EBWR (C. H. BEAN AND F. D. McCUAIG)

The plutonium Recycle Demonstration Experiment is being conducted jointly by the Argonne and Hanford Laboratories. The experiment will utilize plutonium fuel to demonstrate the feasibility of plutonium recycle in a light water, thermal system. The main objective of this experiment is to obtain data on the isotopic behavior of plutonium as it is irradiated in a thermal reactor such as EBWR.

Very few changes were made to the EBWR plant for this experiment. The principle changes were in the fuel and core loading. The fuel element design is patterned after the EBWR Core-2 reference design.⁽³²⁾ Design data for the EBWR plant, core geometry, and fuel loading for the core are described in the safety analysis for the experiment.⁽³³⁾

The reactor core consists of three separate fueled zones with a total of 148 elements. The fabrication of this fuel is also a joint effort between Argonne and Hanford. Hanford has developed and is fabricating the plutonium test zone fuel. This is a mixed oxide of $1.5w/oPuO_2$ in depleted UO_2 . This fuel is fabricated by loading oxide particles into Zircaloy-2 tubes using a combination Nupac and Vipac process.⁽³⁴⁾ The fuel is compacted to 86-89 per cent of theoretical density.

The plutonium test core is surrounded by uranium fuel, which is called the driver fuel for the experiment. Argonne is responsible for the fabrication of this fuel. The driver fuel consists of both 6% enriched and natural uranium in the form of sintered UO_2 pellets loaded into Zircaloy-2 tubes. This is a fairly conventional type of fuel with the exception of the addition of a small quantity of rare earth burnable poisons, Eu_2O_3 and Sm_2O_3 , to the 6% enriched fuel loading.⁽³⁵⁾ The driver elements containing the enriched fuel, which occupy two rows in the core adjacent to the plutonium test fuel, are referred to as shim elements. It is pos-

sible that reactivity in the innermost row of shim elements may have to be periodically increased to restore reactivity of the overall system. The driver fuel loading, along with all the components for the plutonium test zone element assembly is being fabricated by United Nuclear Corporation to ANL Metallurgy Specification No. Pu Recycle Driver-63 dated 27 August 1963 on Contract No. 31-109-38-1622.⁽³⁶⁾

All fuel elements contain fuel rods in a 6 x 6 array loaded into 0.157 cm ($\frac{1}{16}$ in.) nominal wall thickness Zircaloy-2 square cans. The design of the plutonium fuel elements differs from the driver elements in that any individual rod may be withdrawn from a fuel element after periodic irradiation steps during the course of the experiment. This will permit isotopic analysis of the plutonium as the burnup proceeds without having to dismantle whole fuel elements.

The lower end of the plutonium fuel rod snaps into a holder, or grid, and the upper end is held in a guide. Rods can be individually removed with a special tool, which is used to grasp the upper end of the rod, and a firm pull, 12 to 18 lbs., releases the lower end of the rod from its socket. Additional rods may then be inserted to maintain the fuel loading in place of the one removed. The fuel rods for these elements are delivered from Hanford to Argonne and the element assembly is completed at Argonne.

A total of 882 acceptable PuO_2-UO_2 fuel rods have been received at ANL. This amount is sufficient to load 24 fuel elements with 36 fuel rods per element. Acceptable components were delivered to ANL to complete the assembly of 24 elements. These elements were available for loading into the reactor core by January, 1965.

The fuel rods for the driver fuel elements are not removable and they are positioned at the bottom of the element by slotted end plugs. Differences in thermal expansion of the rods are allowed by locating the bottom slotted end of the rod on the lower grid support structure with freedom for the opposite end to move axially, guided by holes in the upper grid. Figure 57 shows a schematic drawing of a driver fuel element illustrating the lower end fitting, fuel can, spacer, supporting grids and fuel rod components.

A number of considerations were involved in

⁽³²⁾ Avery, R., and Kelber, C. N., *Physics Analysis of Proposals for EBWR Core 2*, ANL-6306 (April, 1961).

⁽³³⁾ Toppel, B. J., Vogelberger, P. J., Jr., and Wimunc, E. A., *Safety Analysis Associated with the Plutonium Recycle Experiment in EBWR*, ANL-6841 (to be published).

⁽³⁴⁾ Sharp, R. E., Burgess, C. A., Hague, J. R., and Lohsinger, R. J., *UO_2-PuO_2 Fuel Elements for the Plutonium Recycle Demonstration Experiment*, Trans. Am. Nucl. Soc., 7, (2) 403 (November, 1964).

⁽³⁵⁾ Bean, C. H., McCuaig, F. D., and Handwerk, J. H., *Fabrication of Driver Fuel Elements Containing Rare Earth Burnable Poisons*, Trans. Am. Nucl. Soc., 7, (2) 410-411 (November, 1964).

⁽³⁶⁾ *Annual Report for 1963, Metallurgy Division*, ANL-6868, pp. 117-119.

lection of the burnable poisons and the way they were added to the shim fuel. Boron and boron compounds were rejected as burnable poisons because of the losses and poor homogeneity that occurred during high-temperature firing ($1650^{\circ}\text{C}+$) of the oxide pellets in a hydrogen atmosphere. Variations of as much as $\pm 20w/o$ of contained boron were observed in individual pellets.

Physics calculations showed that the addition of small quantities of europium and samarium to the shim fuel would produce the desired effect of minimizing reactivity variation with burnup. It was calculated the $0.158w/o\text{Eu}_2\text{O}_3$ and $0.0288w/o\text{Sm}_2\text{O}_3$ was all that was required.

Both Eu_2O_3 and Sm_2O_3 are ceramics with properties comparable to UO_2 . They both have high thermal stability, high compressive strength, low thermal expansion, high modulus of rupture, high hardness values, and low thermal shock resistance. When added to UO_2 in the amounts required, the rare earth additions had no measurable effect on the final density of fuel

pellets. Density values for 100 evaluation fuel pellets ranged from 10.23 g/cc to 10.31 g/cc with an average of 10.27 g/cc. This is well over the specified minimum density of 10.20 g/cc. With these physical and mechanical properties for the rare earth oxides it is not likely that their addition will have any adverse mechanical or physical effects on the performance of the fuel.

Weight loss measurements were obtained on mixed rare earth-uranium oxides in a vacuum of 1×10^{-6} torr at temperatures up to 2200°C . The rate of volatilization of europia, samaria, and urania were sufficiently similar to discount any probability of oxide separation due to thermal gradients either during the firing of fuel pellets or in reactor service.

The rare earth oxides are stable compounds with melting points in excess of 2000°C . At the sintering temperature of UO_2 pellets, 1650°C or higher, the rare earth additions form a solid solution with the UO_2 . This is an optimum condition for promoting and maintaining homogeneity. There are no reactions between

112-3639R

FIG. 57. Natural and Enriched UO_2 Driver Fuel Element.

Eu₂O₃, Sm₂O₃ and Zircaloy-2 at the interface temperature indicating satisfactory compatibility with the fuel jacket.

Water corrosion studies were conducted at ANL on compacts of 97w/oUO₂-3w/oEu₂O₃ and 97w/oUO₂-3w/oSm₂O₃. Specimens were tested in both oxygenated and deoxidized 360°C water at a pressure of 193.3 kg/cm², (2750 psi), for test times to 138 hours. All specimens with rare earth additions showed a greater resistance to corrosion than did control specimens of UO₂ without the rare earth additions.⁽³⁷⁾ It was concluded that lesser additions of rare earth oxides to UO₂ such as is used in the Pu Recycle driver fuel would not adversely affect the corrosion resistance of the fuel in the event of accidental exposure to coolant water.

Because the composition of materials that form solid solutions is uniform over a broad temperature range, it is unlikely that thermal gradients in the fuel will cause migration of the rare earth oxides. Unlike boron, the rare earth additions do not aggravate volume swelling tendencies of the fuel, for they do not produce helium atoms. These properties should contribute to the radiation stability of the rare earth burnable poisons.

There is a large difference in the density and particle size between the rare earth oxides and urania. These variables cause segregations to occur during mechanical mixing or blending of the different oxides. The best homogeneity that could be obtained in finished pellets made with either wet or dry blending techniques was $\pm 22w/o$ of the specified amount.

The ideal way to overcome the problem of homogeneity is to prepare the mixed oxides by coprecipitation. Because of the expense and contamination problems associated with poison materials in enriched uranium processing facilities, the relatively small quantity of oxide fuel required for this loading did not justify this approach.

Experiments were continued at Argonne and at United Nuclear's Chemical Operations at Hematite, Missouri, on two other methods for adding the rare earth oxides to urania. Both processes consisted of preparing master blends of high-density fused mixed oxides, which were then blended with much larger quantities of UO₂ to obtain the desired composition. Both processes yielded pellets with satisfactory homogeneity of the rare earth oxides for the core loading.

The process developed at Argonne consisted of pneumatically impacting at 1200°C and 17,577 kg/cm²

master blends of 2w/o Sm₂O₃ in UO₂ and 10w/o Sm₂C in UO₂. The material was impacted at Hanford by the Nupac process. Pulverized material from these master blends was mixed with UO₂ to give 1868 ppm of Sm₂O₃ which was then pelletized and fired in hydrogen at 1700°C. The Sm₂O₃ was uniformly dispersed with a variation of less than 2w/o of the amount added.

The second process consisted of firing a master blend of mixed oxides in hydrogen at a temperature that would promote fusion of the oxides. This material, when blended with UO₂ and processed into fuel pellets, also produced a satisfactory product with a homogeneity of $\pm 3.8w/o$ with a 95% confidence level. This process proved to be more compatible with existing production facilities and was used by United Nuclear Corp. to produce the shim driver fuel.

Homogeneity variations within individual fuel pellets, between pellets, and within pellet batches were difficult to evaluate. Both regular chemical analytical procedures and neutron scanning in the Juggernaut reactor at Argonne showed no detectable variations in homogeneity of commercially produced material. A special X-ray fluorescence spectrometry procedure was developed by the Mallinckrodt Laboratory for detection of the low levels of europium and samarium specified. Results were reported with an analytical error of 5 ppm for europium and 3 ppm for samarium. Analyses for Eu₂O₃ and Sm₂O₃ were obtained from a minimum of five pellet samples in each batch of oxide which was processed. The results for all material processed were within the range for experimental data obtained during development.

All of the 6% enriched fuel rods for the shim zone loading have been fabricated, corrosion tested, and inspected. All of the oxide fuel pellets, Zircaloy-2 end plugs, stainless steel retainer springs, and Zircaloy-2 tubing are available for the normal driver fuel rods, and 50% of these rods have been fabricated.

The components for assembling the fuel rods into fuel elements are all fabricated with the exception of Zircaloy-2 fuel element cans. These are being fabricated at a rate of ten cans per week. As fuel element cans become available all driver fuel elements will be assembled at United Nuclear Corporation and delivered to Argonne for loading into the reactor core.

Detailed records were maintained for all materials used for structural and fuel components; inspection of all structural components; and for all fuel fabrication, testing, inspection, and loading. Each fuel rod and each fuel element have individual identification markings cross referenced with all fabrication and inspection records.

⁽³⁷⁾ Annual Report for 1963, Metallurgy Division, ANL-6868, pp. 195-196.

.. Control Rod Fabrication for the Plutonium Recycle Demonstration Experiment in EBWR (C. H. BEAN)

Because of the questionable condition of the Inconel rivets⁽³⁸⁾ in the boron stainless steel control rods used for previous EBWR operation, and because rods of greater worth were desirable for the new core, eight new enriched boron stainless steel rods were obtained. The boron stainless steel rods contain 2w/o highly enriched ($\approx 90\%$) B^{10} in place of natural boron. One

transition sections have failed in service. Due to differential thermal expansion between Zircaloy-2, ($7.63 \times 10^{-6}/^{\circ}\text{C}$), and stainless steel, ($17.3 \times 10^{-6}/^{\circ}\text{C}$), sufficient strain can occur in the outermost rivets at the design operating temperature, (0.010 cm at 250°C), to cause a shear type failure of the rivet shank. The tongue-and-groove joint eliminates the stress due to

FIG. 58. Boron Stainless Steel Control Rod with Zircaloy-2 Follower.

hafnium rod was also obtained as a spare for the existing central oscillator rod.

The absorber portion of the boron stainless steel rod is joined to the follower section by means of an assembly rod. A tongue-and-groove joint replaces the original riveted transition sections. Rivets in these

⁽³⁸⁾ Annual Report for 1963, Metallurgy Division, ANL-6868, p. 119.

differential thermal expansion of the absorber and follower materials.

Figure 58 shows details of the boron stainless steel control rods. The control rod components are held in alignment when assembled by means of a central 1.27 cm ($\frac{1}{2}$ in.) square Type 304 stainless steel bar which is integral with the cross guide follower and extends throughout the length of the control rod. By removing

the handling tip from the upper end of the control rod, the rod may be disassembled for ease of handling or replacement of either the absorber or follower section independently.

Specifications were prepared for the boron stainless steel and for the hafnium required for control rod fabrication. Specifications were also prepared for the fabrication of the control rods. The boron stainless steel was procured from the Carpenter Steel Company on Contract No. 31-109-38-1671. Hafnium was converted to strip by Wah Chang Corp. These materials

were furnished by the Laboratory to Dresser Products, Inc., who fabricated the control rods.

Detailed records, in accordance with Argonne specifications, were furnished by all suppliers showing the results of analyses, tests, and inspections performed on all materials used. Identification of all material used was maintained throughout the control rod fabrication. Records showing the location of this material as referenced to permanent identification markings on each control rod were provided by the control rod fabricator.

3. Ultrasonic Evaluation of Tubing (R. H. SELNER)

The plutonium recycle program is a joint Argonne-Hanford program. Argonne, under one phase of the program, is responsible for procuring the driver fuel which is contained in Zircaloy-2 tubing of 9.44 mm ID and 0.686 mm wall. The quality of the Zircaloy-2 tubing is being checked by ultrasonic techniques prior to and after loading on a random-sample basis at Argonne. Tubes inspected prior to loading are not necessarily inspected again after loading.

Each tube that has been selected for testing is examined for longitudinal and transverse defects. In the longitudinal test, a 5 mc, focused transducer is positioned a certain distance from the tube center in order to obtain maximum conversion of longitudinal energy to shear energy at the tube surface. In the transverse test, the transducer is set at some angle (calculated for a 45° shear wave in Zircaloy-2 and maximized on reference notches) from the normal to the longitudinal axis of the tube.

Loaded and unloaded tubes with series of electromachined notches on both the OD and ID serve as

the standards. Prior to actual testing, the system is calibrated by means of these notches.

Results to date are summarized as follows:

1. Lots 4 and 18 of unloaded tubes contained tubes which appeared to have transverse defects from 0.051 to 0.076 mm deep. Analysis revealed that these defects were metal build-ups on the ID (apparently introduced during operation of an air gage). Borescopic examination and an eddy current technique were also used in the inspection of tubes with suspected build-ups. Such build-ups were readily apparent upon borescopic examination.

2. Lot 28 had one tube which contained an ID longitudinal defect approximately 0.051 mm deep. Eddy current and borescopic examination verified the presence of this defect. This lot was rejected.

3. Fifty per cent of the tubes in lot 29 were inspected as a result of the defect detected in lot 28. The same sampling will be used in lots 30 and 31.

4. Twenty-seven loaded tubes have been inspected and no defects were detected.

C. DEVELOPMENT OF ALLOY FUELS AND JACKET MATERIALS

1. Thorium-Uranium-Plutonium Phase Diagram (B. BLUMENTHAL)

The thorium-uranium-plutonium alloys are potentially useful fast reactor fuels. Thorium with its high melting point of 1725°C ⁽³⁹⁾ appears to be particularly attractive for high temperature reactor operations. Because of its f.c.c. crystal structure it does not have the anisotropic thermal expansion properties of the orthorhombic uranium and, for the same reason, it does not undergo anisotropic irradiation growth. Its creep strength, however, is relatively low and comparable with that of uranium. Kittel, Horak, Murphy and Paine⁽⁴⁰⁾ have shown that the binary thorium-uranium alloys with up to 20% uranium behave well under irradiation and swell by only about 10% at 650°C and at 4a/o burnup. Not enough is known about the binary thorium-plutonium alloys to make a reasonable evaluation.

In the course of the present research⁽⁴¹⁾ two isothermal sections of the ternary thorium-uranium-plutonium system were investigated at 700 and 900°C . These sections were developed from data of three series of thorium-plutonium alloys with and without small uranium additions. X-ray diffraction, metallography and a microprobe analysis showed that most of the ternary alloys are alloys in which a thorium phase is in equilibrium with the phases of the binary uranium-plutonium system. The phases of this system melt at much lower temperatures than pure thorium. Therefore, the useful alloys are restricted to those compositions in which the high-melting thorium solid solutions are in equilibrium with alpha, beta or gamma uranium and in which the plutonium is distributed between either of these two phases.

This is shown in Figure 59, where the range of useful alloys is indicated by shading. Alloys in this range contain no liquid phase at temperatures of at least up to 900°C and do not separate into two liquid layers upon melting. The presence or absence of a liquid phase was easily established by metallography of quenched specimens.

Another important aspect of the system, however, the question of the stability range of the thorium beta phase of the ternary systems has not yet been resolved satisfactorily. A plot of the lattice parameter of alpha thorium versus the concentration for alloy series of 0 to 60% plutonium and 2 or 4% uranium showed breaks which can reasonably be interpreted if it is assumed that the thorium beta phase is stable at temperatures down to 610°C . A similar plot for the binary thorium-plutonium system might also be interpreted in that way, but since these breaks are very weak the evidence is far from being conclusive.

An attempt was made to resolve the question of the stability range of the beta phase by dilatometric and electrical resistivity measurements. Only limited and uncertain information was obtained by these methods. The most direct way, high-temperature X-ray diffraction was not available to us at that time. A high-temperature Debye Scherrer camera for use with plutonium alloys at temperatures up to 1100°C is presently being checked out. J. A. C. Marples of the U.K.A.E.R.E. at Harwell, following our discussions at the Libby-Cockcroft Conference at Miamisburg, Ohio, then was kind enough to examine a binary thorium-plutonium alloy with 34.4a/o plutonium in a high-temperature diffractometer at 803°C . At this temperature

FIG. 59. Th-U-Pu Phase Diagram at 900°C (Tentative).

⁽³⁹⁾ Kato, H., *Metallurgical Progress Report No. 14 for the Period of January 1, 1962 to March 31, 1962*, USBM-U-921 (March, 1962) p. 15.

⁽⁴⁰⁾ Kittel, J. H., Horak, J. A., Murphy, W. F., and Paine, S. H., *Effects of Irradiation on Thorium and Thorium-Uranium*, ANL-5674 (1963).

⁽⁴¹⁾ *Annual Report for 1963, Metallurgy Division*, ANL-6868, pp. 120-125.

there were no β -thorium lines and the α -thorium lines were quite sharp since the initially worked surface layer had recrystallized. The lattice parameter at this temperature was $5.0368 \pm 0.0004\text{\AA}$. This confirmed

the original phase diagram by Poole, Williamson and Marples⁽⁴²⁾ and puts a question mark on the validity of the interpretation of the ternary system shown in Figure 59. The work is being continued.

2. Effect of Oxygen Content and Heat Treatment on the Lattice Spacing of High-Purity Thorium (B. BLUMENTHAL AND JOHN E. SANECKI)

We have completed the chemical analyses and lattice parameter measurements of the best grades of thorium that are presently available in this country. Crystal-bar thorium supplied by Metal Hydride, Inc. is low in hydrogen (2 ppm), carbon (7 ppm) and nitrogen (5 ppm), but high in oxygen (45 to 90 ppm) and iron (15 to 80 ppm). Electron beam melted thorium, here represented by a button made specially for this investigation by the Ames Laboratory, courtesy of F. H. Spedding and D. T. Peterson, is very low in

TABLE 21. EFFECT OF HEAT TREATMENT ON LATTICE PARAMETER OF ARC MELTED CRYSTAL BAR THORIUM

No.	Heat Treatment			Lattice Parameter, a_0 $\text{\AA}$
	Temperature, $^{\circ}\text{C}$	Time	Cooling	
1	700	2 hr	Furnace Cooled	5.0865
2	700	2 hr	Oil Quenched	5.0887
3	700	3 wk	Water Quenched	5.0897
3	Subsequently 700	2 hr	Furnace Cooled	5.0871

TABLE 22. EFFECT OF HEAT TREATMENT ON LATTICE PARAMETER OF CRYSTAL BAR THORIUM

No.	Heat Treatment			Lattice Parameter, a_0 $\text{\AA}$
	Temperature, $^{\circ}\text{C}$	Time, hr	Cooling	
1	As Received			
2	700	2	Furnace Cooled	5.0842
3	700	2	Oil Quenched	5.0848
4	900	2	Furnace Cooled	5.0855
5	900	2	Oil Quenched	5.0857
5	Subsequently 900	2	Furnace Cooled	5.0851

TABLE 23. EFFECT OF HEAT TREATMENT ON LATTICE PARAMETER OF HIGH PURITY AMES THORIUM

No.	Heat Treatment			Lattice Parameter, a_0 $\text{\AA}$
	Temperature, $^{\circ}\text{C}$	Time, hr	Cooling	
1	500	0.5	Furnace Cooled	5.0857
2	900	2	Furnace Cooled	5.0863
3	900	2	Water Quenched	5.0861

oxygen (6 ppm), but high in nitrogen (130 to 175 ppm), tantalum (200 ppm) and tungsten (200 ppm). This circumstance enabled us to determine the effect of oxygen on the lattice parameter of heat-treated specimens. The lattice parameter of thorium increases with impurity content, temperature and duration of heat treatment and subsequent cooling conditions. Specifically, the lattice parameter increases with the interstitially dissolved impurity content. That part of the lattice parameter increase, however, that is due to the oxygen contamination can be reversed by taking the oxygen out of solution with a subsequent heat treatment (Tables 21 and 22). The low-oxygen Ames thorium does not show this reversibility and this metal has the same lattice parameter after various heat treatments (Table 23).

The room-temperature lattice parameter of the highest-purity thorium is $5.0840 \pm 0.0001\text{\AA}$, its theoretical density is 11.728 g/cm^3 in agreement with the best literature values.

The data suggest strongly that genuinely high-purity thorium may be prepared by a combination of the iodide decomposition process (Metal Hydride process) and subsequent electron beam melting (Ames process).

⁽⁴²⁾ Poole, D. M., Williamson, D. K., and Marples, J. A. C., *Preliminary Investigation of the Plutonium-Thorium System*, J. Inst. Met., 56, pp. 172-176 (1957/58).

3. Properties of Thorium-Uranium-Plutonium Alloys (B. BLUMENTHAL)

Heat Treatment and Thermal Expansion

The alloys with potentially good metallurgical properties contain up to 25a/o uranium and 10a/o plutonium as shown by the shaded section of Figure 59. From this composition range two alloys were selected for intensive study. They contain:

80w/oTh-10w/oU-10w/oPu and
70w/oTh-20w/oU-10w/oPu.

These alloys were fabricated from commercial materials into irradiation pins of 3.66 mm diameter (0.144 in) heat treated for 24 hours at 850°C and water quenched or, alternately, were given the same heat

treatment, but were subsequently reheated for one hour at 700°C and furnace cooled. The 850°C heat treatment was intended to homogenize the alloys and dissolve its impurities. The subsequent 700°C heat treatment was intended to pre-expose the specimens to a thermal condition which they might see in the reactor.

The structures produced by the fabrication process and the heat treatments are shown in Figures 60a and 60b. The spherical or oblong α -uranium particles are imbedded in a thorium matrix. This latter phase shows a precipitate when quenched from 850°C and when furnace cooled from 700°C. Since in such a structure

a. Heat-treated for 24 Hours at 850°C and Water Quenched. As polished.

b. Heat Treated 24 Hours at 850°C and Water Quenched, Subsequently Reheated to 700°C and Furnace Cooled. As polished.

FIG. 60. Structure of 70w/oTh-20w/oU-10w/oPu Alloy Heat Treated as Indicated.

the anisotropic uranium is entirely surrounded by the isotropic matrix, the material should behave well under irradiation. Because of this structure, however, the solidus temperatures of these two alloys are similar to those of the binary uranium-plutonium alloys and an extrapolation of these temperatures into the ternary system together with some indications obtained from high-temperature electrical resistivity measurements resulted in the following low solidus and high liquidus temperature estimates:

Alloy	Estimated Temp. (°C)	
	Liquidus	Solidus
80/10/10	1525	925
70/20/10	1470	940

Dilatometry brought out another important phenomenon. If a cast specimen is heated to a temperature of within 100 to 150°C of the solidus temperature, it begins to creep under the stresses produced by its own weight and the pushrod. Upon heating and cooling a hysteresis loop is formed that becomes smaller and smaller as the cycle is repeated. The hysteresis eventually becomes negligibly small after 8 to 10 cycles. Prior heat treatment of the specimen at the maximum temperature of the cycle practically eliminates the hysteresis. Raising the temperature beyond the previous maximum makes it reappear. An explanation may be possible by assuming that two superimposed phenomena are effective, one being homogenization of the original cast structure when a nonequilibrium low melting phase is eliminated and replaced by the equilibrium structure, the other one being the first stage of creep which proceeds fast enough to be observed by conventional dilatometry.

In the 80/10/10 alloy breaks in the dilatometric curves were observed at $369 \pm 7^\circ\text{C}$, probably caused by the precipitation of a second phase from the thorium matrix, at about 600°C where the α uranium transforms to β uranium over a narrow range of temperatures, and at about 736°C where β -uranium transforms to γ -uranium again over a narrow range of temperatures. In the 70/20/10 alloy a break at about 350°C equivalent to the low temperature break in the 80/10/10 alloy was observed upon cooling. The $\alpha_U \rightarrow \beta$ and $\beta_U \rightarrow \gamma_U$ transformations began at 587 and 739°C respectively.

The coefficient of thermal expansion of the 80/10/10 alloy over the temperature range from 25 to 600°C varied from 12.2 to $13.2 \times 10^{-6} \text{ cm/cm/}^\circ\text{C}$ for stabilized alloys (alloys that show no significant hysteresis). Similar large variations in the coefficient of expansion were previously observed by Baumrucker* on thorium-plutonium alloys and it appears that

* Unpublished data.

structural complexity and the slowness with which true equilibrium is obtained are responsible for this variation. Substantial supercooling was observed in all measurements of both alloys and for that reason only the results of the heating curves are considered.

The 70/20/10 alloy was stabilized by a 24 hour anneal at 850°C before making the dilatometric measurements. The linear coefficient of expansion for the temperature range of 25°C to 587°C was found to be $13.1 \times 10^{-6} \text{ cm/cm/}^\circ\text{C}$. The coefficient of expansion is smaller for lower temperature ranges.

Fabricability

The irradiation specimens were fabricated by rolling and swaging. Early in the program, alloys with 60w/o thorium-20w/o uranium and 20w/o plutonium were successfully cast by the injection casting process. Alloys with 70w/o thorium and more, however, had too high a liquidus temperature to be cast by the same method. The quartz and Vycor tubes used as mold materials softened at the required high casting temperature. Impervious graphite appeared to be a reasonable substitute, but because of the success of fabrication by rolling and swaging no further effort was made to develop a high temperature mold.

High purity alloys could easily be cold rolled by 50% reduction. When the same method was tried with alloys made from commercial thorium, ingot uranium and reactor grade plutonium, the alloys cracked in the first or second rolling passes. Metallographically these alloys showed considerable thorium dioxide contamination in the form of dendrites.

After several trials a process was developed by which arc melted alloys of so-called commercial purity could be fabricated into irradiation pins. The process consists of:

1. A 24 hour heat treatment at 850°C followed by water quenching to dissolve and keep in solution as much as possible of the impurity content of the alloys.
2. Hot rolling at 450°C for a total reduction of 50%.
3. A repetition of the heat treatment described in (1).
4. Swaging at 450°C for a total reduction of 30%.
5. Continuation of heat treatments and swaging until the desired size is obtained.

The entire process including the heat treatments was carried out in the nitrogen atmosphere of our glovebox system without any additional protection of the specimens. The finished specimens had a smooth and clean surface. They were machined to size to meet the standards for irradiation pins.

The process was monitored by hardness tests. The hardness tests of the alloys of commercial purity

ranged from 50 to 60 R_B numbers for the heat treated materials to 70 to 75 R_B for the worked materials. The high-purity alloys are softer. Their hardnesses range from 18 to 35 R_B for the heat treated alloys to about 60 R_B for the worked alloys.

Potential Cladding Materials for Thorium-Uranium-Plutonium Alloys

Stainless steel was considered as a cladding for the thorium-uranium-plutonium alloys because of its availability in tubular form, its known technology and its excellent resistance to molten sodium. Compatibility tests of Type 304 stainless steel with fuel as described by C. M. Walter⁽⁴³⁾ were carried out with three alloys

96w/oTh-4w/oU
86w/oTh-4w/oU-10w/oPu
76w/oTh-4w/oU-20w/oPu

The penetration of the stainless steel into the fuel and the fuel into the stainless steel was determined metallographically after 7, 17, 42 and 51 days at a temperature of 650°C. The results are shown in Figure 61. It is obvious that the penetration of the fuel into the cladding is large enough to eliminate this type of stainless steel and possibly also all other types from consideration as high temperature cladding materials for thorium-uranium-plutonium alloys. The penetration of the cladding into the fuel is even greater. The penetration is only slightly greater for the plutonium bearing alloys than for the binary thorium-uranium alloy. The diffusion follows the parabolic rate law.

A single microprobe analysis of a section of the 76-4-20 alloy carried out at the Mound Laboratory showed that the iron and nickel component of the stainless steel diffused farthest into the fuel in agreement with the metallographic observations of the band width. The depth of the chromium diffusion was very small. On the other hand, neither thorium nor uranium penetrated into the stainless steel, but plutonium did.

These results suggested that pure chromium metal might be a satisfactory cladding for plutonium bearing alloys. We then made a few spot checks, the results of which are shown in Table 24. These spot checks were carried out for 17 days at a temperature of 650°C. They were made with two alloys containing

80w/oTh-10w/oU-10w/oPu
70w/oTh-20w/oU-10w/oPu

selected as a result of a parallel investigation of the binary thorium-uranium-plutonium phase diagram.

⁽⁴³⁾ Walter, C. M., *Interdiffusion Between Uranium-5w/o Fissium Alloy and Type 304 Stainless Steel*, ANL-6816 (March, 1964).

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FIG. 61. Interdiffusion of Type 304 Stainless Steel and Thorium-Uranium-Plutonium Alloys at 650°C.

TABLE 24. INTERDIFFUSION OF THORIUM-URANIUM-PLUTONIUM ALLOYS AND SOME CLADDING MATERIALS FOR 17 DAYS AT 650°C

Cladding Material	Fuel			
	80w/oTh-10w/oU- 10w/oPu		70w/oTh-20w/oU- 10w/oPu	
	Penetration (cm ⁻⁴)			
	Into Cladding	Into Fuel	Into Cladding	Into Fuel
V-20Ti	—	10 ^(a)	—	9 ^(a)
Ni	— ^(b)	— ^(b)	— ^(c)	265
Ni-20Cr	8	116	11	108
Cr	—	2.5 ^(a)	—	2.3 ^(a)

^(a) Total band width in cladding and fuel. No separate bands are discernible.

^(b) Did not bond.

^(c) Broke apart at band/cladding interface.

In these spot tests ductile chromium metal of rather low purity was compared with pure nickel, a nickel-20w/o chromium alloy and a vanadium-20w/o titanium alloy. Initially, we had difficulties in creating a good bond between the chromium and the fuel. We succeeded, however, in several experiments and, for the above mentioned conditions, the chromium metal

showed the lowest penetration rate of the materials investigated.

From the standpoint of compatibility both vana-

dium-20w/o titanium alloy and chromium appear to be suitable cladding materials for thorium-uranium-plutonium alloys.

4. High-Temperature Mechanical Properties of Refractory Metals and Alloys

(F. L. YAGGEE AND E. R. GILBERT)

Studies of the high-temperature properties of the refractory alloys V-10w/oTi, V-20w/oTi and Mo-0.5w/oTi-0.8w/oZr have been continued during the past year and extended to include measurements beyond the short time tensile data previously reported.⁽⁴⁴⁾ During this period tungsten and W-25w/oRe have been added to the above list of alloys being investigated and V-10w/oTi has been dropped because of its poor high-temperature strength as compared to V-20w/oTi. Current work in progress includes investigation of the time, temperature, stress and strain-rate

as tubing of various sizes. V-20w/oTi tubing has been produced at ANL whereas Nb-1w/oZr tubing has been obtained from commercial sources. Although the same degree of fabrication technology has not been achieved to date for Mo-0.5w/oTi-0.08w/oZr, W and W-25w/oRe, work is in progress toward this end. Chromium-base alloys may be of great interest in the future if their fabrication technology is developed to the point where they become commercially available in rod, sheet and tubular geometries.

Since variations in consolidation methods, fabrication schedules and thermal treatments can appreciably alter the mechanical properties of these refractory metals and alloys, uniaxially loaded tests are conducted on rod and sheet material obtained from more than one source. Burst tests are conducted on triaxially stressed tubular specimens, when available, to circumvent the usual doubts accompanying any predictions of multiaxial performance from uniaxial test data. Such predictions are likely to be in serious error in those cases where an attempt is made to use total strain at fracture as a guide for determining the percent useful life remaining in a stressed component.

Studies of the effect of environment on material properties have been started with initial emphasis on molten sodium. Preliminary tests in this area involve the pre-exposure of uniaxially stressed sheet tensile specimens to flowing sodium followed by property measurements in vacuum or an inert gas atmosphere. An equipment design is also being developed to permit the continuous measurement of material creep and stress rupture properties in an environment of reactor grade flowing sodium.

Test results obtained during the past year are presented and described in the following paragraphs.

Constant-Strain-Rate Uniaxial Tensile Properties

The test equipment consists of a resistance heated, vacuum tensile furnace mounted on an Instron Universal Tensile Machine. Specimens are stressed uniaxially at a constant predetermined crosshead rate and strain measurements are taken directly from the specimen gauge length by means of a high temperature mechanical extensometer. Test data are continuously

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FIG. 62. Stress versus Strain for Mo-0.05w/oTi-0.08w/oZr, V-20w/oTi and Nb-1w/oZr Rod Tested in Tension at 650°C.

dependence of the material properties over a wide temperature range (25–2500°C) in order that the generated data have wide applicability in reactor planning and design.

All of the alloys selected for study satisfy to some degree the criteria for an acceptable reactor fuel cladding material. Material requirements include good compatibility with uranium- and plutonium-bearing metallic fuels and molten sodium, adequate high temperature strength and a low neutron capture cross section. Fabricability and commercial availability are further considerations. All of the candidate materials being investigated are available from several different commercial sources in both rod and sheet form. The technology for V-20w/oTi and Nb-1w/oZr is sufficiently advanced to make these materials available

⁽⁴⁴⁾ Annual Report for 1963, Metallurgy Division, ANL-6868, p. 131.

TABLE 25. HIGH TEMPERATURE MECHANICAL PROPERTIES OF REFRACTORY METALS

Temperature (°C)	Ultimate Tensile Stress (kg mm ⁻²)	Yield ^(a) Stress (kg mm ⁻²)	Elongation ^(b) (%)	Uniform ^(c) Elongation (%)	Reduction of Area (%)	Elastic Modulus (103 kg mm ⁻²)
Nb-1w/oZr, stress relieved at 850°C for 1 hour, average strain rate $2.7 \times 10^{-4} \text{ sec}^{-1}$						
RT	53.2	47.4	28	7.3	90	12.4
640	43.4	42.0	19	1.9	93	8.4
650 ^(d)	48.2	44.2	19	1.9	87	12.4
800	36.2	34.6	24	1.3	83	12.4
850	36.2	34.4 ^(e)	14 ^(f)	(g)	87	(g)
950	35.9	34.8 ^(e)	15 ^(f)	(g)	90	(g)

Nb-1w/oZr, recrystallized at 1200°C for 1 hour, average strain rate $2.7 \times 10^{-4} \text{ sec}^{-1}$

650	26.9	24.7	34	7.9	98	13.0
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V-10w/oTi, extruded 1110°C, recrystallized structure, average strain rate $2.7 \times 10^{-4} \text{ sec}^{-1}$

RT	48.4	37.2	38	16.4	62	23.9
RT	50.6	39.5	38	17.3	61	14.3
650 ^(h)	49.9	45.0 ^(e)	34	15.2	53	(g)
750	37.3	27.1	42	10.7	69	8.1

V-20w/oTi, extruded 1110°C, recrystallized structure, average strain rate $2.7 \times 10^{-4} \text{ sec}^{-1}$

RT	70.3	62.6	34	16.7	56	17.7
RT	70.6	64.2	36	20.2	56	18.4
650	66.2	45.8	37	15.6	44	12.0
750	46.3	38.3	36	7.0	56	14.3
800	41.5	35.9	48	5.0	50	9.6

Mo-0.5w/oTi-0.08w/oZr-0.012w/oC, stress relieved at 1200°C for $\frac{1}{2}$ hour, average strain rate $2.1 \times 10^{-4} \text{ sec}^{-1}$

RT	77.6	77.5	(i)		(i)	
RT	79.2	63.0	2.0		1.9	
RT	79.3	75.3	19.5 ⁽ⁱ⁾		18.3 ⁽ⁱ⁾	
RT	83.7	74.2	12.5		10.5	
350	64.9	57.4	14 ^(f)		85	
350	62.4	59.9	22		88	
450	58.9	57.1	19.5 ^(f)		86	
650	56.0	49.1	23		86	
650	57.4	55.0	22		89	
650	55.7	55.0	17.7 ^(f)		85	
800	53.8	49.7	20		85	

Mo-0.5w/oTi-0.08w/oZr-0.017w/oC, stress relieved at 1230°C for $\frac{1}{2}$ hour, average strain rate $2.1 \times 10^{-4} \text{ sec}^{-1}$

29	100	93.2	22		71	
650	68.8	66.0	19		84	
650	70.1	69.0	21		86	
650	72.4	72.4	>19		>82	
650	74.9	72.1	22		87	

TABLE 26. CHEMICAL ANALYSES OF REFRACTORY ALLOY TENSILE SPECIMENS

Nominal Alloy Composition (w/o)	Chemical Composition							
	Weight Percent					ppm		
	Mo	V	Nb	Ti	Zr	C	N	O
Mo-0.5Ti-0.08Zr	Bal.	—	—	0.55	0.09	120	<1	<7
Mo-0.5Ti-0.08Zr	Bal.	—	—	0.49	0.10	170	<1	<1
Nb-1Zr	—	—	Bal.	—	1.0	271	151	96
V-20Ti	—	Bal.	—	22.2	—	290	390	750
V-10Ti	—	Bal.	—	9.2	—	380	385	370

plotted as load-strain function on an automatic read-out recorder.

Stress-strain curves for Mo-0.5w/oTi-0.08w/oZr, Nb-1w/oZr and V-20w/oTi tested in vacuum, 2×10^{-5} torr or better, at 650°C are given in Figure 62. The uniaxial tensile properties for rod specimens of these alloys are listed in Table 25. The chemical analysis for each alloy is given in Table 26.

Fractured specimens of the vanadium, niobium and molybdenum alloys tested at 650°C are shown in Figure 63. The vanadium base alloys exhibit a greater uniform elongation than either the niobium or molybdenum base alloys as illustrated in Figure 63 by the small amount of necking before fracture. In contrast the niobium and molybdenum alloys show localized strain, necking, before fracture. Values of the uniform and total elongation for the alloys tested are listed in Table 25.

Since a large uniform elongation is associated with a high strain-hardening exponent a plot of log true stress versus log true strain should show a greater slope in the region of plastic strain for the vanadium-base alloys than for either the niobium or molybdenum alloys. Such is the case as shown in Figure 64. A material exhibiting uniform elongation has the ability to resist localized deformation by means of a strain-hard-

(a) Measured at 0.002 strain offset.

(b) Measured as change in 2.54 cm gauge length after specimen is removed from furnace.

(c) Total strain at maximum load.

(d) Specimen stress relieved at 850°C for 2 hours in a different vacuum furnace.

(e) Measured with crosshead travel and may not correspond to 0.002 offset yield stress measured with extensometer.

(f) Measured as change in total length of reduced cross section—3.18 cm for Nb-1w/oZr, V-10w/oTi, V-20w/oTi, 4.00 cm for Mo-0.5w/oTi-0.08w/oZr—after specimen is removed from furnace.

(g) Not measured in absence of extensometer.

(h) Specimen surface oxidized during test due to air leak in vacuum furnace.

(i) Test terminated before specimen failure.

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FIG. 63. Fractured Specimens of: (a) Recrystallized V-20w/oTi, (b) Recrystallized V-10w/oTi, (c) Recrystallized Nb-1w/oZr, (d) Stress Relieved Nb-1w/oZr, and (e) Stress Relieved Mo-0.5w/oTi-0.08w/oZr-0.012w/oC, tested at 650°C.

ening mechanism. Thus, as localized deformation tends to occur resistance to further deformation in this area increases through strain hardening causing further deformation to occur elsewhere along the gauge length. Eventually the strain hardening ability is saturated or dominated by another effect and some localized deformation takes place just prior to failure. This behavior is typical of the V-Ti alloys.

Since Nb-1w/oZr and Mo-0.5w/oTi-0.08w/oZr depend upon dispersion hardening for their high strength, they do not strain harden appreciably and therefore exhibit severe localized deformation "necking" at low values of strain. This behavior is associated with a low strain hardening exponent. This combination of very high tensile strength and low uniform strain (early necking) contributes to the difficulties in fabricating the Mo-0.5w/oTi-0.08w/oZr alloy into small diameter tubing. The lower strength of the Nb-1w/oZr alloy and the degree of strain hardening occurring in the recrystallized condition shown in Figure 64 facilitates its fabricability into tubing.

Curves showing the variation in the tensile properties of V-10w/oTi, V-20w/oTi, Nb-1w/oZr and Mo-0.5w/oTi-0.08w/oZr with temperature are given in Figures 65 and 66.

Constant-Load Tensile Properties

The creep properties of V-20w/oTi sheet specimens have been measured at 650°C using the automatic load holding device on the Instron Universal Testing Machine. Results of these tests are shown in Figure 67. Specimens in the recrystallized condition show a greater creep strength than they do in the stress relieved condition. The reason for this difference in creep strength is not understood; however, additional alloy heat treatments are being studied to learn more about this effect. From Figure 67 it can be seen that V-20w/oTi has higher creep strength than Type 304 stainless steel⁽⁴⁵⁻⁴⁸⁾ for similar values of strain rate and that the stress dependence is different for the two

⁽⁴⁵⁾ Simmons, W. F., and Cross, H. C., The Elevated Temperature Properties of Stainless Steels, ASTM Spec. Tech. Bull. No. 124 (Jan. 1952).

⁽⁴⁶⁾ Dulis, E. J., Smith, G. V., and Houston, E. G., *Creep and Rupture of Chromium-Nickel Austenitic Stainless Steels*, ASM Trans. **45**, 42 (1953).

⁽⁴⁷⁾ Brickner, K. G., *New ASTM-ASME Code Data for T₃ 304 Stainless Steel*, (U.S. Steel, Monroeville, Pa.) private communication (1964).

⁽⁴⁸⁾ Simmons, W. F., *Type 304 Stainless Steel Data* [to be published in Revision of ASTM STP No. 124 (1964.)].

106-8317

FIG. 64. Log True Stress versus Log True Strain for Mo-0.5w/oTi-0.08w/oZr, V-20w/oTi and Nb-1w/oZr Rod Tested in Uniaxial Tension at 650°C.

materials. At stress levels below those investigated the slope of the curve for V-20w/oTi in Figure 67 must become steeper since its continuation would result in an appreciable creep rate at zero stress.

Although the V-20w/oTi alloy represents an improvement over the stainless steels in its compatibility with uranium- and plutonium-bearing metallic fuels, it is desirable to improve its creep strength over that of stainless steel by means of alloy additions and/or strengthening heat treatments. Studies are being conducted to determine the effect of heat treatment and additions of chromium on the creep strength, uniform elongation, and compatibility features.

Very little creep has been observed in stress relieved specimens of Mo-0.5w/oTi-0.08w/oZr and Nb-1w/oZr tested below their macroscopic yield stress at 550°C.

Constant-Pressure Tube Burst Properties

Burst-test equipment for determining material performance under a triaxial stress scheme was put into service during the past year. Tubular specimens are stressed by an internal gas pressure, of either argon, helium or nitrogen, and maintained at a constant test temperature between 25 and 1200°C to rupture. Radial-strain measurements are made by interrupting the test at selected intervals for diameter measurements. The test specimen is connected to a high pressure storage vessel of sufficient volume to permit large radial strains to failure without affecting the total system pressure which is read with an accuracy of 1% or better. Specimens can be tested in either a vacuum (1×10^{-6} torr or better) or an inert gas environment.

A typical tube burst specimen is shown in Figure 68a. The overall specimen length is 10.2 cm and the gauge length, defined between the end reinforcing collars, is 7.6 cm. The inside edge of both collars is machined with a radius to avoid local stress raising conditions resulting from large radial strain. Specimens

106-8312

FIG. 65. Ultimate Tensile Stress and Total Elongation vs. Temperature.

106-8313

FIG. 66. Yield Stress and Reduction of Area vs. Temperature.

are purged with helium several times, then evacuated for a minimum of 30 minutes before being heated to the test temperature and pressurized. Likewise the furnace chamber is evacuated to 1×10^{-6} torr or better before heat is applied. The specimen temperature is monitored by two thermocouples; one located at the midpoint of the gauge length and one located at the lower re-enforcing collar.

Initial tube burst tests were made with seamless Type 304 stainless steel specimens to prove out the equipment. The rupture life of Type 304 stainless steel pressurized with helium and tested in argon at 550°C is plotted as a function of tangential stress in Figure 69. The true radial strain exhibited by two specimens with rupture lives of 153 hours and 324 hours is about 12% as illustrated in Figure 70. The specimen which ruptured in 324 hours is shown in Figure 68b. A measurement of radial strain was made on this specimen after 322 hours at temperature, just two hours before the catastrophic failure. A pinhole leak was detected on the tube surface opposite the rupture during reload-

ing of the specimen and was sealed by heli-arc welding.

Testing of Nb-1w/oZr alloy tubing at 550°C has just started. The first specimen of this alloy to be ruptured is shown in Figure 68c. The rupture occurred spontaneously at a tangential stress of 34.2 kg-mm^{-2} . This same specimen had previously withstood 200 hours under a tangential stress of 22.3 kg-mm^{-2} and 136 hours under a tangential stress of 29.6 kg-mm^{-2} . The measured total true radial strain after 336 hours at temperature was approximately 0.5%. True radial strain after failure measured at two points approximately 1.27 cm above and below the rupture was no greater than 1.25%.

Figures 68b and c illustrate the great contrast in the rupture of a material exhibiting a large uniform elongation and one exhibiting a small uniform elongation prior to failure. In this respect Type 304 stainless steel behaves in a manner similar to the vanadium-base alloys tested. This high uniform elongation behavior is desirable in a fuel jacketing material both from the standpoint of relaxing stresses set up by thermal gradients, fission gas formation and differences in expansivities of fuel and jacket alloys, and from the standpoint of sustaining large plastic deformations without failure during fabrication.

The difference in alloy behavior under multiaxial and uniaxial stresses can be illustrated by comparing the 1.25% true radial strain at rupture of the Nb-

106-8304

FIG. 67. Creep of V-20w/oTi Sheet and Type 304 Stainless Steel at 650°C .

39884

Approx. 4/3X

(a) Typical tube-burst specimen, overall length 10.2 cm, gauge length 7.6 cm.

40245

Approx. 5/4X

(b) Seamless Type 304 stainless steel as ruptured after 324 hours at 550°C. Tangential stress 23.2 kg-mm⁻².

40395

Approx. 4/3X

(c) Nb-1w/oZr after spontaneous rupture at 550°C under tangential stress of 34.2 kg-mm⁻².

FIG. 68. Tube-Burst Specimens before and after Failure.

1w/oZr tube specimen shown in Figure 68c with the 20% true strain of Nb-1w/oZr rod specimens (at 650°C) listed in Table 25. The triaxial stress state impressed on the tubular geometry restricts the amount of plastic strain occurring before failure, while the uniaxial stress state is less restrictive on rod specimens even though the alloy itself exhibits low uniform strain (necking) at fracture.

Structural Effects

The mechanical properties of refractory alloys are known to be highly sensitive to the internal material structure. Evidence of this fact has been noticed in the vanadium, molybdenum, and niobium-base alloys tested. The V-20w/oTi alloy exhibits a yield stress of 46 kg-mm⁻² for extruded rod and 33 kg-mm⁻² for recrystallized sheet at 650°C. Similar differences are

106-8332

FIG. 69. Tangential Stress vs. Rupture Life for Seamless 304 Stainless Steel Tubing in Argon at 550°C.

106-8343

FIG. 70. True Radial Strain vs. Time for Seamless 304 Stainless Steel Tubing in Argon at 550°C.

observed for Nb-1w/oZr in the stress relieved and recrystallized conditions and between two lots of commercially procured Mo-0.5w/oTi-0.08w/oZr as reported in Table XXV. Metallographic examinations are being made to resolve these differences.

Strain-Rate Effects

Specimens of Mo-0.5w/oTi-0.08w/oZr have been tested at 650°C using different strain rates in an effort to find an optimum rate for material fabrication. The results of these tests are shown in Figure 71. At high strain rates, greater than $2 \times 10^{-2} \text{ sec}^{-1}$, the ultimate tensile stress decreases. It would appear that fabrication of this alloy should be easier at strain rates corresponding to lower ultimate stress levels. It is hoped that this information may be useful in fabrication when the strain rates correspond to those normally used.

Young's Modulus of Vanadium-Niobium-Molybdenum Alloys

Young's modulus values for V-10w/oTi, V-20w/oTi, Nb-1w/oZr and Mo-0.5w/oTi-0.08w/oZr are listed in Table 25. Additional values for V-20w/oTi are plotted against temperature in Figure 72. These include both dynamic⁽⁴⁹⁾ and static measurements.

⁽⁴⁹⁾ Hill, W. H., and Wilcox, B. A., *Elevated Temperature Dynamic Moduli of Vanadium, Titanium, and V-Ti Alloys*, MC WADDTR 60-245, Ad 243479 (May 1960).

106-8316

FIG. 71. Ultimate Tensile Stress and Total Elongation vs. Strain Rate for Mo-0.5w/oTi-0.08w/oZr Tested in Tension at 650°C.

106-8327

FIG. 72. Young's Modulus vs. Temperature for V-20w/oTi.

Static Young's Modulus of Tungsten and Tungsten-25w/oRhenium

The static Young's moduli of vacuum arc-cast tungsten rod, powder metallurgy-consolidated tungsten sheet and powder metallurgy-consolidated W-25w/oRe sheet have been measured in vacuum* over the temperature range 800 to 2000°C at a strain rate of $2.2 \times 10^{-4} \text{ sec}^{-1}$. All of these were wrought materials in the stress-relieved condition. The measured values of static Young's modulus are given in Tables 27 and 28.⁽⁵⁰⁾

The following comments reflect some general obser-

⁽⁵⁰⁾ Sims, C. T., and Jaffee, R. I., "Further Studies of Properties of Rhenium Metal," AIME Trans. **206** (8) 913-917 (1956).

* Maximum pressure at test temperature was 1.8×10^{-5} torr.

TABLE 27. STATIC YOUNG'S MODULUS FOR UNALLOYED TUNGSTEN

Temperature °C	Literature Dynamic Young's Modulus (10 ³ kg mm ⁻²)	Literature Static Young's Modulus (10 ³ kg mm ⁻²)	Static Young's Modulus V.A.C. Wrought W-Rod ^(a)		Static Young's Modulus P.M., Wrought W-Sheet ^(b)	
			E	σ	E	σ
			10 ³ kg mm ⁻²	kg mm ⁻²	10 ³ kg mm ⁻²	kg mm ⁻²
RT	39-42	—	—	—	—	—
RT	—	33-36	—	—	—	—
800	36-38	—	37 ^(e)	21.4	—	—
800	—	24-34	32 ^(d)	35.6	34 ± 2 ^(d)	8.5
1000	36-37	—	35 ^(e)	21.4	—	—
1000	—	24-26	27 ^(d)	28.5	33 ± 3 ^(d)	6.5
1200	35-36	—	34 ^(e)	11.4	—	—
1200	—	22-25	24 ^(d)	17.5	31 ± 1 ^(d)	6.4
1400	34-35	—	35 ^(e)	11.4	—	—
1400	—	18-23	19 ^(d)	17.1	23 ± 1 ^(d)	6.0
1600	33-34	—	—	—	—	—
1600	—	14-21	13 ^(d)	5.5	16 ± 2 ^(d)	5.0
1800	32-33	—	—	—	—	—
1800	—	8-18	12 ^(d)	4.3	14 ± 2 ^(d)	3.5
2000	30-31	—	—	—	—	—
2000	—	3-17	10 ^(d)	3.6	14 ± 1 ^(d)	2.8
2200	26-30	—	—	—	—	—
2200	—	13	—	—	—	—

(a) 0.635 cm diameter reduced section.

(b) 0.15 cm thick sheet; 0.635 cm wide reduced section.

(e) Unrelaxed modulus.

(d) Relaxed modulus.

variations on the recently measured modulus values for tungsten and for W-25w/oRe.

Unalloyed Tungsten

Below the recrystallization temperature range (approximately 1200 to 1600°C, depending upon prior material history and the applied stress) the measured static modulus is in close agreement with the literature values for dynamic modulus given in Table 27. However, above this temperature range the measured static modulus is in closer agreement with the literature values for static modulus. This difference in the measured static modulus above and below the recrystallization temperature range is attributed to a lowering of the yield point, through recrystallization, to a strain level below the resolution capability of the mechanical extensometer. Therefore, the relaxed static modulus is observed above this temperature range and the unrelaxed modulus is observed below this temperature range.

The slope of the stress-strain curve for vacuum arc-

cast (V.A.C.) tungsten rod appears to be stress dependent, so that both the unrelaxed and relaxed static moduli are observed below the recrystallization temperature range. This is indicated in the modulus values for tungsten rod shown in Table 28. The powder metallurgy-consolidated (P.M.) tungsten sheet did not exhibit a stress dependence.

Tungsten-25w/o Rhenium

The measured static modulus of this alloy lies between the values for unalloyed tungsten and those for unalloyed rhenium at all temperatures below the recrystallization temperature range. However, the measured static modulus of this alloy sheet after recrystallization at 2360°C is observed to be higher when obtained by a regressing temperature technique than when the measured modulus is obtained on heat up. This behavior is consistent with observations reported for single crystals, which do not show the same degree of relaxation of Young's modulus, and therefore suggests a possible grain-size dependence. The larger-grained recrystallized material will have less grain-boundary area and might therefore be expected to exhibit less relaxation. Young's modulus data for unalloyed rhenium and W-25w/oRe above the recrystallization temperature range are not available in the literature for comparison.

The powder metallurgy-consolidated W-25w/oRe sheet did not exhibit a stress dependence such as was observed for vacuum arc-cast tungsten rod.

TABLE 28. STATIC YOUNG'S MODULUS FOR RHENIUM AND TUNGSTEN-25 w/o RHENIUM SHEET

Temperature °C	Dynamic Young's Modulus ^(a) for Unalloyed Re 10 ³ kg mm ⁻²	Static Young's Modulus P.M. Wrought W-25 Re Sheet ^(a)	
		E ^(b)	E ^(c)
		10 ³ kg mm ⁻²	10 ³ kg mm ⁻²
RT	47	—	—
800	42	35 ± 2	—
1000	40	33 ± 2	42 ± 4
1200	37	30 ± 1	37 ± 5
1400	—	22 ± 2	32 ± 3
1600	—	18 ± 2	25 ± 3
1800	—	13 ± 1	21 ± 2
2000	—	11 ± 1	17 ± 1
2200	—	10 ± 1	12 ± 1

(a) 0.076 cm thick sheet; 0.635 cm wide reduced section.

(b) Measurements on heat up; specimen recrystallized during heat up.

(c) Measurements on cool down; specimen in recrystallized condition.

Bend Ductility of Tungsten-25w/o Rhenium

As a part of a program to determine the properties of refractory metals, a comparative evaluation was made of W-25w/oRe alloy sheet obtained from three commercial sources.

The property to be used as a criterion is bend ductility as a function of temperature, since this property has an immediate bearing on the fabrication of this material. Since the mechanical properties of refractory

TABLE 29. DUCTILE-BRITTLE TRANSITION TEMPERATURE OF WROUGHT W-25w/oRe SHEET

Material Source	Method of Consolidation	Ductile-Brittle Transition Temperature for 90° Bend without Fracture (°C)	
		1T	4T
A	Powder Metallurgy	−95	−115
A	Vacuum Arc Cast	−130	−125
B	Vacuum Arc Cast	−95	−132
C	Powder Metallurgy	−90	−112

metals and alloys are influenced by such variables as the consolidation and fabrication procedures, material purity, and metallurgical condition (stress-relieved versus recrystallized), a series of bend tests have been initiated based on a consideration of these variables. Material consolidated by powder metallurgy procedures and that consolidated by vacuum arc casting are both being tested. The nominal as-rolled thickness is 0.076 cm (0.030 in.) in all cases.

Bend test specimens have been made from material in two conditions; as-received, stress-relieved; and recrystallized (at 2000°C).

The bend tests are being conducted in accordance with the procedures outlined in report MAB-192M of the Materials Advisory Board. Test specifications require a constant crosshead rate (loading rate) of 2.54 cm/min (1 in./min) and a bracketing of the ductile-brittle transition temperature within 14°C (25°F).

Bend tests for a 1T and a 4T bend radius have been completed on material received from all three vendors in the as-received, stress-relieved condition. The preliminary results are given in Table 29.

5. Metallographic Procedure for Plutonium Alloys (B. BLUMENTHAL AND D. E. BUSCH)

The process of metallographic specimen preparation by vibratory grinding and polishing developed by S. Matras⁽⁵¹⁾ was adapted to plutonium work. The process uses, in a modified form, the commercial Syntron* vibratory polishing unit. It features various fixtures that guide the specimens over the polishing surface. Metallographic specimen preparation is essentially reduced to three steps:

- (1) Grinding on 600 grit silicon carbide paper under a 500 gram load.
- (2) Intermediate polishing with Linde B alumina on nylon cloth under a 500 gram load.
- (3) Final polishing with Linde B alumina on micro-cloth with no load or only a 50 gram load.

Since the time required to remove the scratches produced by the 600 grit silicon carbide paper was rather long, we have inserted a fine grinding step between Steps 1 and 2. This step utilizes 5 micron particle size alumina by Micro Abrasive Corporation, Westfield, Massachusetts, on Struers DP cloth (grade MOL)

⁽⁵¹⁾ Matras, S., *Vibratory Grinding and Polishing of Metallographic Specimens*, ANL-6975 (to be published).

* Syntron Company, Homer City, Pa.

FIG. 73. Intermediate Polishing Apparatus (in back) and Fine Polishing Apparatus (in front).

under a 500 gram load in a machine similar to the one used for grinding. Photograph of equipment is shown in Figure 73.

We have obtained very satisfactory results with this process. Surface deformation of metallographically soft and sensitive specimens is reduced to a bare mini-

mum. Usually little etching is required to develop the structure. Retention of inclusions is excellent. Individual specimen preparation takes more time than conventional hand preparation, but since the process is able to handle 6 to 12 specimens simultaneously, the total time required is the same.

D. DEVELOPMENT OF CERAMIC FUELS

1. Properties of Uranium and Plutonium Monosulfides

a. Uranium Monosulfide (D. R. MESSIER)

Work was resumed on the development of methods for the synthesis of uranium monosulfide from fused salt mixtures. Such methods are attractive because of their simplicity and adaptability to large scale production compared to the gas-metal reaction method presently in use.⁽⁵²⁾

Two types of experiments were carried out. The first involved the reaction of UF_4 with a H_2 - H_2S gas mixture in a molten halide eutectic following the procedure described by Yoshioka.⁽⁵³⁾ The second concerned an electrolytic preparation similar to that described by Didchenko and Litz.⁽⁵⁴⁾

Attempts to prepare US through the reaction of dissolved UF_4 with H_2S gas were carried out under various experimental conditions. Both LiCl-KCl and LiF-NaF eutectic melts were used as reaction media. When chloride melts were used without predrying, good yields of black product were obtained by bubbling H_2S through the melt for several hours at 570°C . X-ray examination showed that the product was a mixture of UOS and UO_2 . However, under "dry" conditions, i.e., when the chlorides were predried with HCl gas or a fluoride melt at 750°C was used, no visible product was obtained. The fact that US was not obtained under any conditions is in agreement with the results of Allbutt and Junkison⁽⁵⁵⁾ who recently made similar attempts to prepare US.

The unpromising results with the gas bubbling method led to attempts to electrolytically synthesize US. For this purpose, an apparatus similar to that described by Didchenko and Litz⁽⁵⁴⁾ was constructed.

The experimental procedure consisted of dissolving a sulfide and UF_4 or UCl_4 in a fused chloride medium and applying an emf to induce reaction. For a typical run, the application of the emf resulted in a rapid rise in back-emf to a characteristic value for a given temperature and melt composition. The back-emf then

remained constant until the apparent completion of the reaction which was indicated by a rapid rise in current and simultaneous fall in back-emf. Table 30 summarizes the results obtained under various experimental conditions.

Despite the use of HCl and electrolytic predrying of the melts, heavy oxygen contamination still existed. The main products again were UO_2 and UOS. The commercial Na_2S used in the early runs was extremely hygroscopic and appeared to be a likely source of oxygen contamination. Therefore, attempts were initiated in which other sulfides were used as sulfur sources.

Molybdenum cathodes similar to those successfully employed with sodium sulfide were quickly dissolved when used with calcium and lead sulfides. The electrolysis of melts containing lead sulfide with a graphite cathode resulted in the apparent production of lead and sulfur. However, except for a difference in back-emf, the calcium sulfide result with a graphite cathode was similar to the sodium sulfide results. The causes of these differences in behavior are probably complex, and could involve factors such as differences in deposition potentials among the various cations, concentration polarization due to the fairly high current densities used (approximately 0.5 a/cm^2), secondary electrode reactions, etc.⁽⁵⁶⁾

The major experimental problem continues to be oxygen contamination. More experiments are planned with CaS to determine whether the problem can be overcome. It is possible that good results may only be attainable when high-purity materials are used under glovebox conditions.

b. Plutonium Monosulfide (O. L. KRUGER AND J. B. MOSER)

The sintering characteristics and properties of PuS are being studied as part of a broad program to evaluate potential nuclear fuels. Material for this study was prepared by the gas-metal reaction described previously.⁽⁵⁷⁾ Briefly, the method consists of reacting partially decomposed plutonium hydride with hydrogen

⁽⁵²⁾ Shalek, P. D., *Preparation and Properties of Uranium and Thorium Monosulfides*, J. Am. Cer. Soc. **46** (4) 155-161 (1963).

⁽⁵³⁾ Yoshioka, Y., *Preparation of Uranium Monosulfide*, U.S. Pat. No. 3,119,653 (January 28, 1964).

⁽⁵⁴⁾ Didchenko, R., and Litz, M., *Preparation of Lanthanide and Actinide Monosulfides by Fused Salt Electrolysis*, J. Electrochem. Soc. **109** (3) 247-250 (1962).

⁽⁵⁵⁾ Allbutt, M., and Junkison, A. R., *The Preparation and Properties of Uranium Monosulfide and Uranium Monophosphide* (Presented at Libby-Cockcroft Meeting, Hanford, May 1964).

⁽⁵⁶⁾ Delimarskii, Iu. K., and Markov, B. F., *Electrochemistry of Fused Salts*, (Sigma Press, Washington, D.C., 1961).

⁽⁵⁷⁾ *Annual Report for 1963, Metallurgy Division, ANL-6868*, p. 139.

TABLE 30. RESULTS OF EXPERIMENTS ON THE ELECTROLYTIC PREPARATION OF US

Run No.	Batch Composition		Temp. (°C)	Applied emf (Volts)	Back emf (Volts)	Time (mins.)	Products
	Components	Amount (g)					
E-4	UF ₄	4	500	5.0	3.5	125	U, UOS, UO ₂ + alkali metal
	Na ₂ S·XH ₂ O	30					
	LiCl-KCl	90					
E-9	UCl ₄	4	700	5.0	3.4	60	UOS, UO ₂
	Na ₂ S·XH ₂ O	30					
	NaCl-KCl	90					
E-16	UCl ₄	4	700	5.0	2.6	100	Analysis Incomplete
	CaS	1					
	NaCl-KCl	90					

sulfide over the temperature range 400 to 600°C. The resulting sulfide powder is then homogenized for four hours under vacuum at temperature of 1600 and 1500°C, respectively. The material prepared by this technique was characterized by means of chemical analysis, X-ray diffraction and metallographic examination.

Emphasis has been placed on the purity of PuS because the presence of oxygen may adversely affect its thermal properties. High-purity material will be needed to establish reference values so that the effects of impurities can be studied. Plutonium sulfide was found to contain about 0.01w/o oxygen and 0.01w/o nitrogen when high-purity plutonium metal was used in its preparation. This high degree of purity was achieved only by using high-purity gases and in a leak-tight apparatus.

TABLE 31. LATTICE CONSTANTS OF PuS, Pu₂S₃ AND PuP PHASES IN VARIOUS PLUTONIUM-SULFUR AND PLUTONIUM-PHOSPHOROUS COMPOSITIONS

Compound	Lattice Constant (Å)	
	This Work	Other
PuS	5.5383 ± 0.0001	5.525 ± 0.001 ^(a)
	5.5393 ± 0.0001	
	5.5402 ± 0.0001	
	5.5408 ± 0.0001	
	5.5409 ± 0.0001	
Pu ₂ S ₃	8.4182 ± 0.0001	8.4373 ± 0.0005 ^(a)
	8.4193 ± 0.0001	
PuP	5.6562 ± 0.0001	5.644 ± 0.004 ^(b)
	5.6572 ± 0.0001	
	5.6598 ± 0.0001	

^(a) Zachariasen.

^(b) Gorum.

06-8024

100×

FIG. 74. Predominantly PuS (light) with some Pu₂S₃ (dark); as polished.

Some results of precision lattice constant determinations are shown in Table 31. Plutonium monosulfide in equilibrium with Pu₂S₃ had a lattice constant of 5.5409Å, while the lattice constant of pure PuS was 5.5383Å. Further work is needed to determine the dependence of the PuS lattice constant on composition. Values are given in Table 31 for Pu₂S₃ in equilibrium with PuS after annealing at 1600°C.

The microstructure of almost pure PuS is shown in Figure 74. The PuS phase is light with dark Pu₂S₃ located at grain boundaries. Compositions with higher sulfur contents have microstructures containing more of the dark Pu₂S₃ phase.

The sintering characteristics of PuS were investigated. Powder was crushed to a particle size of <44μ, coated with 0.5w/o Carbowax binder and pressed at 2110 kg/cm². Pellets 0.762 cm in diameter by 1.25 cm

106-8031

FIG. 75. Density and Weight Loss of PuS Pellets Sintered under Vacuum at Various Temperatures.

106-8034

FIG. 76. Density and Weight Loss of PuS Pellets Sintered under Argon at Various Temperatures.

long were sintered under a vacuum of $<5 \times 10^{-5}$ mm Hg or in a flowing high-purity argon gas at atmospheric pressure for two hours at intervals of about 100°C.

The changes in density and percent weight loss of the PuS pellets with sintering temperature are shown in Figures 75 and 76. Pellets heated in vacuum attained a density of about 94% theoretical at an optimum sintering temperature of about 1600°C with a weight loss of 1.2% including 0.5w/o binder. At temperatures above 1600°C a slight decrease in the density of the PuS pellets was accompanied by a rapid increase in the rate of vaporization.

106-8030

FIG. 77. Thermal Expansion of PuS.

Sintering under an argon atmosphere greatly reduced the amount of weight loss at temperatures above 1600°C as shown in Figure 76. A maximum density of about 92% theoretical was reached at 1700°C. Above 1800°C a rapid increase in the rate of vaporization was observed.

The theoretical density of PuS, calculated for a stoichiometric compound with a lattice constant of 5.540Å (average of values listed in Table 31) was 10.59 g/cm³. The density of plutonium sesquisulfide was found to be 8.526 g/cm³. This value is based on the assumption that Pu₂S₃ is isostructural with Ce₂S₃-Ce₃S₄ as proposed by Zachariasen.⁽⁵⁸⁾

The average value for the room temperature electrical resistivity of PuS was 2450 ± 150 micro-ohm-cm. This value is considerably higher than the range of 112 to 359 micro-ohm-cm reported for US.

The average linear thermal expansion coefficient of PuS for the temperature 18 to 960°C was $18.54 \times 10^{-6}/^\circ\text{C}$. A typical dilation curve is shown in Figure 77. This high rate of expansion was unexpected since the coefficient for US is $11.6 \times 10^{-6}/^\circ\text{C}$ for the same temperature range.

(58) Zachariasen, W. H., *Crystal Chemical Studies of the 5f-Series of Elements. VI. The Ce₂S₃-Ce₃S₄ Type of Structure*, Acta Cryst. **2**, 57-60 (1949).

2. Properties of (Th, U, Pu) Phosphide Bodies

a. Uranium Phosphide (Y. BASKIN AND J. T. DUSEK)

The compound uranium monophosphide is a potential ceramic fuel material with many interesting properties. Some of these have been reported previously along with details on preparation of the compound.⁽⁵⁹⁾ Research on UP has continued and the more recent results are presented here.

Heating of UP in vacuum above 1400°C invariably resulted in a decrease in its unit cell size of 5.589Å, which value corresponded to that for the stoichiometric compound. Contraction of the lattice was due to preferential loss of phosphorus, which is known to produce this effect. The lattice parameter reached a minimum value of 5.583Å on heating at 2000°C, and did not change with prolonged heating at this temperature. The cell size showed a slight increase to 5.584Å with heating at 2200°C, but increased substantially to 5.588Å upon heating at 2300°C. These values were for material examined at room temperature and no data are available for material at the elevated temperatures. Nevertheless, the presence of free uranium in grain boundaries of material fired above 2000°C indicated that the metal was eliminated from the lattice on cooling and that departure from stoichiometry was even greater at the firing temperature.

Above 2200°C in vacuum the UP lattice loses uranium preferentially and the compound appears to melt at 2300°C, presumably because of the presence of a liquid phase. In this respect, its behavior is similar to that of UN. Samples fired at 2300°C in vacuum bonded to the tungsten sheet, most probably as a result of the reaction between free uranium and tungsten. Tungsten and UP show little sign of reaction in the absence of free uranium (above 2200°C). Reaction of UP and tantalum was negligible below 2200°C in vacuum, but became catastrophic at this temperature. Investigation of this reaction has not been completed but indications are that it also occurs through the agency of uranium metal.

As discussed above, due to dissociation of UP at elevated temperatures its melting temperature in vacuum is about 2300°C. Its apparent melting point in hydrogen is 2540°C and 2600°C in helium. X-ray analysis of the melted samples indicated considerable dissociation of UP both in hydrogen and helium, suggesting that the melting point of stoichiometric material may be higher than 2600°C. Experiments are under way to obtain the melting point of stoichiometric UP by sealing it in a tungsten crucible. Various methods will be tried with the aim of ascertaining when melting has occurred, without destroying the crucible.

⁽⁵⁹⁾ Annual Report for 1963, Metallurgy Division, ANL-6868, pp. 142-148.

FIG. 78. Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) Curves for UP in Static Air. Material was sintered at 1800°C, ball milled, and passed through a 400 mesh screen. Specimens were diluted with Al_2O_3 and heated at 5°C per minute.

Thermogravimetric analysis (TGA) experiments were conducted to gain further information on the oxidation of UP. A TGA curve representing oxidation of UP is shown in Figure 78, along with a DTA curve for the same material. Data obtained from thermogravimetric analysis corroborated the X-ray diffraction results, namely, that the first two DTA peaks represented oxidation of UP, yielding UO_2 and P_2O_5 . Oxidation rates were somewhat more rapid in the temperature range corresponding to the second peak. The nature of the reaction yielding the gentle slope on the TGA curve between 650°C and 750°C is not known. The different rate for this reaction suggests another oxidation mechanism, possibly oxidation of the uranium tied up in the amorphous phase. The slope on the curve representing the $\text{UO}_2 \rightarrow \text{U}_3\text{O}_8$ reaction was moderately steep and corresponded to the third DTA peak. The small DTA peak at 800°C did not involve any weight gain and apparently represented interaction of the oxides to form a uranium phosphate compound with the formula of $2\text{UO}_{2.67} \cdot \text{P}_2\text{O}_7$. The actual weight gain of 30.55% was only slightly short of

TABLE 32. STATIC OXIDATION RESULTS

Sample No.	Temp. (°C)	Time at Temp. (hr)	Weight Gain* (%)	Oxygen Content, %		Crystalline Phases Present	UP Lattice Constant (Å)
				From Weight Gain**	Chemical Analysis		
Original	—	—	—	—	0.32	UP _(vs) , UO _{2(vw)}	5.589***
9	190–210	270	1.87	2.15	2.29	UP _(vs) , UO _{2(vw)} , UP _{2(vw)}	5.591***
10	220–240	95	3.87	4.03	—	UP _(vs) , UO _{2(w)} , UP _{2(w)} , U ₃ P _{4(vw)}	5.591***
11	230–250	110	5.85	5.82	5.55	UP _(vs) , UP _{2(vw)} , UO _{2(w)} , U ₃ P _{4(vw)}	****
12	250–270	57	7.68	7.44	—	UP _(vs) , UP _{2(w)} , UO _{2(w)}	
13	250–270	68	10.02	9.39	9.30	UP _(s) , UP _{2(m)} , UO _{2(m)}	
14	250–270	68	12.09	11.08	—	UP _(s) , UP _{2(m)} , UO _{2(m)}	
15	250–270	92	14.15	12.68	12.6	UP _(s) , UP _{2(ms)} , UO _{2(ms)}	
16	260–280	130	17.31	15.01	—	UO _{2(s)} , UP _{2(mo)} , UP _(ms)	
17	270–290	67	19.29	16.44	15.6	UO _{2(s)} , UP _{2(m)} , UP _(m)	
18	280–300	117	21.46	17.92	—	UO _{2(sv)} , UP _{2(w)} , UP _(w)	
19	290–310	130	23.53	19.30	18.6	UO _{2(vs)} , UP _{2(w)} , UP _(w)	
20	310–330	178	25.55	20.59	20.4	UO _{2(vs)} , UP _{2(vw)}	
21	370–500	470	27.89	22.06	21.0	UO ₂	
22	490–510	91	29.91	23.30	—	UO _{2(s)} , β-U ₃ O _{7(m)}	
23	500–520	112	31.12	23.97	22.3	U ₃ O ₈	
24	520–580	180	32.02	24.50	23.7	(UO ₂) ₂ P ₂ O _{7(vs)} , U ₃ O _{8(m)}	
25	600–620	64	32.33	24.72	24.2	(UO ₂) ₂ P ₂ O ₇	
26	640–800	185	32.08	24.55	25.7	(UO ₂) ₂ P ₂ O ₇	

* Experimental weight gains were recalculated in terms of the UP constituents, which comprised 97.3% of the original material.

** Oxygen contents derived from weight gain also include amount present originally (0.32%).

*** Lattice constants were accurate to ± 0.001 .

**** UP pattern was too diffuse in high-angle region for accurate lattice-constant determination.

NOTE: vs = very strong, s = strong, ms = moderately strong, m = moderate, w = weak, and vw = very weak.

the calculated weight gain of 30.73%, the difference being attributed to volatility of P₂O₅. Further weight gain on cooling was attributed to oxidation of the phosphate to (UO₂)₂P₂O₇, but probably also to some moisture pickup.

Results of the static air oxidation study involving fine UP powder (calcined at 1400°C), are presented in Table 32. Although not shown, the TGA curve for this material was identical to that shown in Figure 78. Chemical analysis essentially confirmed that the weight gains were a result of oxygen pickup. The UP structure showed signs of degradation when the sample exhibited an oxygen pickup of 1.87%. The high angle X-ray reflections became somewhat diffuse and the lattice showed a small expansion. These two phenomena may have been caused by the presence in the UP structure of oxygen atoms in interstitial positions, producing an enlarged and strained lattice. While the UP lattice did not exhibit further expansion with additional oxygen pickup by the sample, the patterns became steadily more diffuse with increasing oxygen content, making it impossible to obtain accurate lattice constants.

A diffuse pattern for UO₂ was visible in the X-ray pattern of material showing a 1.87% weight gain. A

faint pattern for UP₂ was also visible, and these two phases become more prominent as the sample reacted with additional oxygen. As mentioned previously,⁽⁶⁰⁾ higher phosphides formed during oxidation of UP as displaced phosphorus atoms reacted with the underlying monophosphide. While some U₃P₄ formed, formation of UP₂ clearly was favored. A similar situation was noted when UP was reacted with phosphorus vapor under low pressures at 300°C. Large quantities of UP₂ formed, while only small amounts of U₃P₄ resulted. Evidently, phosphorus atoms reacted rapidly with UP at low temperatures under both oxidizing and reducing conditions, and formation of UP₂ was favored over that of U₃P₄.

The X-ray patterns for UO₂ were too diffuse to permit accurate measurement of the lattice constant. Thus, it was not possible to secure information about the O/U ratio through X-ray means. However, based on weight gain data it appeared that the UO₂ in sample No. 21 (Table 32) was hyperstoichiometric. Possibly, the UO₂ in samples exhibiting less weight gain than No. 21 also had O/U ratios greater than two. No s

⁽⁶⁰⁾ Annual Report for 1963, Metallurgy Division, ANL-6868, p. 147.

a crystalline phosphate compound was detected until the temperature was raised above 520°C. The maximum weight gain observed, 32.33%, fell somewhat short of the value of 32.71% calculated for oxidation of UP to $(\text{UO}_2)_2\text{P}_2\text{O}_7$. The discrepancy was presumably caused by loss of P_2O_5 . Prolonged heating of $(\text{UO}_2)_2\text{P}_2\text{O}_7$ at temperatures above 640°C resulted in weight loss, again probably due to volatilization of P_2O_5 .

A series of UP pellets were prepared and fired for one hour in vacuum at temperatures ranging from 1600°C to 2200°C. Some of the powder was pelletized without any further treatment, while other powder was ball milled for five hours. Results are given in Table 33 and show the effect of ball milling on sintered density, which was marked for pellets fired at the lower temperatures. Ball milling resulted in some improvement in green density, but its main effect appeared to be that of increasing the activity of the powders. There was little improvement in sintered density on firing above 2000°C, since further densification was offset by weight losses which increased rapidly above this temperature. Weight losses for UP at 2200°C were about four times greater than those at 2000°C.

Pellets were fired for different time periods at 2000°C and all had identical firing schedules up to that temperature. The data presented in Table 34 show only moderate density changes with increased soaking time; however, grain growth was significant. Grain size was about three times larger in the samples fired for five hours as compared to those fired for five minutes. Considerable coalescence of pores also took place with additional heating.

In order to produce larger specimens for some mechanical and thermal property measurements, the technique of hot-pressing UP was investigated. UP that had been homogenized at 1400°C was crushed to powder having an average particle size of 2.5 μ . Several parameters were varied in an effort to produce specimens having an L/D ratio over 3, as shown in Table 35. In the initial experiments, cracking of the specimens was common. This cracking resulted from the specimens sticking to the graphite mold and punches. This sticking did not permit the specimens to contract on cooling, and stresses which developed caused the specimens to crack. The use of a thin layer of powdered charcoal between the specimen and the graphite punches eliminated sticking at the ends. The transverse cracking was reduced significantly by lower-

sintering temperature and shortening the firing cycle. This is shown by the specimens pressed at temperatures which did not exceed 1625°C and at cycles of less than twenty minutes. By this procedure UP

TABLE 33. SINTERED DENSITY* AS A FUNCTION OF FIRING TEMPERATURE, AND POWDER TREATMENT (ONE HOUR AT TEMPERATURE)

Sintering Temperature	1600°C	1700°C	1800°C	2000°C	2200°C
Untreated	86.8	90.3	93.0	95.6	96.1
Ball Milled	93.7	95.6	95.9	96.6	96.7

* Percent of Theoretical Density (10.2 g/cm³).

TABLE 34. SINTERED DENSITY* AS A FUNCTION OF FIRING TIME (UNTREATED POWDER)

Property of Pellets	Time at 2000°C, minutes			
	5	20	60	300
Density, Percent of Theoretical	90.7	93.1	93.6	95.5
Average Grain Size, mm	0.0060	0.0088	0.0120	0.0160

* Percent of Theoretical Density (10.2 g/cm³).

TABLE 35. HOT-PRESSING OF UP USING GRAPHITE MOLDS AND AN ATMOSPHERE OF FLOWING ARGON

Firing Time (mins.)	Peak Mold (°C)	Soak Time (mins.)	Press kg/cm ²	Pellet L/D	Percent (U.D.)	Phases	Remarks
85	1750	30	150	1.64	89.0	UP UO _{2(w)} *	End Broken
72	1670	21	140	1.85	—	UP UO _{2(w)}	End Broken
75	1780	30	175	—	—	UP UO _{2(w)}	Good
82	1740	50	705	3.63	—	—	Cracked
100	1760	50	175	3.98	—	—	Cracked
85	1800	57	175	3.91	82.7	UP UO _{2(w)}	Cracked
50	1625	15	140	3.91	82.6	UP UO _{2(w)}	Good
42	1615	18	600	3.69	92.0	UP UO _{2(w)}	Good

* w = weak.

could be fabricated to densities as high as 92% of theoretical.

b. Thorium Phosphide (Y. BASKIN)

Thorium phosphide shows promise as a ceramic nuclear fuel material because of its refractoriness and other attractive high-temperature properties. Compounds in the system Th-P have been synthesized previously, but few property determinations have been made at elevated temperatures. The present investigation was conducted with the aim of obtaining such data in order to evaluate the fuel potential of ThP.

Thorium phosphide was prepared by reaction of phosphine gas with finely divided thorium obtained by successive hydriding and dehydriding steps.⁽⁶¹⁾ The active powder was brought in contact with PH₃

⁽⁶¹⁾ Annual Report for 1963, Metallurgy Division, ANL-6868, p. 148.

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FIG. 79. Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) Curves for ThP in Static Air. Material was calcined at 1300°C in vacuum. Specimens were diluted with 3 parts powdered alumina and heated at 5°C per minute.

TABLE 36. SOME PROPERTIES OF THORIUM PHOSPHIDE

Color	— Dark Blue
Crystallographic Structure	— Rock-Salt
Lattice Constant	— 5.833Å
Density	— 8.83 g/cc
Melting Point	— 2900° ± 50°C
Electrical Resistivity (R.T.)	— 34 μohm-cm
Sinterability	— Fair to Moderate
Volatility in Vacuum at 2200°C	— Very Low
Oxidation-Resistance	— Excellent
Resistance to Moisture	— Fair
Average Chemical Analysis	— 88.57% Th, 11.12% P, 0.31% O
Average P/Th Ratio	— 0.97

gas at temperatures above 550°C to initiate the reaction. A mixture of Th_3P_4 and thorium resulted when a stoichiometric amount of PH_3 was reacted with the metal. Homogenization of the reacted material in vacuum at 1200°C to 1300°C produced slightly hypostoichiometric ThP, with P/Th ratios ranging from 0.99 to 0.95. Chemical analysis also showed the presence of from 0.3 to 0.4 *w/o* oxygen in the ThP, with virtually all of it being present in a secondary ThO_2 phase. The homogenized ThP powder was not pyrophoric and could be safely handled in air.

Some properties of thorium phosphide are listed in Table 36. Among the more unusual properties are the dark blue color, the relatively high electrical conductivity and the high melting point. Sinterability of the compound was only fair; material fired at 1800°C for two hours exhibited densities ranging from 70 to 78%

of the theoretical value. Only slightly higher densities were achieved by increasing the sintering temperatures to 2000°C and 2200°C. Thorium phosphide exhibited very low weight losses upon heating in vacuum at 2200°C. In spite of their greater surface area, pellets of ThP experienced smaller weight losses than those of UP under identical conditions.

Oxidation of thorium phosphide ($\text{ThP}_{0.99}$) was investigated by the DTA and TGA techniques and the results are shown in Figure 79. The TGA curve shows the occurrence of very rapid oxidation between 650°–680°C, with the reaction being virtually complete by the time the latter temperature was attained. The weight gain of 27.4% corresponded to complete oxidation of essentially stoichiometric ThP to a mixture of ThO_2 and P_2O_5 . X-ray diffraction analysis of the oxidized material only revealed the presence of ThO_2 ; phosphorus pentoxide was presumed to be present in an amorphous or vitreous phase. Retention of all the phosphorus pentoxide after heating to 950°C was unusual and could only be explained by assuming that it was tied up with thorium oxide in a vitreous phase having a much lower vapor pressure than P_2O_5 (which is very volatile above 500°C). Similar retention of P_2O_5 was observed during studies of the oxidation of UP.⁽⁶²⁾

The DTA thermogram corresponding to oxidation of thorium phosphide ($\text{ThP}_{0.99}$) shows a major, asymmetric peak at 670°C, and a minor peak at 560°C. The relatively good oxidation resistance of ThP, as evidenced by the high temperature of its major exothermic peak, is attributed to the existence of a protective amorphous coating of $\text{ThO}_2\text{-P}_2\text{O}_5$, similar to that with UP, and to the greater stability of the compound itself. On the basis of other DTA studies involving ThP as well as DTA studies of the oxidation of UP, it is presumed that the minor peak was caused by oxidation of the very fine fraction of the powder and that the asymmetry of the major peak was caused by delayed oxidation of the coarser fraction. X-ray diffraction analysis of oxidized material also revealed ThO_2 as the only crystalline phase; no sign of a thorium phosphate compound was observed.

c. Plutonium Monophosphide (O. L. KRUGER AND J. B. MOSER)

The preparation, sintering and properties of PuP are being studied in order to evaluate this material as a nuclear fuel. Material for this study was prepared by either the gas-metal reaction⁽⁶³⁾ in a manner similar to that for the preparation of PuS, but with the use of

⁽⁶²⁾ Baskin, Y., *Oxidation Behavior of Uranium Monophosphide*, J. Am. Ceram. Soc., (in press).

⁽⁶³⁾ *Annual Report for 1963, Metallurgy Division, ANL-6868*, p. 139.

phosphine gas, or by the reaction of the elements in a pressure vessel.⁽⁶⁴⁾

The PuP produced by the gas-metal reaction was not as pure as the PuS produced by the pressure vessel, addition reaction even though the gases used in the phosphide preparation were thought to be ultra-pure. The best PuP produced to date contained 0.052w/o oxygen and 0.067w/o nitrogen.

For the reaction of plutonium and phosphorus in a pressure vessel, pieces of plutonium were reacted with hydrogen at about 200°C and then dehydrided at 600°C. This procedure produced sintered plutonium that was easily crushed to a particle size of <44 μ . Plutonium and red phosphorus powders were sealed in a pressure vessel that was heated slowly to between 550°C and 650°C, held for five hours and cooled. Excess phosphorus was separated from the PuP powder by distillation. X-ray photograms of the powder showed single-phase PuP and chemical analysis gave values for the oxygen and nitrogen content of 0.15 and 0.02 respectively. Pellets were prepared by vacuum sintering at 1600°C and further studies on this material are in progress.

The lattice constant of PuP produced by the gas-metal reaction (see Table 36) in equilibrium with plutonium was 5.6562Å. Comparison of this value with the value of 5.644Å obtained on material made with the pressure vessel reaction showed that there may be a substantial increase in lattice constant with increasing phosphorus content within the PuP phase field.

The sintering characteristics of PuP were determined on material crushed to <44 μ . The PuP particles were coated with 0.5% Carbowax and pressed at 2110 kg/cm². Pellets formed were sintered under a vacuum of $<5 \times 10^5$ mm Hg for 2 hours at increasing temperature intervals of 100°C.

The change in density and percent weight loss is shown in Figure 80. A maximum density of 88% of theoretical density was achieved at a sintering tem-

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FIG. 80. Density and Weight Loss of PuP Pellets Sintered under Vacuum at Various Temperatures.

perature of 1600°C with a weight loss of 2.1%. Above this temperature the rate of vaporization increased rapidly while the sintered density decreased only slightly. The calculated density of PuP with a lattice constant of 5.6598Å and 9.893 g/cm³.

Melting points of PuS were measured in a tungsten filament furnace. Plutonium monosulfide melted at 2330°C under a pressure of 1 atm. The rate of vaporization of PuP heated above 2400°C under a pressure of 1 atm was so great that the sight glass fogged and the melting point could not be measured. A sample heated under two atmospheres of pressure melted at a power setting on the furnace that corresponded to a temperature of about 2900°C. This value is quite high for a plutonium compound and further work is needed to determine a more exact melting point. The melting point of PuP probably lies between the melting point of UP (2540°C) and that of ThP (3000°C).

3. Binary Compound Systems

a. Phase Studies in the System ThP-UP (Y. BASKIN)

A study of the system ThP-UP was undertaken to obtain information on the phase relationships and physical properties of the binary compositions. Studies are being conducted on the individual compounds, both

of which exhibit many interesting properties that make them potential nuclear fuel materials.

Both UP and ThP were made by reacting the metal powders with PH₃ at low temperatures, followed by homogenization in vacuum at 1400°C.⁽⁶⁵⁾ Initially, powders were blended, pelletized and fired in vacuum;

⁽⁶⁴⁾ Annual Report for 1963, Metallurgy Division, ANL-6868, p. 149.

⁽⁶⁵⁾ Baskin, Y., and Shalek, P. D., *Synthesis of Uranium Monophosphide by the Phosphine Reaction*, J. Inorg. Nucl. Chem., **26**, 1679-1684 (1964).

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Fig. 81. Preliminary Phase Diagram of System ThP-UP.

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Fig. 82. Differential Thermal Analysis (DTA) Curves for ThP, ThP-UP Solid Solutions and UP in Flowing Oxygen. All samples were fired at 1800°C in vacuum and then ground up to pass 200 mesh screen. Specimens were diluted with 3 parts powdered alumina and heated at 5°C/minute.

first at 1800°C, then at 2000°C and finally at 2200°C. Broadened and diffuse X-ray reflections indicated that equilibrium was not reached, probably as a result of poor mixing. Another series of pellets was prepared,

but this time the powders were intimately mixed and further comminuted by ball milling. Equilibrium was attained by firing these pellets in vacuum for 7 hours at 2000°C. Shalek found similar difficulty in completely reacting ThS and US, and ultimately used a firing temperature of 2050°C.⁽⁶⁶⁾

X-ray diffraction and metallographic analysis disclosed that ThP and UP exhibited complete mutual solubility. This was not surprising in view of the small difference in lattice constant values between the two compounds, and the fact that such systems as ThO₂-UO₂, ThC-UC, ThS-US, and others are mutually soluble. Lattice constants of compositions at 12.5% intervals across the system fell on a fairly smooth curve that exhibited a slight positive deviation from linearity (Vegard's Law).

Melting temperatures of selected compositions in the system also fell on a fairly smooth curve. A preliminary phase diagram of the system, based on X-ray and melting temperature data, is shown in Figure 81.

Sintered densities generally showed an increase with increasing amounts of UP, from 81% of theoretical for ThP to 95% of theoretical for UP. Weight losses in vacuum at 2200°C were also higher toward the UP end of the system despite the lower surface area of the pellets. However, this might have been expected since ThP exhibited a much higher melting temperature in helium than UP, 2900°C versus about 2600°C.

Oxidation behavior of ThP-UP solid solutions was studied by the DTA technique, and the results are shown in Figure 82. The major exothermic peak of ThP (670°C) was shifted to slightly lower temperatures with increasing UP content, but, otherwise, the changes were minor. ThO₂ was the only crystalline phase observed in the oxidized residues of ThP, but this changed to a ThO₂-UO₂ solid solution for binary compositions, with the UO₂ content rising with increasing uranium content in the original sample. A moderate peak at 740°C appeared for the sample containing 25%ThP-75%UP. This peak was identical to one occurring with UP and has been identified as being associated with the UO₂ → U₃O₈ reaction.⁽⁶²⁾ In confirmation, U₃O₈ was observed in both X-ray patterns. An unknown phase appeared in the residue of sample 50%ThP-50%UP and again, somewhat stronger, in the 25%ThP-75%UP sample. The pattern may represent that of a (thorium, uranium) phosphate, but it has not yet been identified.

⁽⁶⁶⁾ Shalek, P. D., *Preparation and Properties of Uranium and Thorium Monosulfides*, J. Am. Ceram. Soc., 46 (4) 155-161 (1963).

b. Uranium Carbide-Uranium Sulfide (G. D. WHITE AND J. T. DUSEK)

The system UC-US is being investigated to ascertain the effect of US on the behavior of UC. The preliminary phase equilibrium diagram⁽⁶⁷⁾ indicated that no compounds were formed. This diagram showed the presence of two solid solution regions, a UC(S) which has a maximum of 4*m/o*US in solution at 1600°C, and a US(C) which contains 40*m/o*UC at 1600°C. The region between is composed of two saturated solid solutions. The compounds UC and US have unit cell sizes of 4.96Å and 5.49Å respectively and the saturated solid solutions UC(S) and US(C) equilibrated at 1600°C and quenched have unit cell sizes of 4.98Å and 5.32Å respectively. One of the interesting properties of this system is the large improvement in inertness to room atmosphere imparted to sintered UC specimens by small US contents. Consequently an oxidation study was done in which use was made of thermogravimetric and differential thermal analyses.

All powders to be analyzed were prepared by crushing sintered specimens under alcohol and, after evaporation of the alcohol, screening to the desired particle size. The sized powders were mixed with an equal weight of Al₂O₃ powder for analysis. Analyses were done on commercially available equipment.

The specimens for thermogravimetric analysis were reduced to -140M and mixed with Al₂O₃ powder. The mixed powders were placed in an alumina crucible with a porous bottom which was suspended on the balance and heated in static air at 5°C/minute up to 1000°C. Weight changes were automatically recorded on a strip chart recorder.

The plots of percent weight change versus temperature are shown in Figure 83 for UC, UC-4*m/o*US, UC-60*m/o*US, UC-80*m/o*US, and US. UC begins to gain weight at 250°C slowly and at 320°C the weight gain becomes very rapid. Oxidation is virtually complete at 360°C. The UC-4*m/o*US begins gaining weight at the same temperature as UC but the rapid weight gain parallels that of UC 25° higher. Oxidation is complete at 400°C. The specimens of UC-60*m/o*US and UC-80*m/o*US produced very similar plots except for their heights, which are the total gains in weight. Both started gaining weight at 375°C and the very rapid gain in weight occurred between 415°C and 450°C. The plots above 450°C were parallel. The US began to gain weight at 375°C and the weight gain was rapid from 415°C to 425°C. A less rapid weight gain occurred between 425°C and 575°C where the maximum weight in was recorded. The weight of each of the specimens decreased from its maximum up to the 1000°C termi-

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FIG. 83. Thermogravimetric Plots for Compositions Heated in Air at 5°/min. Powders of each composition were prepared by crushing sintered specimens to pass a 140M sieve and were diluted by an equal weight of Al₂O₃.

nation. This decrease was proportional to the amount of sulfide in the specimen. Also the maximum weight gain was greater than that calculated for the complete oxidation of the composition to U₃O₈ for all compositions except UC; this difference was also in proportion to the amount of sulfide in the composition. The final weights for each specimen were less than those calculated for complete conversion to U₃O₈ with expulsion of initial anions. The excessive maximum weights could be explained by sulfur retention in the structure after oxidation and the subsequent decrease in weight by the expulsion of sulfur. However the decrease to below the calculated U₃O₈ value can not be explained unless the U₃O₈ begins to lose oxygen below 1000°C. On cooling the weight did increase but not up to the calculated value for the conversion of the composition to U₃O₈. X-ray diffraction on the oxidized specimens produced reflections for U₃O₈ only.

Differential thermal analyses were done on the same compositions as above. Specimens were crushed to -140M and mixed with Al₂O₃ powder. The heating rate was 5°C/minute up to 1000°C and the atmosphere was static air. The cup holding the specimen had a porous bottom; consequently, conditions were very similar to those for the thermogravimetric analyses.

The differential thermal curves for UC and UC-4*m/o*US were similar; two exotherms occurred as shown in Figure 84, the weaker at 350°C and the stronger at 390°C to 395°C. The first exothermic ef-

⁽⁶⁷⁾ Annual Report for 1963, Metallurgy Division, ANL-6868, p. 155.

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FIG. 84. Differential Thermal Plots for Compositions Heated in Air at 5°/min. Compositions were sintered, crushed to pass 140M, and diluted by an equal weight of Al_2O_3 .

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FIG. 85. Differential Thermal Analysis Plots for Powders Diluted with an Equal Weight of Al_2O_3 Oxidized in Water-Saturated Argon at a Temperature Rise of 5°/min. Powders were prepared by crushing sintered specimens of the compositions and taking the $-100\text{M} + 325\text{M}$ fraction.

fect of the UC-4m/oUS specimen was weaker than that of the UC. No other differential heat effects were present up to 1000°C. The curves for the other three compositions contained three common heat effects: a large exotherm at 410°C to 430°C, a weak exotherm at 530°C to 560°C, and a weak endotherm at 750°C. In addition the US specimen exhibited a weak exothermic effect at 615°C. X-ray analyses of specimens heated to a temperature immediately above the largest exotherm and also to 1000°C revealed the presence of only U_3O_8 . It is thought that the weak differential thermal effects present on the plots for US-rich specimens at higher tem-

peratures are associated with the reaction of sulfur still present in the oxide and the expulsion of the sulfur from the lattice of the oxide after the oxidation is complete. This correlates with the excessive weight gain and loss of the US-rich specimens discussed above.

Further differential thermal analyses were run on specimens of UC, UC-60m/oUS, and US crushed to $-100\text{M} + 325\text{M}$. The powders were again mixed with Al_2O_3 powder and were heated at 5°C/minute to 1000°C in flowing, water-saturated argon. Additional oxidations in water-saturated argon were done to appropriate temperatures to determine the reactions causing the observed thermal effects.

All three compositions produced differential thermal plots containing three distinct exothermic effects shown in Figure 85. Each of these exotherms was broad and was terminated on the upper side by the beginning of the next exotherm. The first exothermic effect for UC reached a maximum at 315°C, for UC-60m/oUS at 405°C, and for US at 400°C. All three of these exotherms began approximately 100°C below the peak temperatures. The second exotherm peaked at 500°C for each of the compositions. The maximum was reached on the third exotherm at 775°C, 730°C, and 675°C for UC, UC-60m/oUS, and US respectively. The peak of the first exotherm for UC occurs approximately 35°C lower than the lower of the two exothermic peaks for UC oxidized in air; whereas, the US and UC-60m/oUS produced initial exotherms which reached maxima at approximately the same temperature as their single exotherms in air.

X-ray diffraction of a UC specimen heated in flowing, water-saturated argon in the DTA apparatus to just above the first maxima produced strong reflections for UC and weak reflections for UO_2 . A specimen heated to just below the second maximum produced X-ray reflections which were strongest for UO_2 and much weaker for UC and very weak for U_3O_8 . Heated to just above the second maximum, a UC specimen produced X-ray reflections of very great strength for U_3O_8 and of much less intensity for UO_2 . A specimen heated to just above the maximum of the third exotherm still contained a small percentage of UO_2 . However specimens heated to 1000°C were completely oxidized to U_3O_8 .

Specimens of US heated to temperatures just below and just above the maximum of the first exotherm and just above the maximum of the second exotherm produced weak reflections for UOS and strong, diffuse reflections, which could be either UO_2 or US or mixture of the two, as the cell parameters for these two compounds are separated by only 0.020Å. When heated to just above the maximum of the third exotherm a specimen produced very strong reflections for U_3O_8 and weak reflections for UO_2 . At 1000°C oxidation was

complete. The overlapping presence of oxide phases from one temperature to the next seemed to indicate that the spread and discreteness of the exothermic effects were more a function of particle size spread than of specific oxidation reactions. A specimen of US crushed to -325M was analyzed under conditions the same as above. The initial exotherm came at approximately the same temperature but was much more intense and less broad and the second was broad and much less intense. The total spread of the heat effects was greatly reduced. X-ray analysis on this thermograph has not been done.

Most significant in these results is that the UC specimen began to react in water-saturated argon at almost as high a temperature as in air and the US and UC-60*m/o*US began at approximately the same temperature as in air. In view of the fact that these specimens were exposed to the flowing, water-saturated argon overnight at room temperature, the reaction of atmosphere water with these powders at room temperature must produce a very small amount of oxide restricted to a thin layer on the surface. This oxide coating would then act as a barrier to further oxidation unless the ratio of surface area to volume of the particles is large enough that the heat of reaction raises the temperature of the powder to the ignition temperature. Powders of UC can be made nonpyrophoric in air by exposing them to moisture in an inert atmosphere or by spreading them into a very thin layer before exposing them to air.

Specimens of the composition UC-20*w/o*US were prepared for irradiation. The specimens in the form of cylindrical pellets were approximately 20% enriched and had a diameter between 0.6350 and 0.6477 cm and a length of approximately 1.27 cm. Total length of pellets made was 101.6 cm, of which 20.32 cm contained an axial hole 0.250 ± 0.005 cm in diameter.

The US was prepared by reacting H_2S with fully enriched uranium metal powder. The UC, depleted in U^{235} content, was produced by arc melting. Both materials were crushed to pass an 80M sieve and two lots of the composition were formulated. Each of the lots was ball milled in xylene, dried, mixed with 1% of 2:1 stearic acid-Acryloid binder which was dissolved in xylene, cold-pressed, and vacuum sintered at 1750°C for three hours. The first lot, because of insufficient ball milling, resulted in pellets of insufficient density; consequently the pellets were crushed, ball milled, and refabricated. The second lot was milled for a longer time initially and the pellets produced were of required density.

Densities of the pellets from both batches were between 89 and 91% of theoretical. The unit cell sizes of the UC(S) solid solution were $4.991\text{\AA}$ for the first batch and $4.974\text{\AA}$ for the second. Unit-cell sizes could

FIG. 86. Etched Polished Section of a Sintered Pellet of 20% Enriched UC-20*w/o*US. After the first sintering the pellet was reduced to a powder, which was pressed and sintered again.

not be determined for the US(C) solid solution because the X-ray reflections were too weak. Microphotographs of polished and etched specimens are shown in Figures 86 and 87. The lack of equilibrium in the specimens of the second batch is evident from the lattice parameters and the microstructure, the dark phase is US. Further reduction of particle size of the second batch would have improved the equilibrium attainable at the sintering conditions.

For some mechanical and thermal property measurements, specimens having a length to diameter ratio of over three were needed. Hot-pressing seemed to be a suitable method for producing these specimens, and the fabrication of compositions within the binary UC-US is being investigated.

Uranium carbide prepared by either arc-melting of the elements or by preparation from a zinc-magnesium melt was used. The arc-melted UC was crushed to minus 80 mesh and then ball milled for six hours. The precipitated UC is a fine powder, and was used without further treatment. Specimens hot-pressed by graphite molds under the conditions shown in Table 37 were found to be cracked when removed from the mold.

Uranium sulfide prepared by the metal- H_2S gas re-

39694

250X

FIG. 87. Etched Polished Section of Sintered Pellet of 20% Enriched UC-20w/oUS.

compositions showed many interesting properties. The preliminary phase diagram showed a melting maximum at UP-30w/oUS and a minimum at UP-90w/oUS. X-ray diffraction analysis did not reveal any compound formation at either of these compositions; however, bonding was apparently enhanced in the composition UP-30w/oUS and weakened in the latter composition. Microhardness and weight-loss measurements were conducted on samples of the two intermediate compositions and the end members to learn whether analogous effects could be discerned in these two properties, which are also strongly influenced by bond strength.

Microhardness measurements showed a general increase in hardness with rising US content. UP had a room temperature Vicker's hardness value of 245 kg/mm², UP-30w/oUS a value of 239 kg/mm², UP-90w/oUS a value of 279 kg/mm², and US a value of 286 kg/mm². As seen in Table 38, samples showed very small weight losses on firing in vacuum at 1800°C, although US exhibited the largest loss. Weight losses at 2200°C were much more pronounced; UP showed a smaller loss than US, but the composition UP-90w/oUS had the greatest loss. However, as pellets of the inter-

TABLE 37. HOT-PRESSING OF COMPOSITIONS IN THE SYSTEM UC-US

Material	Firing Time (mins.)	Peak Mold (°C)	Soak Time (mins.)	Press kg/cm ²	L/D Ratio	Percent Theoretical Density	Phases	Remarks
UC	53	1485	17	705	3.7	88.1	UC	Cracked
UC-20w/oUS	101	1625	4	140	—	—	UC-US	Cracked
UC-20w/oUS	100	1600	40	175	5.2	—	—	Cracked
US	55	1730	30	120	1.3	85.0	US	Good
US	44	1490	11	560	1.1	95.2	US UOS _(w) *	Good

* w = weak.

action was homogenized at 1900°C and then crushed to pass a 400 mesh screen. This material was hot-pressed in graphite molds, and specimens having densities up to 95.2% of theoretical were formed. These specimens were short having an L/D ratio of up to 1.3, however, it appears that US is amenable to hot-pressing with only a minimal amount of oxidation.

A mixture of UC-20w/oUS was also used in these experiments. The two materials were ball milled for eight hours and specimens were then hot-pressed. The specimens were found to be cracked when removed from the mold, and additional work will be necessary to determine the parameters for hot-pressing these mixtures.

c. Uranium Phosphide-Uranium Sulfide (Y. BASKIN)

Earlier studies⁽⁶⁸⁾ revealed that UP and US exhibited complete mutual solubility, and that the intermediate

mediate compositions were less dense (and had greater surface areas) than those of the pure compounds, only limited comparisons can be made among the weight-loss results. It is possible that if all other factors were equal the weight losses across the compositional range would also rise with increasing US content, as did the microhardness values.

Only minor changes occurred in the lattice constants of the two binary compositions on refiring at 2200°C, and these appeared to parallel changes in the major constituents. In the case of UP, the slight decrease in lattice constant was a result of selective loss of phosphorus. For the US, the increase in cell size was probably due to loss of dissolved oxygen from the lattice. Analysis of the material that condensed on the crucible top during firing of samples of composition UP-30w/oUS at 2200°C, revealed that US was preferentially lost from these pellets. The condensate had a somewhat

⁽⁶⁸⁾ Annual Report for 1963, Metallurgy Division, ANL-6868, p. 156.

smaller lattice constant than that of the pellets indicating higher US content. This behavior was consistent with the greater volatility of US as compared to that of UP.

d. Uranium Carbide-Uranium Phosphide (G. D. WHITE AND Y. BASKIN)

A study was initiated in the system UC-UP to determine phase equilibrium relationships and possibly some physical properties in the system. The individual compounds have been studied and are of interest as fuel compounds.

The UC was made by reacting uranium and carbon in an arc-melting furnace. The product was crushed and ball milled to a particle size of $<15 \mu$. X-ray diffraction on the powder produced only reflections for UC with a unit cell size of $4.958\text{\AA}$. The UP was produced by reacting PH_3 with finely divided uranium metal, which was made by hydriding and dehydriding uranium metal chips. The UP was calcined at 1400°C and after screening had a particle size of 2.5μ . The lattice constant of the UP was $5.589\text{\AA}$; the oxygen content was $0.15w/o$ with all of the oxygen being tied up as a secondary UO_2 phase.

Specimens for phase equilibrium studies were prepared by mixing the powders in a mortar and pestle, adding 1% of 2:1 stearic acid-Acryloid as a solution in xylene, and cold-pressing. A number of equilibrations were run in vacuum at 1800°C on selected compositions. A period of six hours was found to be sufficient for attainment of equilibrium. Compositions of 10% intervals across the system were fired in vacuum; intervals

TABLE 38. WEIGHT LOSSES AND LATTICE CONSTANT CHANGES FOR SEVERAL COMPOSITIONS IN THE UP-US SYSTEM (SAMPLES HEATED IN VACUUM)

	UP	UP- 30 ^{w/o} US	UP- 90 ^{w/o} US	US
Weight Loss/Hour at 1800°C , %	0.20	0.22	0.31	0.46
Weight Loss/Hour at 2200°C , %	1.24	2.51	3.75	3.28
Pellet Density, Percent of Theoretical Value	88	83	67	89
Lattice Constant After 2 Hours at 1800°C , $\text{\AA}$	5.586	5.563	5.501	5.486
Lattice Constant After 2 Hours at 2200°C , $\text{\AA}$	5.584	5.560	5.502	5.489

of 2% were used for compositions near the end members.

The reacted specimens were examined by X-ray diffraction and the unit cell sizes determined for the phases. The unit-cell size of UC did not change on firing but the lattice parameter for UP decreased to $5.586\text{\AA}$. This decrease is attributed to the selective loss of phosphorus from the lattice. The change in lattice parameter of UC with the addition of UP was negligible. Additions of UC to UP went into solution to a limit of approximately 4% with an accompanying reduction in lattice parameters from $5.586\text{\AA}$ to $5.560\text{\AA}$. There was much less solubility in this system than in the UC-US system.⁽⁶⁹⁾ However, this would be expected in view of the much larger difference in non-metal radii between carbon and phosphorus as compared to that between carbon and sulfur.

4. Mechanical Properties of Uranium Compounds (C. R. TOTTLE)

Uranium compounds have many suitable properties for application as reactor fuel materials, but little quantitative information is available to assist design from the structural strength standpoint, or to simplify the interpretation of radiation damage. A Riehle testing machine has been equipped with a high-vacuum furnace, provided with a tungsten heating element and tungsten tools, to carry out bend tests at high temperature on bars approximately 6 mm^2 in cross section and 5 cm long. The separate influences of testing strain rate, and processing variables such as density, form part of the study, which initially has centered on uranium dioxide.

High-density UO_2 (95% plus, theoretical density) shows a modulus of rupture of the order of 850–900

kg/cm^2 , at room temperature, with a brittle fracture, i.e., showing little evidence of plastic deformation. Decrease in density has a marked effect in reducing strength, and high strain rates show a small increase in rupture strength for a given green density. At 1000°C , the breaking strength increases to around 1200 kg/cm^2 for high density and slow straining. Decrease in density (92% T.D.) and increase in strain rate ($\times 10$) both lower the strength to about 1000 kg/cm^2 . The first signs of deformation become evident

⁽⁶⁹⁾ Shalek, P. D., and White, G. D., "Studies in the System Uranium Carbide-Uranium Sulphide," *Carbides in Nuclear Energy*, 1, 266–272, MacMillan and Company, Ltd., London (1964).

40403

FIG. 88. UO_2 Bars Deformed by Bending under Four Point Loading at 1500°C .

in the microstructures of specimens broken at 1000°C , as branching cracks close to the fracture.

When temperatures are raised to 1250°C , the breaking strength also rises, but more noticeably from 1000° to 1250°C than from room temperature to 1000°C . High density and slow strain (27 g/sec) gives moduli of rupture around 1750 kg/cm^2 , with a fall in strength at very rapid strain (350 g/sec) to 750 kg/cm^2 and a marked drop with fall in density. Deformation is mainly elastic, with a value of Young's modulus of 1900 kilobars, and small permanent deflections of about 0.025 mm over an outer span of 3 cm in four-point loading.

At 1500°C , the material begins to behave in a very similar manner to a ductile metal when slowly strained. Load-deflection curves show an initial elastic portion, of Young's modulus roughly 200 to 250 kilobars (almost an order of magnitude less than at 1250°C) with an increasing rate of deflection suddenly changing to a well-defined upper and lower yield point, followed by a rise to a maximum stress and frequently a drop to the breaking load, plastic deformation continuing during this whole period. The yield

point appears to be unaffected by density, and the resultant deflection to reach almost 1 mm over the 3 cm span, i.e., an increase of $40\times$ that measured at 1250°C (see Figure 88). The breaking strength is lowered at 1500°C , as would be expected from this ductility, to about 1000 kg/cm^2 . Lower density has little influence on strength, but gives higher ductility. All measurements at 1500°C have so far been at low strain rates. Table 39 shows the results obtained to date.

Microscopic examination, and density measurements before and after testing, suggest that the main mechanism of deformation in the tension stress region is that of propagation of cracks between pores, most of which occur in the grain boundaries in high-density stoichiometric UO_2 . The size of pores (in these samples) increases at lower density, more than the number of their distribution, so that the cracks propagate in a similar manner, but have a shorter inter-pore distance to traverse, and obviously a modified triaxial stress system motivating their propagation. Temperature obviously has less effect until the value exceeds 1250°C , and presumably extra slip systems become available at 1500°C to cause plastic flow around the stress concentrations before cracking. Density shows a drop of over 5% after rupture at 1500°C , so that some enlargement of pores must result during the plastic flow. This may be of some importance in irradiation damage at the center of UO_2 fuel pieces, where the temperatures may well be of the order of 1500°C .

TABLE 39. MECHANICAL TESTS ON UO_2

Number of Samples in Batch	Density		Modulus of Rupture		Mean Load Rate g/sec	Temperature $^\circ\text{C}$
	Mean g/cc	Standard Deviation	Mean kg/cm^2	Standard Deviation		
5	10.58	0.009	843	128.0	68.0	R.T.
5	10.44	0.07	598	37.2	68.0	R.T.
5	10.26	0.025	943	18.2	680.0	R.T.
4	10.55	0.003	1239	92.0	63.4	1015
5	10.47	0.027	1097	61.9	575.3	1025
5	10.51	0.016	1044	81.7	1114.4	1020
4	10.60	0.01	1759	98.2	27.2	1250
2	10.62	0.005	1624	53.0	194.8	1255
5	9.85	0.24	1234	93.8	199.5	1250
4	10.52	0.01	377	10.8	362.4	1250
4	10.23	0.05	792	13.4	416.4	1250
5	10.45	0.05	1017	95.2	19.5	1500
5	9.86	0.04	916	118.0	18.1	1500

5. Anelasticity of Some Uranium Compounds (R. J. FORLANO)

The main objective of this program is to determine the elastic moduli by a dynamic method and to correlate those results with internal friction measurements.

Uranium dioxide compacts of controlled grain size and porosity are desired as samples for anelasticity

determinations. A study was performed to determine the effects of sintering time, temperature, and minor additions on the grain size and porosity of UO_2 compacts. Pellets with different amounts of Nb_2O_5 and TiO_2 were prepared by cold-pressing, with the aid of 2% Carbowax, and were sintered at 1750°, 1650°,

FIG. 89. Effect of Minor Additions and Sintering Temperature on Density of UO_2 .

FIG. 90. Effect of Minor Additions and Sintering Temperature on the Grain Size of UO_2 .

1500°, and 1450°C for four hours in hydrogen atmosphere. The results of these treatments are shown in Figure 89. Polished sections of all the specimens were prepared and the grain size measured with the results shown in Figure 90. The specimens with a maximum density were those with an addition of about 0.4% by weight Nb_2O_5 and sintered at 1750°C. Titanium dioxide was not as effective with respect to density increase; however, for amounts of 0.3% or less, at all sintering temperatures, a greater increase in the grain size was noted than that obtained with equivalent amounts of Nb_2O_5 . This is in disagreement with the results published by Arthur and Scott,⁽⁷⁰⁾ who did not detect any increase of grain size caused by additions of TiO_2 when the sintering temperature was below 1620°C. Figure 89 shows that for a certain sintering temperature an increase in the amount of the minor addition results in a decrease in density. This behavior is somewhat similar to a solarization phenomena, which consists of a decrease in density in sintered bodies due to the increase of the treatment, time or temperature. Williams et al.⁽⁷¹⁾ attribute this phenomena to the limiting effect of grain growth or diffusion processes in sintering. Williams⁽⁷²⁾ in a later paper did not rule out bloating due to the entrainment of gases in closed pores as the cause. Amato et al.⁽⁷³⁾ agreed with this theory. The decrease in density, in the present investigation, was always accompanied by the presence of a liquid phase, hence it is felt that consideration should be given to the possibility of the formation of minute cracks during cooling due to a different thermal expansion of the glassy phase and the grains.

The elastic modulus was determined by the dynamic method introduced by Förster,⁽⁷⁴⁾ which is suitable for high temperature measurements. Briefly, it consists of exciting one of the mechanical resonant frequencies of the material with an electromagnetic driver. Another transducer detects the amplitude of vibration of the sample. At resonance the amplitude reaches a maximum, which is determined with a vac-

uum tube voltmeter. The mode of vibration is determined by the Lissajou pattern impressed in a cathode-ray oscilloscope. Young's modulus and the shear modulus for specimens with rectangular cross section are given by,

$$G = \frac{4LRmf_t^2}{S}$$

$$E = \frac{0.94645 Cmf_f^2}{B}$$

where:

E is the Young's modulus (kilobars*).

G is the shear modulus.

C is a shape factor obtained from Hasselmann's Tables⁽⁷⁵⁾ as a function of the dimension of the cross section parallel to the direction of vibration, the length of the specimen and Poisson's ratio.

m is the mass of the test piece (g).

f_f is the resonant frequency of the first mode of flexural vibration.

B is the dimension of the cross section perpendicular to the direction of vibration.

L is the length of the test piece.

f_t is the resonant frequency of the first mode of torsional vibration.

S is the area of the cross section.

R is a shape factor obtained from Hasselmann's Tables,⁽⁷⁵⁾ as a function of the length of the shorter side and the length of the longer side of the cross section.

The internal friction (Q^{-1}) values can be obtained from the logarithmic decrement or they can also be obtained from the half-width of the resonant peak. The first method is advisable in the case of very low values of Q^{-1} and the second method for relatively high Q^{-1} (when the half-width is of the order of several cycles).

The Young's modulus for four bars of UO_2 at room temperature was determined. Two of the bars were brought to the final dimensions by lapping. The other two were tested as obtained after sintering. The dimensions, density and elastic modulus of these samples are shown in Table 40. The Poisson's ratio was assumed to be 0.3. Bars 1 and 2 were prepared by forming the UO_2 powder plus binder in a steel die at 140 kg/cm² and repressing isostatically at 3850 kg/cm². The specimens were sintered in hydrogen at 1700°C for 4.5 hours and the resulting O/U ratio was

* Kilobar is equal to 10⁹ dynes/cm².

⁽⁷⁵⁾ Hasselmann, D. P. H., *Tables for the Computation of the Shear Modulus and Young's Modulus of Elasticity from the Resonant Frequencies of Rectangular Prisms*, Published by the Carborundum Company, Niagara Falls, New York.

⁽⁷⁰⁾ Arthur, G., and Scott, D., *The Effect of TiO_2 Additions on the Sintering of UO_2* , Trans. British Cer. Soc. **63** (8) 417-429 (1964).

⁽⁷¹⁾ Williams, J., Barnes, E., Thackray, R. W., and Murray, P., *The Non-Stoichiometric Oxides of Uranium*, Trans. British Cer. Soc. **56**, 608-623 (1957).

⁽⁷²⁾ Williams, J., *The Sintering of Uranium Oxides*, J. Nucl. Matls. **2** (1) 92-93 (1960).

⁽⁷³⁾ Amato, I., Colombo, R. L., and Pootti, A. M., *On a Case of Solarization During Steam Sintering of UO_2 Pellets*, J. Nucl. Matls. **8** (2) 271-272 (1963).

⁽⁷⁴⁾ Förster, F., *Zeitschrift für Metalkunde* **29** (4) 109-115 (1937).

TABLE 40. DIMENSIONS, DENSITY AND ELASTIC MODULUS OF UO_2 AT ROOM TEMPERATURE

Sample	After Sintering					After Lapping							
	Width cm (1)	Depth cm (1)	Length cm	Weight g	Density g/cc (2)	Width cm	Depth cm	Length cm	Weight g	Density g/cc (2)	E_f Kilobars (3)	E_e Kilobars (4)	G Kilobars (5)
1	0.712	0.711	6.459	34.1734	10.62	0.564	0.417	6.459	15.9332	10.53	2056	2070	794
2	0.741	0.738	6.350	34.5539	10.61	0.538	0.480	6.350	17.2532	10.54	2062	2062	794
3	0.819	0.465	7.351	29.0712	10.54	—	—	—	—	—	1813	1856	714
4	0.818	0.470	7.350	29.1831	10.49	—	—	—	—	—	1846	1851	705

(1) Average of 3 measurements.

(2) Density determined by the Arquimedes' method.

(3) Young's modulus calculated from the flatwise flexural vibration.

(4) Young's modulus calculated from the edgewise flexural vibration.

(5) Shear modulus calculated from the expression: $\mu = (E/2G) - 1$, where μ is Poisson's ratio and E the average of E_f and E_e , Young's moduli for flatwise and edgewise flexural vibrations, respectively.

2.005. They were finished by automatic lapping to a dimensional accuracy of 0.005 cm. Bars 3 and 4 were prepared by isostatically pressing the powder and binder at 3850 kg/cm², granulating, forming in a steel die at 420 kg/cm² and repressing isostatically at 3850 kg/cm². They were sintered in hydrogen at about 1700°C for 4.5 hours. The resonant frequencies were excited by two methods. In the first one the specimen was supported on foam rubber and driven by placing the needle of a record cutting head (Astatic X-26) against the bar. The vibrations were detected by the needle of a phonograph cartridge (Astatic L-12). The second method consisted of suspending the specimen from two Pt wires, 0.0254 cm in diameter and 41 cm long, placed 0.2 cm from the nodes of the sample with

one wire attached to the needle of the record cutting head and the other to the phonograph cartridge. The flexural resonant frequency of bar 1 was determined by both methods and the results were reproducible. In the case of bars 2, 3 and 4 it was not possible to excite consistently the flexural resonant frequency by the second method of excitation. This was attributed to the fact that these specimens were heavier. In Table 40 can be seen that the Young's modulus of the finished bars was larger than for the unfinished specimens. Probable causes might be: (a) lack of precision in the parallelism and dimensions of bars 3 and 4, (b) dissimilar microstructure due to the different fabrication procedures, and (c) skin effect put in evidence by the lapping of specimens 1 and 2.

6. Thermal Stability of Ceramic Materials (E. D. LYNCH)

All phases of the thermal stability of ceramic materials have become of increased importance as a result of interest in higher operating temperatures and special operating conditions of nuclear reactors.

The use of high fuel-center temperatures for prolonged time presents the problems of volatility of fuel materials, migration of fuels, and compatibility of fuels with gaseous and solid contaminants and coolants.

The purpose of this program is to determine the effects of compositions, temperature, time, and atmospheric environment on the evaporation and rate of evaporation of ceramic materials. Of immediate interest are the urania-based fuel materials and those materials associated with them as solid solution agents,

dispersed media, coatings, property stabilizers, sintering aids, and impurities. An additional phase of this work is the study of control of the rate of loss of fuel and fuel migration.

An apparatus has been constructed for the study of evaporation of materials as affected by variations in the testing environment of temperature, pressure, and atmosphere. The apparatus used for this study consists of a tungsten element resistance furnace vacuum coupled to a recording semimicroanalytical balance. The system is so constructed that vacuum or either inert or hydrogen atmospheres may be used. The capabilities of this apparatus are 2700°C in vacuum and 2500°C for the pressure range 5×10^{-6} torr to 1.5 atmospheres in an inert gas or in hydrogen. The re-

40320

250X

FIG. 91. Magnesium Oxide before Heating. Etched 1 minute with 50% H_2SO_4 .

40409

FIG. 92. Weight Loss Data for Polycrystalline MgO.

Recording balance has an automatic weighing range of 400 mg and is direct reading to 0.1 mg weight change.

An analysis of the evaporation characteristics of

magnesium oxide has been initiated. For this purp high-purity polycrystalline MgO has been used. This material was prepared by a sintering operation and has a density of 3.55 g/cc, approximately 99.5% theoretical density. A representative microstructure of this material is shown in Figure 91.

Test samples of this material were prepared by diamond sawing sections of approximately 2 cm² surface area. Samples for test were suspended in the furnace by tungsten wire.

Samples were heated in the temperature range of 1200°–1400°C at a pressure of 1×10^{-5} torr for a minimum of 15 hours before testing in order to insure stabilization of the sample weight. Samples were heated to test temperature level and temperature maintained constant while recording the weight change of the sample as a function of time.

Typical evaporation curves for MgO are shown in Figures 92 and 93. These curves show that evaporation rate stabilizes rapidly with time and evaporation is a linear function over a prolonged time period.

40408

FIG. 93. Weight Loss Data for Polycrystalline MgO.

These data were obtained at a pressure of 1×10^{-5} torr.

Evaporation rates calculated from these data are shown in Figure 94. At this time evaporation has not been measured at 1×10^{-5} torr below 1788°K and samples have been held at approximately 1650°K for 15 hours without weight change. A rapid change in rate occurs above 2000°K for MgO. The data above 2250°K begins to show a spread which is associated with an oxidation of the tungsten suspension by the evaporation of oxygen as a species. Changes in suspension technique are being tried to correct this problem.

Samples after evaporation in vacuum show a greatly eroded surface and attack along grain boundaries. The extent of thermal etching and erosion may be seen from comparison of the surfaces on original and evaporated surfaces shown in Figure 95.

The magnesium oxide has shown extensive grain growth during the evaporation heat treatment. Precise

grain size measurements have not yet been made but typical grain growth may be seen from Figure 96.

An apparatus was constructed to measure thermal diffusivity and specific heat at room temperature on small disk-shaped specimens. This apparatus was used in accordance with the method developed by Parker et al.⁽⁷⁶⁾ At room temperature, measurements on metals⁽⁷⁷⁾ were in good agreement with accepted values, and this work was expanded to measure ceramic standards and uranium compounds. In addition, two furnaces are being installed in a glovebox and will be used for measuring the thermal diffusivity and specific heat of plutonium compounds at high temperature.

⁽⁷⁶⁾ Parker, W. J., Jenkins, R. J., Butler, C. P., and Abbott, G. L., *Flash Method of Determining Thermal Diffusivity, Heat Capacity and Thermal Conductivity*, J. Appl. Phys. **32**, 1679 (1961).

⁽⁷⁷⁾ *Annual Report for 1963, Metallurgy Division, ANL-6868*, p. 162.

40407

FIG. 94. Rates of Evaporation of Polycrystalline MgO in Vacuum.

FIG. 95. Surface Roughening Due to Heating at Temperature Shown. In Vacuum (1×10^{-5} torr)

40320

96-a. Unheated

250×

40322

(1×10^{-5} torr)

96-b. 1928°C

250×

40324

(1×10^{-5} torr)

96-c. 2008°C

250×

40323

(1×10^{-5} torr)

96-d. 2060°C

250×

FIG. 96. Change in Microstructure of MgO Resulting from Heat Treatment.

7. Development of Thermal Diffusivity for Ceramic Materials (J. B. MOSER AND O. L. KRUGER)

a. Room-Temperature Properties of Uranium Compounds

The compounds investigated were arc-cast uranium monocarbide, pressed and sintered uranium dioxide,

106-8018

FIG. 97. Single Oscilloscope Trace of Temperature Rise of Uranium Carbide Specimen 2 mm Thick. Horizontal: 50 msec/cm. Vertical 0.85°C/cm. Energy level 0.35 cal/cm².

106-8019

FIG. 98. Multiple Oscilloscope Trace of Temperature Rise of Uranium Carbide Specimen 2 mm Thick. Horizontal 20 msec/cm. Vertical 0.85°C/cm. Energy level 0.44 cal/cm².

TABLE 41. THERMAL PROPERTIES OF STANDARDS AT ROOM TEMPERATURE

Material	Density D (g cm ⁻³)	Thermal Diffusivity α (cm ² sec ⁻¹)	Specific Heat C_p (cal g ⁻¹ °C ⁻¹)	Thermal Conduc- tivity K (cal cm ⁻¹ sec ⁻¹ °C ⁻¹)
Armco Iron	7.86	0.20	0.11	0.17
Graphite	1.73	0.80	0.17	0.24
Aluminum Oxide	3.51	0.075	0.18	0.047

hot-pressed high-density uranium monosulfide and hot-pressed uranium phosphide of varying densities. The apparatus was described adequately before⁽⁷⁷⁾ but the following additions were made for the work with ceramics. A spring-loaded chromel-alumel thermocouple (with wires 2 mm apart) was pressed against the central area of the back surface of the sample. Liquid indium alloy applied in a thin layer improved electrical contact on the nonmetal samples and was necessary to obtain reliable diffusivity and specific heat data. In order to obtain reproducible energy pulses for the specific heat measurements, the capacitor was discharged into the flashtube after the voltage had reached a predetermined value as indicated on a modified stripechart recorder.

An output signal from the sweep delay circuit of the oscilloscope was amplified and this signal triggered the flashtube a short time after the start of the trace. A single trace of the temperature rise of a 2 mm uranium carbide sample is shown in Figure 97. Use of a multiple trace on the same specimen expanded the horizontal scale 2½ times, and reduced the measurement error in $t_{\frac{1}{2}}$ as shown in Figure 98.

Table 41 shows the standards selected for the purpose of checking the effect of the liquid metal film on the thermal properties of a metal, a semiconductor and an insulator.

Table 42 shows the room-temperature thermal properties of various uranium fuel materials as determined in this investigation. In all cases chemical analyses of the main constituents were carried out to determine the stoichiometry of the compounds. Metallographic examination to determine the homogeneity of the material and its pore distribution was carried out on some materials especially those where some conclusions are drawn as regards the effect of porosity on the reported measurements. All materials were analyzed for oxygen content.

Uranium Monocarbide

The values reported for uranium monocarbide are the average of four determinations. The specific heat value of 0.048 cal g⁻¹ °C⁻¹ is in agreement with the IAEA⁽⁷⁸⁾ standard of 12.1 cal/mole or 0.0484 cal g⁻¹ °C⁻¹. The value of the thermal conductivity found in this investigation is 0.055 cal cm⁻¹sec⁻¹ °C⁻¹ corrected to 100% theoretical density. This agree

⁽⁷⁸⁾ *The Uranium-Carbon and Plutonium-Carbon Systems*, International Atomic Energy Agency, Tech. Report Series 14 (1963).

TABLE 42. THERMAL PROPERTIES OF NUCLEAR MATERIALS AT ROOM TEMPERATURE

Material	Percent of Theoretical Density	Thermal Diffusivity α ($\text{cm}^2 \text{sec}^{-1}$)	Specific Heat C_p ($\text{cal g}^{-1} \text{°C}^{-1}$)	Thermal Conductivity K ($\text{cal cm}^{-1} \text{sec}^{-1} \text{°C}^{-1}$)	Oxygen (w/o)
Uranium Monocarbide	98.8	0.085	0.048	0.054	0.0046
Uranium Dioxide	91.3	0.023	0.063	0.014	12.35
Uranium Monosulfide	96.4	0.040	0.045	0.019	0.32
Uranium Monophosphide	73.5	0.053	0.045	0.018	—
Uranium Monophosphide	82.6	0.051	0.046	0.020	—
Uranium Monophosphide	88.8	0.054	0.046	0.023	0.26

with Russell's⁽⁷⁹⁾ value of 0.055 at room temperature as well as with Secrest's⁽⁸⁰⁾ determination of 0.06.

Uranium Dioxide

The value found for the specific heat $0.063 \text{ cal g}^{-1} \text{°C}^{-1}$ falls between 0.057 for $\text{UO}_{2.00}$ and 0.065 $\text{UO}_{2.25}$ as reported by Westrum and Grønvold⁽⁸¹⁾ for 298.15°K . The thermal conductivity of $0.015 \text{ cal cm}^{-1}\text{sec}^{-1} \text{°C}^{-1}$, as corrected to zero porosity by application of the density ratio, compares to 0.018 given by Godfrey et al.,⁽⁸²⁾ who worked with stoichiometric material at room temperature.

Uranium Monosulfide

The specific heat found for US, $0.045 \text{ cal g}^{-1} \text{°C}^{-1}$, agrees with the experimental work at 25°C reported by Westrum and Grønvold⁽⁸¹⁾ and the figure calculated by Kopp's rule. The value of $0.019 \text{ cal cm}^{-1}\text{sec}^{-1} \text{°C}^{-1}$ was found for the thermal conductivity.

Figure 99 at $30\times$ shows evenly distributed pores and a second phase of UOS throughout the specimen. At the higher magnification of $800\times$ (see Figure 100) the irregular shape of the second phase material and the pores is evident. This type of pore-shape has an

⁽⁷⁹⁾ Russell, L. E., "The Structure and Properties of U-C and (UPu)-C Alloys," *New Nuclear Materials Including Non-Metallic Fuels*, Vol. 1, pp. 409-428, IAEA, Vienna (1963).

⁽⁸⁰⁾ Secrest, A. C., Jr., Foster, E. L., and Dickerson, R. F., *Preparation and Properties of Uranium Monocarbide Castings*, BMI-1309 (January 1959).

⁽⁸¹⁾ Westrum, E. F., Jr., and Grønvold, F., "Chemical Thermodynamics of the Actinide Element Chalcogenides," *Thermodynamics of Nuclear Materials*, pp. 3-37, IAEA, Vienna (1962).

⁽⁸²⁾ Godfrey, T. G., Fulkerson, W., Killie, T. G., Moore, J. P., and McElroy, D. L., *Thermal Conductivity of Uranium Dioxide and Armco Iron by an Improved Radial Heat Flow Technique*, ORNL-3556 (June 1964).

Surface

106-8016R

30X

Fig. 99. Cross Section of 96% Dense Uranium Monosulfide.

106-8015

800X

Fig. 100. Cross Section of 96% Dense Uranium Monosulfide.

exceptionally marked effect in reducing K . The UOS content may also reduce the conductivity somewhat since its value as reported by Warren⁽⁸³⁾ equals $0.009 \text{ cal cm}^{-1}\text{sec}^{-1} \text{°C}^{-1}$ at room temperature. Therefore, the value for the room-temperature thermal conductivity of theoretically dense, high-purity US may be somewhat higher than that reported in Table 42.

Uranium Monophosphide

The distribution of pores and impurities was very uniform throughout the sample for all densities; a

⁽⁸³⁾ Warren, I. H., *Uranium Compounds as Thermoelectric Materials*, Can. Inst. of Mining and Met. Trans. **66**, 147 (1963).

FIG. 101. Cross Section of 89% Dense Uranium Monophosphide.

FIG. 102. Cross Section of 89% Dense Uranium Monophosphide.

40298

FIG. 103. Horizontal Diffusivity Furnace with Infrared-radiation Detector (top) and Thermocouple Pick-up Assembly (bottom).

cross section of the 89% dense material at 30× is seen in Figure 101. The pore shape and UO_2 inclusions were distinguished at a higher magnification and a cross section at 800× is shown in Figure 102. The rounded appearance of both pores and inclusions is typical of the plutonium monophosphide samples tested.

The specific heat of UP was 0.045 to 0.046 cal $\text{g}^{-1} \text{°C}^{-1}$, which compares well with a calculated value of 0.047 cal $\text{g}^{-1} \text{°C}^{-1}$. There are no experimental specific heat values in the literature available for comparison.

The diffusivities vary unsystematically from 0.051 to 0.054 $\text{cm}^2 \text{sec}^{-1}$, averaging to 0.053 ± 0.002 . The invariance of α with density can be explained with the aid of a few simple relations. If the pores are spherical and isotropically distributed and if furthermore the amount of heat transferred across the pores by conduction through the gas and radiation is neglected the following relation is obtained for the thermal conductivity:

FIG. 104. Thermal Diffusivity of Armeo Iron.

40297

FIG. 105. Vertical Tantalum Heater Diffusivity Furnace.

$$K_M = K_T (1 - P) \quad (1)$$

where the subscripts M and T denote measured and theoretical properties, respectively, and P denotes porosity as a volume fraction. This is the simplest and most frequently employed porosity correction for heat-conduction data, and it often describes experimental results to moderately high temperatures.

Substituting the density equation:

$$D_M = D_T (1 - P) \quad (2)$$

in the expression for the measured thermal diffusivity

$$\alpha_M = \frac{K_M}{D_M C_P} \quad (3)$$

the following relation is obtained

$$\alpha_M = \frac{K_T}{D_T (1 - P) C_P} \quad (4)$$

Only if K_M follows relation (1) can one write:

$$\alpha_M = \frac{K_T}{D_T C_P} \quad (5)$$

and α_M will be independent of porosity.

The thermal conductivity of theoretically dense UP calculated by equation (5) is 0.025 cal $\text{cm}^{-1} \text{sec}^{-1} \text{°C}^{-1}$.

b. High-Temperature Apparatus

A horizontal tantalum-wound furnace for heat pulse studies in vacuum or inert atmospheres was completed and is shown in Figure 103 (page 108). The thermocouple detection unit was used to obtain diffusivity data on Armco iron from room temperature to 1000°C. The values obtained are compared with those reported by Rudkin et al.,⁽⁸⁴⁾ as shown in Figure 104

⁽⁸⁴⁾ Rudkin, R. L., Jenkins, R. J., and Parker, W. J., *Thermal*

(page 109). Also shown in Figure 103 is an interchangeable insert designed for use with a radiation thermometer. An infrared detection device incorporating a PbS cell was tested successfully between 200° and 1000°C for use with this apparatus. Between 1000° and 2200°C a vertical vacuum furnace with a split tantalum tube heater as shown in Figure 105 will be used.

Diffusivity Measurements on Metals at High Temperatures, USNRDL-TR-518 (June 1961).

E. EXPERIMENTAL IRRADIATIONS OF FUEL AND CONTROL MATERIALS

1. Irradiation of Thorium-Base Fuels (W. N. BECK)

Six specimens of thorium-base fuels were irradiated in Nb-1w/oZr tubing. The irradiation was performed in a gas annulus temperature controlled capsule, installed in a CP-5 vertical thimble. The fuel specimens consisted of two each of the following compositions: Th-35w/oPu, Th-20w/oU-20w/oPu and Th-20w/oU. Each fuel composition was jacketed in tubing which had an ID of 3.96 mm or 6.52 mm. The large tubing was used to permit the alloys to swell without jacket restraint. The wall thickness of all tubings was 0.38 mm.

After an average 1.1 total *a/o* burnup, the thermocouple readings indicated a redistribution of fuel ma-

terial in two specimens and the capsule was withdrawn from the reactor and nondestructively examined by neutron radiography. All specimens were intact with the exception of a Th-20w/oU-20w/oPu specimen and a Th-35w/oPu specimen, both of which were jacketed in 6.52 mm ID tubing. The average central fuel irradiation temperatures of the pins was respectively 720° and 650°C. The companions of these specimens were being irradiated at an average fuel temperature 120°C lower and were still intact. This capsule will be disassembled and a detailed examination will be made of all specimens.

2. Transient Irradiations of Thorium-Uranium Alloys (C. F. REINKE)

Neutron irradiation of thorium causes a complex series of nuclear reactions leading to the production of uranium-233, a valuable nuclear fuel. Although these reactions are well-known, more information is required about the properties and reactor behavior of thorium and its alloys.

One question that arises concerns the behavior on thermal excursions of thorium-uranium fuels in which the uranium content greatly exceeds its solid-solubility limit. Coalescence of the excess uranium existing as a dispersed phase in such alloys is known to occur on prolonged holding at high temperatures; but little was known about the effect of short-time, fission heating of such alloys to the vicinity of the uranium melting temperature.

Six Th-22w/oU alloy specimens were therefore subjected to elevated temperature transients in the TREAT reactor. The sodium-bonded specimens, which were jacketed with 0.38 mm thick Nb-1w/oZr alloy or Type 304 stainless steel tubing, had no previous irradiation history. Measured cladding temperatures

ranged from 745° to 1434°C. The test conditions and results are summarized in Table 43.

The posttransient examination revealed that the integrity of the jacketing on all six specimens had been maintained. There were no dimensional or volume changes on jacketed specimens in which the transients were below the melting point of the uranium phase. At temperatures above the melting point of the uranium phase, an upward displacement of the fuel occurred inside the jacket, as can be seen in the radiographs in Figure 106. This movement is believed to have been caused by sodium vapor pressure. Small dimensional changes were noted in the specimens subjected to the more severe transients. However, the resultant volume changes were less than 1%.

Metallographic cross sections, shown in Figure 107, indicate that the core-jacket interaction on the Nb-1w/oZr jacketed specimen in which the uranium phase was molten was minor, while that between the core and Type 304 stainless steel jacket was more extensive.

3. Examination of Irradiated Aluminum Alloy Clad UO₂ (L. A. NEIMARK AND R. CARLANDER)

The results of the irradiation of aluminum alloy-jacketed UO₂ pellets have been compiled and evaluated. Two three-rod assemblies containing UO₂ pellets in wrought A-288 aluminum alloy cladding were ir-

radiated in the ANL-2 High Pressure Water Loop in the MTR. The object of the experiment was to determine whether thermal ratcheting is significant in aluminum-clad UO₂ fuel elements. Pertinent information

on the irradiation and postirradiation examination is presented in Table 44. The rods were 406 mm long and 9.6 mm in diameter. They were irradiated horizontally so that the maximum burnup and temperature occurred at one end of the assembly.

Two of the six rods contained pellets with dished ends and the other four rods contained pellets with square ends. Under loop operating conditions the 0.76 mm thick cladding was collapsed onto the fuel in all rods. The three rods from assembly ANL-2-13 showed that the dished pellets caused less residual rod elongation than the square pellets. The results from the ANL-2-16 assembly, however, were contradictory in that the rod with dished pellets elongated considerably more than the others, 3.05 mm compared to 0.51 mm. Submersion leak testing of this rod indicated a defect in the weld closure at the "cold" end. Examination of the weld defect led to the conclusion that it was formed in the welding operation and was present throughout the irradiation. A thorough check of loop coolant activity records substantiated this conclusion.

TABLE 43. TRANSIENT IRRADIATIONS OF Th-22w/oU ALLOY

Specimen No.	Jacket Alloy	Maximum Jacket Temp., °C	Postirradiation Evaluation
152H	Nb-1Zr	999	No jacket failure. No dimensional or volume changes. No core-jacket interaction.
152I	Nb-1Zr	944	No jacket failure. No dimensional or volume changes. No core-jacket interaction.
152K	Nb-1Zr	1434	No jacket failure. Slight diameter and length decrease with resultant volume decrease of 0.4%. Slight core-jacket interaction noted.
152L	304 SS	745	No jacket failure. No dimensional or volume changes. No core-jacket interaction.
152M	304 SS	923	No jacket failure. No dimensional or volume changes. No core-jacket interaction.
152N	304 SS	1245	No jacket failure. Slight diameter and length increase with resultant volume increase of 0.7%. Core-jacket interaction noted.

FIG. 106. Comparison of Radiographs of Specimens 152K (Nb-1Zr Jacketed) and 152N (Stainless Steel Jacketed) with Typical Pretransient Specimen.

Metallographic examination of the three rods in assembly ANL-2-13 and the two square pellet rods in assembly ANL-2-16 showed no central void or columnar grain growth in any rod at any position. Also, the pellets did not coalesce at their interfaces, as is shown in Figure 108.

The defected dished-pellet rod ANL-2-16-6 had a central void surrounded by columnar grains, about 60 mm long at the hot end. The columnar grain growth extended into the dished ends of the pellets, as shown in Figure 109, but no coalescence occurred between pellets. A small reaction was found between the columnar grains and an adjacent ZrO_2 dummy pellet at the hot end of the rod as shown in Figure 110. Movement of UO_2 , like that into the dished ends, has been postulated by Canadian investigators to be plastic flow.⁽⁸⁵⁾ The growth at the hot end appears to have been flattened by the ZrO_2 end pellet. The cold end of the void is shown in Figure 111. Lenticular voids are apparent in the columnar grains around the cer

⁽⁸⁵⁾ Bain, A. S., *Cracking and Bulk Movements in Irradiated Uranium Oxide Fuel Elements*, Trans. Am. Nuc. Soc., 6, 352 (November 1963).

EI-2743

50X

EI-2597

50X

FIG. 107. Typical Cross Sections of Th-22w/oU Alloy Specimens Subjected to Transient Irradiations in which the Uranium Phase was Molten. The left specimen is 152K (Nb-1Zr alloy jacket); the right is 152N (Type 304 stainless steel jacket).

TABLE 44. IRRADIATION SUMMARY OF ALUMINUM ALLOY CLAD UO_2 RODS

Rod	Pellet Profile	Preirrad. Annulus	Burnup, 10^{20} fiss/cc		Heat Flux, w/cm ²		Max., $\tau_s \int_{T_0}^T kd\theta$, w/cm	Total Elong., mm	Fiss. Gas Release, %	Remarks
			Max.	Avg.	Max.	Avg.				
ANL-2-13-1	Square	0.03 mm He	1.4	0.7	136	61	31	0.53	—	No gas detected.
ANL-2-13-5	Dished	0.03 mm He	1.4	0.7	136	61	31	0.13	0.59	
ANL-2-13-8	Square	None	1.4	0.7	136	61	31	0.38	0.77	Defect in weld.
ANL-2-16-6	Dished	0.03 mm He	2.0	0.9	124	52	28	3.05	—	
ANL-2-16-7	Square	0.03 mm He	2.0	0.9	124	52	28	0.13	0.20	
ANL-2-16-9	Square	None	2.0	0.9	124	52	28	0.51	0.26	

tral void. It appears that the center cavity was formed by the movement of the lenticular voids up the temperature gradient to the center. Maximum calculated $\tau_s \int_{T_0}^T kd\theta$ for these rods was 28 w/cm. This is considerably below that at which central voids normally occur in stoichiometric UO_2 .

As noted above, the behavior of the dished-pellet rod ANL-2-16-6 was substantially different from all other rods. Besides elongating, it contained a center void while two adjacent rods did not. It is believed all the differences were caused by the defective weld. Operation with the defective weld would have exposed the UO_2 pellets to loop water. The subsequent steam generation would have oxidized the UO_2 resulting in a lower fuel thermal conductivity. The center void and columnar grains are the result of this lower conductivity. In addition, with the pressure inside and outside the rod the same the cladding would not collapse onto the pellets. This was borne out in the

metallographic examination. The as-loaded annulus was maintained and thermal ratcheting occurred giving the measured elongation.

Significant thermal ratcheting between pellets and cladding did not occur in experimental rods with collapsed cladding. Figure 112 shows particles of brass embedded in the fuel-cladding interface in rod ANL-2-16-9. The brass was from a rod used to push the pellets into the tubes during the original loading. Had ratcheting occurred material would have been dragged along the interface; it was not. The results are in agreement with data obtained by Canadian investigators, that tubing collapsed onto the fuel pellets moves with the fuel in both directions and ratcheting does not occur.⁽⁸⁶⁾

⁽⁸⁶⁾ Motley, M. G. F., and Harvey, A., *The Length Changes of Zircaloy Sheathed UO_2 Fuel Elements During Irradiation*, AECL-1846.

EI-2176

22×

FIG. 108. Typical UO_2 Pellet Interface in Nondefected Aluminum Alloy Cladding.

EI-2161

25×

FIG. 109. Pellet Interface (Top) of Dished Pellet in Rod ANL-2-16-6. Grains have grown into dish but no coalescence occurred between pellets.

EI-2159

25×

FIG. 110. Grain Growth in End UO_2 Dished-Pellet in Rod ANL-2-16-6.

EI-2162

25×

FIG. 111. Cold End of Central Void in Rod ANL-2-16-6. Lenticular voids are evident in columnar grains.

FIG. 112. Particles of Brass in the UO_2 -Aluminum Interface. No ratcheting occurred.

4. Irradiation Behavior of Uranium Sulfide (L. A. NEIMARK, R. CARLANDER, AND C. C. CROTHERS)

Initial examination of irradiated uranium sulfide specimens indicated that high-density (90% of theoretical) liquid-phase sintered US containing UOS as a grain boundary phase did not undergo significant structural change during irradiation. However, low-density (80% of theoretical) solid-phase sintered US containing UOS as discrete particles did change radically in one specimen. The variation has been attributed to a reduction in thermal conductivity caused by lower density and the UOS phase.

The extent of the changes in the low-density sulfide has been more fully assessed with more extensive metallographic examination. The most obvious structural change was the creation of a spherical void at the top of the fuel column next to the helium-filled gas plenum. The cavity is believed to have resulted from fuel melting. The volume expansion on melting was sufficient to bulge the cladding. The area around the cavity was porous and joined a porous pipe of nonsymmetrical shape that extended the length of the fuel. This area contained at least three phases tenta-

tively identified as US (whitish matrix), UOS (medium gray), and UO_2 (dark gray). In addition there was a light gray phase and a white phase that could be US_2 or metallic uranium. These phases were in various forms of association from fine needles to massive particles.

The porous center pipe was characterized by a total absence of another phase with the US. Away from the pipe the proportion of UOS was increased over that in the unirradiated condition. The porous US next to the spherical cavity contained needles of UOS that formed on preferential crystallographic planes as shown in Figure 113. Other grains showed almost complete transformation of US to UOS with an intermediate gray phase shown in Figure 114. The UOS that was formed at the extreme edge of the fuel near the cavity transformed to what is probably UO_2 . The area shown in Figure 115 was near the lower extremity of the UOS- UO_2 transformation.

The thermal conductivity of this low density (80%) sulfide is evidently sufficiently low to create a sub-

stantial thermal gradient in the fuel. Under these conditions the UOS evidently migrated from the center to the colder periphery. In addition, sufficient oxygen must have been present in the gas plenum next to the top pellet to (1) precipitate UOS needles and plates in newly solidified US, (2) transform US to UOS, and (3) transform UOS to UO_2 at the exposed edge surfaces. Since UOS has a lower melting point than US, a lower thermal conductivity, and is more reactive (a tantalum spring in contact with the newly formed UOS was attacked), its presence in the fuel during irradiation is not desirable.

Nine uranium sulfide specimens are under irradiation in the MTR reactor in three instrumented, temperature-controlled capsules. A thermocouple is adjacent to each specimen to measure the cladding surface temperature. Specimen temperatures are controlled by varying the helium-nitrogen ratio in a 0.25 mm annulus between the inner and outer capsule walls.

EI-2112

320×

FIG. 113. UOS on Preferential Crystallographic Planes in US Next to Cavity.

EI-2114

500×

FIG. 115. US-UOS and UOS- UO_2 Transformations at Pellet Edge in Top Pellet.

EI-2100

320×

FIG. 114. Incomplete US-UOS Transformation Next to Cavity.

tion in the MTR reactor in three instrumented, temperature-controlled capsules. A thermocouple is adjacent to each specimen to measure the cladding surface temperature. Specimen temperatures are controlled by varying the helium-nitrogen ratio in a 0.25 mm annulus between the inner and outer capsule walls.

The uranium sulfide is in the form of pressed and sintered pellets having grouped densities of from 85 to 95% of theoretical. The pellets are 6.43 mm in diameter and are clad with 0.30 mm thick Nb-1w/oZr alloy. A 0.05 mm helium-filled annulus exists between the pellets and the cladding. The pellets contain approximately 2w/o UOS phase primarily in the grain boundaries.

The three irradiation capsules are designated ANL-56-8, ANL-56-9, and ANL-56-11. The desired cladding surface temperatures for specimens in these capsules are 650°, 850°, and 650°C, respectively. However, be-

cause of vertical flux variation these temperatures cannot be attained in each specimen in the capsule. The capsules have been moved periodically to positions of higher flux so that the desired temperatures could be attained in the majority of specimens. Desired burnups for specimens in these capsules are 3.3×10^{21} fiss/cc (125,000 Mwd/MT), 2.2×10^{21} fiss/cc (82,500 Mwd/MT), and 2.2×10^{21} fiss/cc, respectively.

The specimens in capsule ANL-56-8 have achieved estimated burnups from 2.7×10^{20} to 4.9×10^{20} fiss/cc at cladding surface temperatures from 535 to 610°C.

EI-3039

0.96×

FIG. 116. Typical Irradiated Specimen (51-5) of Co-30w/oDy₂O₃ Jacketed in Type 304 Stainless Steel.

TABLE 45. IRRADIATION CONDITIONS OF JACKETED PELLETS OF COBALT-30w/oDy₂O₃

Specimen	Integrated Unperturbed Thermal Neutron flux, nvt	Calculated Specimen Temperature, °C
51-3	4.8×10^{21}	300
51-4	6.6×10^{21}	300
51-5	7.6×10^{21}	300

Capsule ANL-56-9 contains four specimens that have achieved estimated burnups from 2.0 to 10^{20} to 3.1×10^{20} fiss/cc. These specimens are presently operating at cladding surface temperatures between 680° and 800°C. The specimens in capsule ANL-56-11 are operating at cladding surface temperatures from 560 to 700°C and have reached burnups of from 1.1×10^{20} to 2.9×10^{20} fiss/cc.

Although some thermocouples are no longer operative, no positive indication of specimen failure has been observed.

TABLE 46. IRRADIATION CONDITIONS OF 15w/oB₄C DISPERSED IN SODA-POTASH GLASS

Specimen	Integrated Unperturbed Thermal Neutron flux, nvt	Calculated Specimen Temperature, °C
51-8	3.1×10^{21}	300
51-9	3.8×10^{21}	550
51-10	2.2×10^{21}	200

EI-3041

1×

FIG. 117. Typical Irradiated Specimen (51-10) of 15w/oB₄C Dispersed in Soda-Potash Glass and Jacketed in Type 321 Stainless Steel.

5. Irradiation of Highly Absorbing Materials (C. F. REINKE)

Three capsules containing jacketed pellets of cobalt-30w/oDy₂O₃ have been irradiated in the MTR. The pellets were jacketed with 0.5 mm thick Type 304 stainless steel. There was approximately a 0.05 mm clearance between the pellet and the ID of the jacket.

Postirradiation examination indicated the specimens were in good condition, as can be seen in Figure 116. A uniform diameter increase of about 0.05 mm was noted on the specimens. The irradiation conditions are tabulated in Table 45.

6. Irradiation of Poisoned Glasses (C. F. REINKE)

Three specimens of 15w/oB₄C dispersed in soda-potash glass have been irradiated in the MTR to integrated unperturbed thermal neutron fluxes ranging from 2.2×10^{21} to 3.8×10^{21} . The specimens were clad with 0.5 mm thick Type 321 stainless steel by firing the glass-B₄C mixture directly in the tube. The

postirradiation examination indicated the specimens were in excellent condition. No changes were noted in either dimensions or density. The irradiation conditions are tabulated in Table 46. Figure 117 shows a typical specimen after irradiation.

F. EXAMINATION OF FULL-SCALE REACTOR FUEL ELEMENTS

1. Examination of EBWR Prototype Fuel Plates (R. CARLANDER AND C. C. CROTHERS)

Two EBWR prototype fuel plates that were tested in the in-pile and out-of-pile sections of the ANL-2 loop at MTR were examined after 1.31 total atom percent burnup in order to provide information regarding the performance of the fuel at high burnups.

The plates were tested at a loop water temperature of 225 to 250°C, and at pH ranging from 5.4 to 7.9. After completion of the test, the plates were measured for changes in length, width, and thickness, and the corresponding total changes, which occurred through irradiation alone, were determined.

The out-of-pile plate decreased in both the length and thickness dimensions, but increased in width. The average change in length, width, and thickness of the in-pile plate was +0.04%, +0.06%, and +2.8%, re-

spectively. The corresponding change in the in-pile plate due to irradiation alone was +0.66%, +0.14%, and +3.9%. The scale thickness varied from 0.02 to 0.04 mm.

The resulting volume change of 3.5% per atom percent burnup was approximately one-third of that which occurred in operating EBWR fuel plates after only 0.5a/o burnup. Also, the scale thickness on the operating fuel plates was 0.23 mm compared to 0.02–0.04 mm on the prototype fuel plates. It is therefore concluded that the prototype plate operated at a lower average centerline fuel temperature than that which occurred in the reactor, resulting in a lower rate of change in volume.

2. Examination of EBWR Fuel Element after 100 Mw Operation (R. CARLANDER)

An EBWR fuel element was subjected to a post-irradiation examination as part of the program to determine the operating characteristics of the fuel element and the irradiation behavior of the fuel with increased burnup and temperature.

The present element was of the "thin" type, made up of plates 5.38 mm thick, and was irradiated to approximately 0.5 total a/o burnup. The average centerline fuel temperature was calculated at 320°C although it has been estimated that it could reach a maximum of 590°C with normal scale buildup.

The element appeared to be in good condition except for rippling of the Zircaloy-2 side plates (Figure 118). Partial descaling had occurred in certain areas of the plates to a somewhat greater extent than had been observed previously (C. F. Reinke and R. Car-

lander, "Examination of Irradiated EBWR Core-I Fuel Elements," ANL-6091). The total thickness of nonadherent and adherent scale was measured to be 0.25 mm, and the resultant maximum volume increase of the fuel plate in the absence of scale was then determined as 10% per a/o burnup. The bond between the core and the cladding was sound and the residual stresses were negligible compared to a previous element irradiated at a calculated center temperature of 280°C to a burnup of 0.39a/o.

Postirradiation annealing studies on samples from a previously examined element indicated that volume increases of the order found in this examination could be expected at ~500°C. It is therefore concluded that the maximum centerline fuel temperature during irradiation was in the area of 500°C.

3. Examination of EBWR Core 1A Spike Element (R. CARLANDER AND L. A. NEIMARK)

A spike element from the 100 Mw core of EBWR was examined after an estimated burnup of 4.5a/o of the uranium atoms in order to provide information as to the performance characteristics of the fuel ele-

ment design and to the irradiation behavior of the fuel.

The fuel rod assembly consisted of 49 Zircaloy-2 fuel rods (9.5 mm diameter, 1.3 m long) in a 7 x 7

106-7841

106-7840

0.1X

FIG. 118. Opposite Sides of an EBWR Fuel Element after 100 Mw Operation.

EI-3152

0.08X

FIG. 119. Irradiated EBWR Spike Element Fuel Rod Assembly.

array supported at the ends by two Type 304 stainless steel end fittings containing fuel rod support grids, and at the midpoint by a Zircaloy-2 center spacer grid. Each rod contained a 1.19 m long fuel column of ceramic pellets of composition $81.92w/oZrO_2$ - $9.01w/oCaO$ - $9.07w/oUO_2$, 93% enriched. The fuel pellets were 8.13 mm in diameter, 12.7 mm long, and were fabricated by compacting a mixture of U_3O_8 , $CaCO_3$, and ZrO_2 at 985 to 112.5 kg/cm² and sintering in air at 1675°C.

The appearance of the fuel rod assembly after removal from the fuel element frame is shown in Figure

119. There was no evidence of warpage of the Zircaloy-2 side plates, distortion of the stainless steel end fittings, or bowing of the Zircaloy-2 fuel rods. No fretting corrosion was observed at the juncture of the fuel rod and the center spacer and the diameter of a measured set of four corner rods was within 0.025 mm of the original diameter. Scale buildup on each rod was minimal and could not be measured. A small amount of scale appeared to have been removed in the region of the center spacer but is believed to have been caused by sliding of the rods in the assembly during handling operations.

G. DEVELOPMENT OF CORROSION RESISTANT JACKETING AND STRUCTURAL MATERIALS

1. Aluminum Alloys for High Temperature Water Service (W. E. RUTHER)

Aluminum alloy corrosion samples exposed in the BORAX-V reactor were examined, weighed and electrolytically defilmed. As received, the outer corrosion product was a dark brown to dark gray color. The brown coloration suggested that some ferrous corrosion product had been deposited on the outer surface.

tests in refreshed autoclaves a metal loss of about 4 mg/cm² would have been predicted solely as the result of the high-temperature exposure.

Two other assemblies were exposed for longer periods (Groups 5 and 6, Table 47). The two sets do not differ substantially in the time at temperatures over 204°C,

TABLE 47. CORROSION OF ALUMINUM SPECIMENS IN THE BORAX-V REACTOR

Group No.	Samples*	Time, days					Reactor Location	Corrosion, mg/cm ²		
		Temp > 204°C	In Air	In Water (cold)	In H ₃ BO ₃ (cold)	H ₃ BO ₃ > 204°C		Metal† Loss, Avg.	Actual Coating	Calculated Coating
1	A288 X8001	51	26	501	33	5	Top N.W.	4.19	8.7	9.5
								4.60	9.5	10.2
2	A288 X8801	51	26	501	33	5	Top S.E.	4.34	8.6	9.7
								4.43	9.3	9.8
3	A288 X8001	51	26	501	33	5	Bottom N.W.	4.57	9.6	10.5
								5.08	10.5	11.3
4	A288 X8001	51	26	501	33	5	Bottom S.W.	4.65	9.6	10.3
								5.22	10.4	11.6
5	A288 X8001	82	26	649	49	10	Bottom S.E.	6.24	11.3	13.8
								6.64	11.9	14.7
6	A288 X8001	84	26	795	151	11	Top N.E.	8.54	12.7	19.0
								8.51	13.0	18.9

(*) A288 composition 0.93Ni, 0.53Fe, 0.11Ti, 0.003Si.

X8001 " 1.10Ni, 0.55Fe, 0.01Ti, 0.12Si.

(†) 7 mg/cm² metal loss is equivalent to a uniform penetration of 0.0254 mm.

The samples were exposed in assemblies of four X8001 and four A288 alloy plates. The area of each flat piece was 21.4 cm². The plates were held together with stainless steel threaded rods and stainless steel spacers.

Four assemblies were exposed for the same period in different spots inside the reactor vessel. All of the specimens of the same alloy within a single assembly corroded to approximately the same extent (±5%). A summary of the exposure and corrosion data is given in Groups 1-4, Table 47. It is apparent that the samples exposed at the bottom of the reactor vessel suffered more corrosion (10-15%, depending on alloy) than those exposed near the top. Whether this indicated an increase of corrosion with radiation would depend on whether the hydraulic conditions were similar for the two locations. It is well known that aluminum corrosion is dependent on the water velocity. From out-of-reactor

so the increased corrosion of Group 6 as compared with 5 would seem to be a result of corrosive attack in the cold reactor (water and boric acid solutions).

In the last two columns of Table 47 the actual weight of corrosion product is compared with that calculated from the metal loss figures. The difference is that amount of corrosion product which is lost to the reactor system. As in previous reactor experience in the EBWR, a significant amount of the coating was released after longer exposures.

Evaluation of the samples exposed in BORAX-V concluded this program. A summarizing and review publication⁽⁸⁷⁾ was prepared.

(87) Draley, J. E., and Ruther, W. E., "Aluminum Alloys" in Chap. 5 of *Reactor Technology—Selected Reviews, 1964*, TID-8540 pp. 215-223 (July 1964).

2. Zirconium Alloys for Use in Superheated Steam (C. A. YOUNGDAHL, S. GREENBERG, AND J. C. TEZAK)

Studies of the behavior in superheated steam of corrosion-resistant zirconium alloys have continued. The work relating to the first phase of relatively successful alloy development has been published.^(88,89) Investigation has continued in the following areas: (a) effect of alloy microstructure on corrosion; (b) the long term corrosion behavior of resistant binary alloys; (c) long term corrosion behavior of resistant ternary alloys; (d) the effect on corrosion rate of greatly reduced steam pressure; (e) further alloy modification for reduced oxygen absorption; and (f) surface electrical studies relating to hydrogen absorption during corrosion.

In the continuation of a study of the influence of alloy microstructure on corrosion behavior, samples of steam resistant zirconium alloys were worked by a high-energy forming (HEF) technique. As-cast samples in ring form (similar to tubing sections) were reduced in diameter at General Atomics (GA) by their Magne-form process, a magnetic pulse technique. A diameter reduction of about 10% was achieved at room temperature (for 5 cm OD rings of 1.5 mm wall thickness), according to the GA report. The ring form was chosen to simulate a fuel cladding section demonstrating a conceivable cladding application technique and to obtain HEF material. At Argonne the samples were subjected to metallographic examination and corrosion test. The as-cast microstructure was substantially retained through the moderate reduction achieved in the rapid-forming process. Sections corrosion tested in deoxygenated, superheated steam at 540°C, 42.2 kg/cm², for 128 days formed smooth, dark, adherent corrosion films free of blister attack, with film cracks at sharp edges, typical of the behavior of the better steam-resistant alloys. Weight gain rates were not unusual for these materials except for the Zr-3w/oNi-0.5w/oFe alloy: for this alloy the rate was significantly lower than that for samples prepared by hot rolling. This result is in accord with results of previous tests of this alloy in the as-cast state. Thus the relative superiority of the as-cast condition appear verified for this material, and it was demonstrated that the preferred state need not be lost in moderate forming. This behavior is in contrast with that of ternaries containing copper and iron, for which

the beta-quenched condition appeared preferable but was not retained in a long-term corrosion test.

Additionally, brief tests relating to formation of surface blemishes often observed on steam-resistant zirconium alloys during exposure to steam led to the tentative conclusion that blemishes are associated with local physical defects in the as-cast structure, which may be reduced through moderate reduction by hot rolling or high energy forming more readily than by cold rolling.

Long-term exposure of Zr-4a/oNi and Zr-4a/oCu (as cast) to 540°C, 42.2 kg/cm² steam was continued. After 385 days the Zr-Cu samples had continued to gain weight at a low rate. Total weight gained was 6.2 mg/cm² (average of three). The Zr-Ni samples' rate of gain was somewhat variable, totalling 9.4 mg/cm² (average of three) after 385 days. Thin edge cracks of the film were apparent at 13X on all samples, but there was no surface blistering. The corrosion product was adherent and colored gray to white. The test has been terminated. The relatively low weight gains are impressive and instructive with respect to the possibility of further improvement in steam corrosion resistance.

Samples of Zr-3w/oNi-0.5w/oFe and Zr-1.1w/oCu-1.2w/oFe in the hot-rolled condition were corrosion tested in 540°C, 42.2 kg/cm², deoxygenated steam for a total of 316 days. The purpose of this test was to determine whether an increase in rate of weight gain observed after 220 days in a previous test had been associated with an overtemperature excursion, or was, in fact, a real phenomenon of increasing rates at extended exposure times. From the recent data it is evident that the excursion did contribute substantially to the increase. In the present test weight gain rates continued to decrease slightly with time, being 3.4 mdd for Zr-Ni-Fe and 2.4 mdd for Zr-Cu-Fe during the most recent period. Surfaces developed relatively adherent coatings of corrosion product without blemishes. The usual film edge cracks were present. Total weight gains were 14 mg/cm² for Zr-Ni-Fe and 10.3 mg/cm² for Zr-Cu-Fe.

The foregoing alloys were tested in water vapor at 650°C and 1.35×10^{-3} kg/cm² (one-torr absolute) and the results compared with those obtained in 42.2 kg/cm² steam at 650°C. The purposes of the test were: (a) to observe the effect of steam pressure on corrosion rate, and (b) to obtain a basis for relating the results of electrical studies (see below) made in the one-torr range to corrosion processes at higher pressures. Samples pre-exposed 0.9 days to the high-pressure steam were transferred to the low-pressure environment and tested for an additional 12.8 days. While weight gains observed were somewhat lower than those of tests at higher pressure, the rates of gain after five days were essentially

⁽⁸⁸⁾ Greenberg, S., and Youngdahl, C. A., *Superheated Steam Attack on Zirconium Alloys Containing Small Amounts of Iron and Copper or Nickel*,* in Corrosion (to be published).

* This is an expanded version of the paper listed in the 1963 Annual Report as "Development of Zirconium Alloys for Use Supercritical Steam at 600 psi" and indicated as submitted to Corrosion.

⁽⁸⁹⁾ Greenberg, S., and Youngdahl, C. A., *Development of Zirconium Alloys for Use in Superheated Steam*, ANL-6714 (to be published).

the same as at 42.2 kg/cm². Lower total gains may have been due to a test temperature significantly lower than 650°C, which prevailed during the first low-pressure exposure period (2.7 days), or possibly to a real effect of low pressure on the initial corrosion behavior. The rate results reveal the lack of pressure influence on the corrosion reaction (at least after the initial exposures) and give additional interest to the results of electrical measurements made in the low-pressure environment.

Zirconium-alloy modification efforts have been initiated for the purposes of: (1) microstructure stabilization during use at elevated temperatures, (2) reduction of oxygen absorption rate in hot, oxidizing media, and (3) strengthening of the material for high-temperature use. It is thought these highly desirable results may be achieved simultaneously as a consequence of similarities in the fundamental mechanisms contributing to each. Alloying elements known to strengthen or harden zirconium are being added to the steam-resistant alloys in the initial work. The corrosion resistance of modified alloys is of first consideration. The steam-corrosion behavior of some experimental alloys containing silicon or beryllium additions is summarized in the following.

Twenty-four alloys containing beryllium or silicon have been arc melted: selected compositions in the 10 to 75a/o range for beryllium and 50 to 75a/o range for silicon were prepared. Ten of the alloys were based on crystal-bar zirconium and the rest on a master alloy of Zr-1w/oCu-1w/oFe. Simple mechanical tests verified the anticipated brittleness of the silicon alloys. The higher beryllium alloys had very high strength but

failed in a brittle manner. The lower beryllium alloy appeared to possess a useful ductility. A number of these materials were further homogenized by levitation melting and casting into copper molds.

Samples were corrosion tested in 650°C, 42.2 kg/cm², deoxygenated steam for 6 to 13 days. Samples based on crystal-bar zirconium were not corrosion resistant. Failure of several alloys based on the master alloy may have been associated with their poor mechanical properties. High-silicon alloys appeared somewhat more corrosion resistant (although highly brittle) than lower-silicon alloys but were not satisfactory. The lower-beryllium alloys were more satisfactory: a 1w/oBe alloy (based on master alloy) displayed a slightly lower weight gain after one week at 650°C than a control alloy containing no added beryllium, and its surface appearance was promising. The alloy modification study is continuing.

It has been found⁽⁹⁰⁾ that steam-resistant zirconium alloys absorb a markedly lower percentage of corrosion product hydrogen in steam at 650°C than at 540°C (at a steam pressure of 42.2 kg/cm² at both temperatures). It has been suggested that temperature-sensitive surface electrical properties may affect the percentage of hydrogen absorbed. Results of measurements of corrosion film resistance, EMF across corrosion films during corrosion, potential between corroding samples and the environment immediately adjacent (in one-torr steam) and conductance between samples and immediate environment (in one-torr steam) appear to lend support to the hypothesis. Techniques to apply an emissive coating to the surfaces of zirconium alloys in order to modify hydrogen absorption are being developed.

3. Corrosion of Stainless Steels and Nickel Base Alloys in Superheated Steam

(W. E. RUTHER, R. SCHLUETER, R. H. LEE, AND D. J. DORMAN)

This program has been oriented towards finding or developing a suitably corrosion-resistant alloy for use as fuel cladding in a nuclear superheat reactor. The results obtained prior to 1964 have been published.⁽⁹¹⁾ During the past year attention was directed towards the corrosion evaluation of modified commercial alloys at 650°C and the behavior of certain commercial alloys at 750°C. A special dual-wall autoclave was designed and built for testing at the higher temperature.

a. Corrosion Behavior at 650°C

Modified Type 304 Stainless Steel

High general corrosion rates and sensitivity of rate to surface preparation had been noted⁽⁹¹⁾ in the testing

of the 300 series stainless steels at 650°C. However, the relatively good neutron economy and the good fabrication experience with these alloys provided an incentive for attempting to improve their steam resistance. Aluminum was an obvious alloying choice based upon experience with Type 406. Other elements chosen—cerium, silicon, yttrium, and zirconium—could also reasonably be expected to increase oxidation resistance.

⁽⁹⁰⁾ Youngdahl, C. A., *Studies of Thermal Ions in the 540°-650°C Steam Corrosion of Zirconium Alloys*. Presented at Libby-Cockcroft Technical Exchange Meeting, April, 19 (to be published).

⁽⁹¹⁾ Ruther, W. E., and Greenberg, S., *Corrosion of Steels and Nickel Alloys in Superheated Steam*, J. Electrochem. Soc. **111** (10) 1116-1121 (October 1964).

all arc-melted buttons were prepared and fabricated into sheet. The results of seven-day corrosion tests of these alloys in refreshed (static) steam at 650°C are shown in Table 48.

Aluminum and silicon were found to be very beneficial additions. Additional aluminum-modified melts were made with the objective of determining the minimum percentage of aluminum for excellent corrosion resistance. Results of 28-day tests under refreshed static conditions are summarized in Table 49.

Unfortunately, the alloy containing enough aluminum ($\sim 4w/o$) to give excellent corrosion resistance was brittle after hot rolling into sheet. An alloy containing $3w/o$ Al and $0.2w/o$ Y had improved fabricability and could be bent (at room temperature) in sheet form without cracking. This alloy has very satisfactory corrosion resistance at 750°C (2 mg/cm² metal loss after seven days) and formed a very thin film, similar to that on Type 406 stainless steel, at 650°C.

Type 304 with $2w/o$ silicon (Table 48) is essentially the same composition as a commercially listed alloy (Type 302B). The latter alloy is recommended for service in high-temperature air. Unfortunately, it is not popular and samples were not available from commercial

TABLE 48. CORROSION OF MODIFIED TYPE 304 STAINLESS STEEL IN STEAM

Seven Days, 650°C, 42 kg/cm ² , 30 ppm O ₂		
Addition	w/o, nominal	Defilmed Metal Loss mg/cm ²
None	—	12.7
Al	4	0.02
Ce	0.1	7.3
		(*)
Si†	2	0.50
Y	0.1	6.4
	4	(*)
Zr	0.1	8.5
	4	4.5

(*) Cracked in fabrication. All samples exposed in electro-polished surface condition.

(†) This sample was exposed 35.0 days.

TABLE 49. CORROSION OF ALUMINUM MODIFIED TYPE 304 STAINLESS STEEL IN STEAM

28 Days, 650°C, 42 kg/cm ² , 30 ppm O ₂	
w/o Al	Defilmed Metal Loss—28 Days Exposure, mg/cm ²
0	18.0
1	17.0
2	8.8
4	0.06
5	0.03

TABLE 50. CORROSION OF MODIFIED INCOLOY 800 IN STEAM

650°C, 42 kg/cm ² , 30 ppm O ₂		
w/o Al	Defilmed Metal Loss, mg/cm ²	
	7.0 Days	15.9 Days
0	8.30	
1.05	4.67	4.21
2.4	1.06	1.04
3.5	0.33	0.61
3.7(+0.3w/oTi)	0.52	0.46
3.9	0.25	0.26

TABLE 51. CORROSION OF MODIFIED INCOLOY 800 IN FLOWING STEAM

650°C, 42 kg/cm ² , 61 meters/sec, 30 ppm O ₂ , 3.8 ppm H ₂					
w/o Al added	Defilmed Metal Loss, mg/cm ²				
	2 weeks	4 weeks	6 weeks	8 weeks	10 weeks
0(*)	1.10	1.74	1.16	1.21	—
1.05	0.93	0.88	0.81	0.90	0.95
2.4	0.51	0.56	0.56	0.51	0.58
3.5	0.82	0.98	1.11	1.21	1.07
3.7(+0.3w/oTi)	0.33	0.38	0.71	0.78	0.78
3.9	0.53	0.72	0.66	0.94	1.02

* The unmodified Incoloy 800 sample had been tested separately from the aluminum bearing samples.

sources. However, it does not suffer from brittleness and provides a very significant improvement in steam corrosion resistance as compared with Type 304.

Modified Incoloy 800

Incoloy 800 is among the alloys favored for superheated steam reactor cladding but earlier corrosion experience⁽⁹¹⁾ with this alloy indicated a sensitivity to surface preparation in the refreshed static autoclave tests. In an effort to prevent this phenomenon, alloys of Incoloy 800 modified with aluminum were obtained from the International Nickel Company. The results of exposures to refreshed static steam, summarized in Table 50, clearly show the improvement afforded by the addition of aluminum.

A dynamic test in 650°C, 42 kg/cm² steam containing 30 ppm oxygen and 3.8 ppm hydrogen was performed at 61 meters/sec velocity with the results shown in Table 51. There is less consistency in the variation of corrosion resistance with aluminum content than in the static test and also less overall improvement as compared with the aluminum free Incoloy 800.

From a fabrication point of view the modified alloys appear quite satisfactory. Heliarc welds were not brittle

and rolling to sheet form is readily accomplished. The International Nickel Company has performed some mechanical-property tests on modified material (2.9% Al) with satisfactory results. They report that the tensile and yield strengths of the modified material were greater than those of Incoloy 800 at room temperature and at 540°C while the percent reduction in area was only slightly less. A stress rupture test at 540°C also showed the modified material to advantage, as compared with Incoloy 800.

Brazed Joints

Type 406 stainless steel brazed with Coast Metals 60 was exposed to flowing steam (~30 m/sec) for 56 days. Temperature was 650°C, and the steam contained 30 ppm oxygen and 3.8 ppm hydrogen. The braze alloy experienced corrosive attack, particularly the excess braze material along the sides of the joint. Most of this has been converted to corrosion product and is easily chipped off with a probe. The joint itself did not appear weakened and the corrosive attack proceeded only slowly into the braze alloy between the joined 406 plates.

TABLE 52. CORROSION IN REFRESHED SUPERHEATED STEAM
750°C, 42 kg/cm², 30 ppm O₂

Alloy	Metal Loss, mg/cm ²					
	7 Days	14 Days	21 Days	28 Days	35 Days	50 Days
304 SS (EP)*	8.3	10.9	14.3	23.0	29.5	34.5
304 SS (GB)	0.6		3.1			
316 SS (EP)	12.2	17.8	17.7	21.9	21.5	
321 SS (EP)	12.9	17.5	25.2	24.4	31.8	
347 SS (EP)	11.9	16.7	24.8	27.9	37.5	
406 SS (EP)	0.4		0.42	0.42	0.55	0.6
Inconel 600 (EP)	9.4	13.5	17.9	12.4	13.8	15.1
Inconel 600 (WG)				1.8		2.3
Inconel 625 (EP)	0.4	0.6	0.6	0.7	0.7	1.27
Inconel X750 (EP)	2.9	2.4	2.4	2.6	3.27	
Incoloy 800 (EP)	6.7	7.2	6.8	6.8	7.2	8.9
Incoloy 800 (GB)						2.9
Rene 41 (EP)	0.96		1.04	1.16	1.33	
Nichrome V (EP)	0.5		0.5			
304 SS + 2w/oSi	0.63				3.3	

* (EP)—Electropolished

(GB)—Grit Blasted

(SG)—Wet Ground 600 Grit, Light Electropolish

b. Corrosion Behavior at 750°C

Although many of the proposed superheat reactors do not contemplate clad temperature as high as 750°C partial loss of steam flow through some channels could easily result in temperatures of this magnitude and even higher. With this possibility in mind, the corrosion performance of selected commercial alloys was evaluated at 750°C. Results are in Table 52.

A few general observations can be made. Alloys which had performed well at 650°C (i.e., Type 406 and Inconel 625) again showed lowest corrosion at the higher temperature. Type 406 showed less metal loss for a given time at 750°C than at 650°C, a continuation of the trend noted earlier. The other alloys could also be rated in about the same order as for 650°C, with slightly increased metal loss values for a given exposure time. The pronounced effect of surface preparation prior to test was again noted.

Significant changes in microstructure are observed as a result of the corrosion exposure at 750°C. Pearl and Gaul⁽⁹²⁾ have reported compositional changes near the surface as a result of exposure at temperatures of 700°C or less. Many of our alloys tested at 750°C for a month or more show changes in the distribution of inclusions or intermetallic compounds throughout the sample in addition to the surface-layer changes. The largest internal changes noted thus far have been the formation of a dispersed cubic phase in Type 321 and the coalescence and ordering of the intermetallic compound in Type 406.

Surface Preparation Effects

An attempt has been made to differentiate between the stress set up in a cold-worked surface and the partial transformation to a ferritic phase as possible causes of the improvement in corrosion resistance noted for such cold-worked surfaces. Type 304 stainless steel samples with cold-worked surfaces (machined, grit blasted or cold rolled) were stress relieved one hour at temperatures of 600, 700, 800 and 900°C. The higher temperatures should be adequate to relieve the stresses without reconverting the ferritic phase to austenite. These samples all continued to show the improved corrosion behavior characteristic of the cold-worked surfaces in low oxygen content steam at 650°C.

⁽⁹²⁾ Pearl, W. L., and Gaul, G. G., *General and Stress Corrosion of High Nickel Alloys in Simulated Superheat Reactor Environment*, GEAP 4165A (March 1963).

4. Light Alloy Suitable for Use with Mercury at Elevated Temperatures

(JAMES Y. N. WANG AND WALTER MCFALL)

This program is essentially complete and the work has been published.^(93,94)

a. The Inhibiting Effect of Dissolved Nickel in Mercury

As indicated in the Annual Report for 1963 (ANL-6868), the effect of nickel addition to the mercury is the development of a uniform protective layer at the surface of titanium samples* exposed at 538°C. No corrosion was observed during a 90-day test.

A microhardness traverse of an exposed specimen (Figure 120) showed a sharp increase in hardness in the layer adjacent the base metal. Spectrographic analysis indicated a high nickel ($>10w/oNi$) and low mercury ($0.1w/oHg$) content in the surface layer.

A similarly appearing layer was also formed when titanium specimens were exposed in a thermal-convection loop to nickel-containing mercury for 90 days. The loop was operated with a maximum temperature of 454°C in the hot leg and 320°C (lowest) in the cold leg with an average flow rate about 5.3 cm/sec (10.5 ft/min). A weight gain of 1.86 mg/cm² was recorded for the hot leg specimen. A cold-leg specimen showed only 0.42 mg/cm² weight gain, and metallographic examination of the surface indicated little or no corrosion at 353°C (average cold-leg temperature). Spectrographic analysis revealed that there was only a trace of nickel deposited on the cold-leg specimen.

Thermal mass transfer to the hot leg was thus observed. It may be that the transfer consisted of the dissolution of the soluble additive (nickel), transfer by convection and diffusion through the system to the surface of the solid metal (titanium), and subsequent interdiffusion. The titanium surface under the layer is not uniform. The nonuniformity is presumably due to initial surface attack before the layer was formed.

A microprobe study of the surface layer of an exposed specimen indicated that there were three levels for both nickel and titanium concentration. Figure 121 a, b, and c are the electron, NiK_{α} X-ray, and TiK_{α} X-ray images, respectively. The pen recordings of X-ray intensity vs. distance of line scans are shown in Figure 122.

Two analyses of the outer zone (nearest the edge)

⁽⁹³⁾ Wang, James Y. N., *Titanium and Titanium Alloys in Mercury—Some Observations on Corrosion and Inhibition*, Nuc. Sci. & Engr. **13**, 18-30 (1964).

⁽⁹⁴⁾ Wang, James Y. N., *The Effect of Metallic Additives in Mercury on the Corrosion of Titanium*, in Corrosion (to be published).

* Throughout this discussion titanium is to be taken as arc-melted crystal-bar titanium rolled to sheet specimens.

were reported as 58w/oNi-51w/oTi and 76w/oNi-26w/oTi respectively. The result of analysis of the inner zone (nearest the base metal) was 12w/oNi-81w/oTi. The fact that these values do not add up to 100% may stem from the fact that no fluorescence corrections were applied, or more importantly from the probability that the absorption correction is not as accurate as it should be. It was not possible to detect mercury in either of the zones or in the base metal.

Since the results of the analyses of the outer layer correspond roughly to the compounds TiNi (stoichiometrically 55.06w/oNi) and TiNi₃ (stoichiometrically 78.61w/oNi) it may be that there are two phases in the outer layer. Also, the nickel content of the inner zone is very close to the reported solubility limit of nickel in β -Ti even though the reaction was conducted below the α - β transformation temperature.

The mechanism of this reaction requires further careful study. In view of the evidence presented, it is believed that the intermetallic compounds formed on the surface of titanium during the corrosion process may act as a diffusion barrier between solid and liquid. Since there was little or no deposition of nickel on the cold-leg specimen of the loop test, one is led to believe that temperature plays an important role in this process.

The intermetallic compounds, TiNi and TiNi₃ have

37660

As Polished

250X

FIG. 120. Vickers Hardness Traverse of Titanium Sample Exposed to Nickel Saturated Mercury at 538°C for 90 Days.

MP600 700X

121a. Electron Image of Edge of Reacted Titanium.

MP602 700X

121b. NiK α X-ray Image of Same Area as Shown in "a".

MP601 700X

121c. TiK α X-ray Image of Same Area as Shown in "a".

FIG. 121. Microprobe Analysis of the Surface Layer Developed on Titanium in Mercury Containing Nickel.

106-8335

FIG. 122. The Pen Recordings of X-Ray Intensity vs. Distance of Line Scans.

been prepared and are being exposed to mercury at 538°C. Examination after exposure for 30 days indicated the compounds are inert in mercury at this temperature.

b. The Inhibiting Effect of Dissolved Zirconium or Aluminum in Mercury

The addition of zirconium, particularly, showed promise in the early stages of this study.⁽⁹³⁾ At 371°C a dark gray surface film was formed. However, at a few locations, this film was penetrated and an accelerated local attack resulted. At 454°C and 538°C, no

visible film was detected but the overall corrosion was markedly reduced.

Two loop tests, identical to the one previously described as to temperature and flow rate, were conducted. In one test the mercury was saturated with zirconium (at 320°C), in the other no additives were used. After 90 days exposure, the hot-leg (454°C) specimens from both tests were completely dissolved. The cold-leg (353°C) specimens were severely attacked.

The presence of aluminum, which is appreciably soluble in mercury at 538°C, greatly reduced the corrosion of titanium exposed to mercury at this temperature under static conditions (weight gain of 0.28

38352

Kroll's Reagent

250X

FIG. 123. Titanium Exposed to Mercury Saturated with Aluminum at 538°C (Static Conditions).

TABLE 53. INTERACTION OF TITANIUM AND ADDITIVES EXPOSED TO LIQUID MERCURY AT 538°C (STATIC CONDITIONS)

Specimen	Test Conditions	Weight Change* mg/cm ² , 14 days	Spectrochemical Analysis of Exposed Surfaces**				
			Hg	Ni	Zr	Mg	Al
Crystal Bar Titanium	Liquid Hg	-16.51	W	—	—	—	—
		-17.60	W	—	—	—	—
		-18.69	W	—	—	—	—
Crystal Bar Titanium	Liquid Hg + Ni (750 ppm)	+4.04	M	M	—	—	—
		+3.92	M	M	—	—	—
Crystal Bar Titanium	Liquid Hg + Ni (750 ppm) + Mg (50 ppm)	-34.10	W	T	—	—	—
		-31.20	W	T	—	—	—
Crystal Bar Titanium	Liquid Hg + Ni (750 ppm) + Al (50 ppm)	-28.56	M	W-M	—	—	W-M
		-29.87	M	W-M	—	—	W-M
Crystal Bar Titanium	Liquid Hg + Al (750 ppm)	+0.26	M	—	—	—	S-VS
		+0.32	M	—	—	—	S-VS
Crystal Bar Titanium	Liquid Hg + Ni (750 ppm) + Zr (50 ppm)	-58.20	M	W	—	—	—
		-57.50	M	W	—	—	—

* "+" refers to weight gain, and

"-" refers to weight loss.

** VS—very strong, above 10%

S—strong, 10 to 1%

M—moderate, 1 to 0.1%

W—weak, 0.1 to 0.01%

T—trace, 0.01 to 0.001%

TABLE 54. INTERACTION OF TITANIUM AND ADDITIVES EXPOSED TO LIQUID MERCURY AT 538°C, (STATIC CONDITIONS)

Specimen	Test Conditions	Weight Loss, mg/cm ² , 14 days	Spectrochemical Analysis of Exposed Surfaces*				
			Hg	Ni	Zr	Mg	Al
Crystal Bar Titanium	Liquid Hg	-16.51	W	—	T	—	—
		-18.69	W	—	T	—	—
		-17.60	W	—	T	—	—
Crystal Bar Titanium	Liquid Hg + Zr (750 ppm)	-0.15	M	—	M	—	—
		-0.94	M	—	M	—	—
		-0.92	M	—	M	—	—
Crystal Bar Titanium	Liquid Hg + Zr (750 ppm) + Al (50 ppm)	-0.89	S-VS	—	—	—	—
		-1.56	S-VS	—	—	—	VS
Crystal Bar Titanium	Liquid Hg + Zr (750 ppm) + Mg (50 ppm)	-2.08	M	—	S	—	VS
		-1.07	M	—	S	—	—
Crystal Bar Titanium	Liquid Hg + ZrN	-2.72	M	—	M	—	—
		-4.57	M	—	M	—	—
		-5.81	M	—	M	—	—
Zirconium Nitride	Liquid Hg	Disintegrated in ten days	—	—	—	—	—
Zirconium Nitride	Liquid Hg + Ti	-23.90	—	—	—	—	—

* VS—very strong, above 10%

S—strong, 10 to 1%

M—moderate, 1 to 0.1%

W—weak, 0.1 to 0.01%

T—trace, 0.01 to 0.001%

mg/cm² after 30 days). No visible surface film was detected as shown in Figure 123. However, a heavy powdery gray scum, presumably an amalgam of mercury and aluminum was formed in the expansion bulb. No scum was observed in the case of zirconium or nickel additions at this temperature. No loop test was performed with aluminum because of the scum formation.

c. The Effect of a Second Additive

The effect of a second additive to nickel-containing or zirconium-containing mercury on the corrosion behavior of titanium was investigated. In this series of tests aluminum or magnesium at a concentration of 50 ppm was used. It is presumed that both metallic additives may have some scavenging and/or wetting effects. Nickel and zirconium were also used in combination. Results of a 14-day exposure at 538°C in a static system are shown in Tables 53 and 54.

Data revealed that there was little effect of the

addition of aluminum or magnesium to the zirconium-containing mercury. However, greatly accelerated attack on titanium was observed in the Hg-Ni-Al, Hg-Ni-Mg and Hg-Ni-Zr systems. A reaction of mutual benefit results when titanium and ZrN are simultaneously exposed to mercury.⁽⁹⁴⁾ It appears that the effects of the addition of one or more metallic additives to the Ti-Hg systems involved a complex mutual interaction.

The mechanism of inhibiting corrosion by mercury is not yet established. In general, liquid metal inhibition is largely attributable to the formation of an insoluble protective film. If no film can be formed (for thermodynamic or physical reasons) there probably will be little or no inhibition. The influence of dissolved species on the electron configuration of a liquid metal such as mercury deserves a diligent study. A change in liquid structure may result, influencing in turn the aggressiveness of the liquid metal.

5. Lithium Corrosion Studies at Elevated Temperatures (J. Y. N. WANG AND WALTER D. McFALL)

Whenever higher operating temperatures can be effected in power-reactor design without undue complications, or impairment of safety, a resulting increase in the efficiency of the reactor can be expected to result in cheaper power. However, higher operating temperatures introduce additional problems in the cooling of reactors. Some of these problems may be solved by the use of a high-boiling, low-density coolant such as lithium, having good heat-transfer properties, provided suitable corrosion-resistant materials for fuel cladding and structural components can be developed. Lithium is also of potential interest as the fuel-cladding bond for use in high-performance, sodium-cooled reactors.

The corrosiveness of lithium at elevated temperatures is well known. Investigations of compatibility of various container materials have been undertaken in the past decade. It has been generally indicated that the materials most resistant to corrosion by lithium are high melting-point, body-centered cubic transition metals, notably molybdenum, tantalum, tungsten, and niobium. Among other factors, impurities in these materials, particularly oxygen, nitrogen and carbon, may dramatically affect the corrosion behavior. Very little quantitative information is avail-

able on refractory metal-lithium systems above 1000°C.

The present study was initiated to investigate corrosion, solubility and mass-transfer effects in lithium systems containing molybdenum, tantalum, tungsten and niobium between 900° and about 2500°C. Variables that effect the corrosion process and the study of which yield insight into protection possibilities are of paramount interest.

Work was initiated during the past year and was largely devoted to solving tangential problems in analysis of lithium and in handling and testing of refractory metal-lithium assemblies at high temperatures. Capsule design and protective loading and sealing procedures were established. Initial results of the corrosion of tantalum and molybdenum in lithium were obtained. High-temperature furnaces especially designed for this work are being procured.

A suitable technique for oxygen analysis in lithium has not yet been established, although neutron activation reportedly shows some promise. It is tentatively planned to use activation analysis in this study. Analysis of lithium for nitrogen has been accomplished with reasonable accuracy by use of a method based on the hydrolysis of lithium nitride to form ammonia and

lithium hydroxide. An analytical apparatus for nitrogen determination has been assembled, and a protective specimen-transfer container has been built. In preliminary runs with known nitrogen concentrations, it was demonstrated that this analytic method is of sufficient sensitivity in the range of 20 to 250 ppm of nitrogen.

Refractory-metal capsules used for the determination of compatibility with lithium are fabricated from high-purity metal (99.95+%). (The capsule serves both as container for specimens of the same metal and as a specimen itself.) The oxygen and nitrogen contents of these materials as furnished by suppliers were 50–100 ppm and 30–50 ppm, respectively.

Pending completion of an inert-atmosphere (recirculating helium) glovebox, an inert-gas "glove-pouch" was developed and used to transfer lithium into and out of refractory test capsules. Loaded capsules are then transferred to the electron-beam welding vacuum chamber. The lithium inside each capsule is protected in transfer by a lucite cap with Viton "O" ring seal. Because of the difference in pressure between the capsule interior (the inert atmosphere in the "glove-pouch" is at approximately normal atmospheric pressure) and its vacuum surroundings in the welder, the lucite cap is readily removed and the capsule is seal welded.

Tantalum (stress-relieved) in both the arc-melted and powder product form was exposed to lithium at 1000°C for seven days. Preliminary results indicated that both materials were susceptible to transgranular attack in liquid lithium. Figure 124 is typical of the surface of these samples. No attack was observed in the vapor phase.

High-purity lithium (from the same source as used in the molybdenum tests discussed below) was used in this test. However, the nitrogen analysis apparatus was not available at the time of the tantalum test.

At 1000°C, powder-product molybdenum exhibited no attack above the liquid level after 4.2 days. However, random penetration below the liquid level, particularly on the bottom portion of the capsule to a depth of about 1.5 mils was observed (Figure 125). No evidence of corrosive attack was observed on the arc-melted molybdenum samples. Microhardness measurements of a transverse section of the sample revealed that there was no disturbed layer discernable at the surface. Analytical results indicated that there was an increase of 30 ppm in nitrogen concentration of the lithium over the initial 30 ppm. Since no corrosion was observed metallographically it is presumed that 60 ppm of nitrogen in lithium has no effect on the

39557

Creighton's Reagent

250X

FIG. 124. Powder-Product Tantalum Exposed to Lithium at 1000°C for 7 Days.

corrosion of arc-melted molybdenum at 1000°C (at least for short exposure). Tests with this and other potential impurities at higher concentrations and at high temperatures are planned.

The density of powder-metallurgy materials is on the order of 97% theoretical. The porosity of these materials may contribute to their low resistance under above test conditions.

Apparatus suitable for use up to 1300°C is being assembled and equipment suitable for use to 2500°C* has been ordered. Pending completion of these facilities, the work at 1000°C serves to provide useful base line information and is also useful as an aid in developing the necessary techniques.

* This equipment is designed for continuous operation to 2000°C and for shorter times to 2500°C.

38945

Powder-Metallurgy Product

250×

40210

Arc-Melted Product

250×

Etched: 10% $\text{K}_3\text{Fe}(\text{CN})_6$ + 10% KOH in Water

FIG. 125. Comparison of Corrosion Behavior of Arc-Melted and Powder-Product Molybdenum Exposed to Lithium at 1000°C for 4.2 Days.

6. Corrosion Mechanisms in Refractory Metal—Liquid Metal Systems (T. F. KASSNER)

An understanding of the mechanism of the corrosion of the refractory metals in impure alkali metals would be an invaluable aid in evaluating and improving the usefulness of these materials in nuclear reactor systems. Unfortunately such an understanding, if it exists at all, does so only in a very fragmentary manner.

It is the purpose in this program to attack the problem by the study of dissolution kinetics under well defined hydrodynamic conditions in environments of interest. Since it is anticipated that the solubility of the refractory metals under such conditions will be extremely small, it is planned to study these systems by use of radiochemical techniques. Pending completion of the required apparatus (including a tantalum still for production of high-purity sodium) other systems are being investigated. Systems are selected that are suitable for perfecting the technique that will be used in alkali metal systems and which are also of some practical interest.

The rotating-disc sample geometry used in these studies was chosen because of the unique hydrodynamic properties of the system. Von Karman⁽⁹⁵⁾ and Cochran⁽⁹⁶⁾ have solved the Navier-Stokes hydrodynamic equations to give the velocity distribution throughout the body of the viscous fluid. This information along with the mathematical boundary conditions for the dissolution process can be used to obtain a solution to the convective-diffusion equation for mass transport.⁽⁹⁷⁾

The dissolution kinetics of Type 304 stainless steel in 58w/oBi-42w/oSn eutectic alloy is of interest because of application to potential corrosion problems of the rotating seal of EBR-II and other sodium cooled reactors. The results of this study have been reported.⁽⁹⁸⁾

The experimental method consists of immersing a 304 SS disc 61 mm in diameter and 2.9 mm thick, in 500 cc of Bi-Sn eutectic alloy. The disc is rotated at constant angular velocity and the liquid is sampled at temperature at specified intervals. The Bi-Sn samples were analyzed for iron, chromium, nickel, and manganese by a spectrographic method in which specially prepared standards were used. The limits of detectability of the analytical method are 0.003w/o for

iron and 0.0005w/o for chromium, nickel and manganese.

Dissolution data have been obtained over a wide range of experimental conditions. The effect of rotational speed of the disc on the dissolution rate was carried out at 860°C, a temperature at which the concentrations of all of the elements could be determined for exposure times greater than 0.5 hour. At 860°C, dissolution runs have been made at rotational speeds of 2, 10, 30, 50, 100 and 150 rpm for times up to 150 hours. The range 2 to 150 rpm defines the region of laminar flow in the vicinity of the disc and covers a range of Reynolds numbers from 1.32×10^3 to 1.0×10^5 . The Reynolds number for the rotating disc geometry is defined as $Re = \omega R^2/\gamma$ where R is the radius of the disc, ω is the angular velocity, and γ is the kinematic viscosity of the Bi-Sn eutectic alloy.

The effect of temperature on the dissolution process was investigated at a rotational speed of 10 rpm for temperatures of 650, 750, 860, 1050 and 1100°C. Additional data at 450 and 650°C at higher rotational speeds indicated that the relative concentrations of Fe, Cr, Ni, and Mn in the Bi-Sn eutectic alloy were still changing for times up to 80 hours. Another apparatus was used to equilibrate the 304 SS with the eutectic alloy for periods up to 500 hours at temperatures of 450, 650, 860 and 985°C to obtain mutual solubility data and the overall heats of solution of the four elements in the eutectic alloy.

The experimental data obtained under the well defined hydrodynamic flow conditions produced by rotating-disc samples can be compared with calculated liquid-diffusion-controlled dissolution rates (for rotating discs) to give insight into the dissolution mechanism. At 860°C, the maximum flux of material from the sample varied with the one-half power of the angular velocity of the disc in the range 2 to 30 rpm. Above 30 rpm the maximum flux was independent of the angular velocity of the disc. The dependence of the dissolution rate on the half power of the angular velocity is in agreement with a liquid-diffusion-controlled dissolution process.

At 10 rpm and temperatures above 700°C, the temperature dependence of the dissolution rate of iron from 304 SS can also be explained in terms of a liquid-diffusion-controlled process. However, the magnitude of the mass flux from the sample was found to be less than that predicted by the convective-diffusion model.

In view of the encouraging results obtained with this method in the six-component stainless steel-bismuth-tin system, a similar type of study of the tantalum-tin

⁽⁹⁵⁾ Von Karman, T., *Z. Angew. Math. Mech.* **1**, 233 (1921).

⁽⁹⁶⁾ Cochran, B. A., *Proceedings of the Cambridge Philosophical Society*, **30**, 365 (1934).

⁽⁹⁷⁾ Levich, V. G., *Physicochemical Hydrodynamics*, pp. 60-72, Prentice Hall, Inc., Englewood Cliffs, N. J., 1962, 2nd ed.

⁽⁹⁸⁾ Kassner, T. F., *A convective Diffusion Study of the Dissolution Kinetics of 304 Stainless Steel in the Bismuth-Tin Eutectic Alloy*, ANL-6985, to be published.

system is in progress in order to quantitatively correlate the dissolution rates with the critical variables of temperature, solute diffusivity, viscosity, thermodynamic solubility and Reynolds number for fluid flow.

The radiochemical analytic techniques being developed and used in the investigation of the Ta-Sn system will be applied to refractory metal-alkali metal systems of interest.

7. Polarization Studies in Liquid Metal Environment (C. A. YOUNGDAHL, S. GREENBERG AND J. C. TEZAK)

The performance of reactor structural materials in liquid metal heat transfer media is limited by corrosion. It is now well known by workers in this field that the presence of dissolved oxygen in the liquid metal influences the degree of attack. The corrosion phenomena include general oxidation attack; e.g., on zirconium a nearly continuous corrosion film is observed after exposure to oxygen-contaminated liquid sodium at elevated temperatures.

The feasibility of extending electrical polarization methods to this area of research, to study and perhaps influence the corrosion process, is being investigated.⁽⁹⁹⁾ In oxygenated sodium the corrosion behavior of a number of structural materials was observed at temperatures between 500 and 700°C. The corrosion and electrical behavior of selected metals of this group were studied in more detail.

The effects thereon of imposed anodic and cathodic polarization currents were investigated over a range of surface current densities from a few mA/cm² to 1 amp/cm². The results of these studies are summarized below and discussed in detail with respect to the phenomena and techniques of work with unalloyed zirconium at relatively low current densities. Effects of imposed current on polarization cell terminal voltage are reported, and the results of preliminary attempts to relate the electrical phenomena to corrosion are given.

The experimental cell apparatus developed in this investigation, shown in Figure 126, provides conditions important to the feasibility of the study. A region of reasonably constant temperature 5 cm long exists near the center of the melt: a somewhat longer useful region is available if differences in temperature of several degrees are tolerable. The sodium, being warmer at the bottom and periphery than at the upper surface is presumably stirred slowly by convection. The entire container is operated above the melting point of sodium to prevent solid accumulations of condensed

sodium in the upper region. The baffle is used to localize the refluxing sodium to as great an extent as possible away from the insulators. Currently a local heater is being added to the electrode under the baffle to insure that condensate does not form on the electrode shank. Without the latter, tests of a few days' duration may be conducted without condensate shorting either at the baffle or upper insulators. The possibility remains of shorting by essentially oxygen-free sodium condensate on the electrode shank near the liquid level: the degree of this interference and means of avoiding it are being studied.

Sodium is exposed to air briefly during transfer into the cell. This exposure is considered tolerable since operation near the oxygen-saturated condition was subsequently insured by addition of sodium peroxide. The possibility exists that a small amount of water vapor (and therefore hydrogen) is introduced by the transfer step operation. High purity materials are used for electrodes. For zirconium, electrodes 15 cm (6 in.) long x 0.65 cm (0.25 in.) diameter, with hemispherical ends, were fabricated from extruded rod of reactor grade material. They were machined to a surface finish of 15 to 20 microinches (38 to 51 microns) and etched briefly before use.

After test, samples are cleaned by water immersion and bristle brushing. Evaluation methods include weight change and film capacitance measurements. Some success was achieved in attempts to remove corrosion product film from zirconium electrodes (to obtain additional and more meaningful weight change data) by overnight immersion in calcium-saturated sodium at 600°C. Film capacitances (an inverse index of film thickness) are measured at room temperature in Hg-30w/o Woods Metal after low-voltage anodization in boric acid to eliminate film short circuits. Recordings of cell terminal voltage versus time at constant polarizing current were also obtained during the tests of zirconium electrodes.

In preliminary tests samples of Zircaloy 2, unalloyed zirconium, and unalloyed niobium were tested in oxygen-contaminated (≈ 400 ppm oxygen) sodium at 500, 600 and 700°C. Visual inspection indicated that un-

⁽⁹⁹⁾ Youngdahl, C. A., Greenberg, S., *Polarization Studies in Liquid Metals*, Presented at USAEC Corrosion Symposium, May, 1964 and at meeting of the Electrochem. Soc., Oct., 1964, Abstract—J. Electrochem. Soc. **111**, 8, P. 199c (Aug., 1964).

alloyed zirconium was to a degree protected at 500°C at a surface current density greater than 450 mA/cm² of cathodic polarizing current. At 700°C cathodic current densities approaching 1 amp/cm² appeared to result in lower weight gains for polarized samples.

In order to magnify the effects and facilitate control of oxygen concentration the near-saturation condition previously described was then adopted, and a survey of materials performance in this unusual environment at 650°C (and also at 540°C for zirconium) was made. Vanadium lost weight rapidly in 18 hours and was embrittled; Type 304 stainless steel appeared useful but exhibited noticeable attack; tantalum formed a voluminous reaction product in 40 hours; platinum dissolved rapidly; Nb-5w/oV formed a voluminous reaction product and displayed a large weight loss in 17 hours; unalloyed zirconium formed a nearly continuous, thin black film, lost weight at 650°C but gained weight at 540°C; and nickel was sufficiently resistant to permit its use as the cell material without substantial attack. These materials (external electrode extension referred to relatively cool nickel tube) displayed a positive EMF of from 9 to 13 mV, at a central sodium temperature of 650°C, (except in the cases of nickel (near zero) and stainless steel (not measured)). The behavior of the potential was in keeping with that of a thermocouple EMF, although the phenomenon was not studied in detail.

106-8328

Fig. 126. Sectional View of Polarization Cell.

TABLE 55. CONDITIONS AND RESULTS OF POLARIZATION EXPERIMENTS ON UNALLOYED ZIRCONIUM ELECTRODES IN HIGHLY OXYGENATED SODIUM AT 540°C

Sample	Pol. Condition mA/cm ² , avg.	Na Condition	Exposure Time, hours	Wt. Change, +mg/ cm ²	Cp* muf
A	Unpolarized	Fresh	20	0.76	.93
B	10.1, anod.	"	20	0.32	127;143
C	19.7 "	"	20	0.36	147
D	4.85 "	"	20	0.95	63
E	Unpolarized	"	67.5	0.93	41
F	"	"	20	0.38	46
G	5.4 anod.	"used"	65	0.41	95
H	21.5 "	"	45	0.26	325
I	21.5 cath.	"	20	0.19	223
J	20 anod.	Fresh	24.7	**	54
K	Unpolarized	"	20	0.84	—
L	Unpolarized	"used"	41.5	0.38	130

Letter sequence indicates order of occurrence of the runs.

* Parallel capacitance for reference area of 11.4 cm².

** Not obtained, but pol. curve suggests thick film: this sample in cell Na and at temp. 3 hr before application of polarizing current.

A more detailed study of unalloyed zirconium electrodes at 540°C produced the results summarized in Table 55. Various correlations are illustrated in subsequent figures. These electrodes displayed dark corrosion-product films on surfaces immersed in liquid sodium and shiny or slightly discolored surfaces on vapor-phase regions. Several small, relatively bare spots were usually found in the darkened (immersed) area. The room-temperature electrical resistance of these areas was far lower than that of the surrounding film. The cause of these spots has not yet been determined. They became less obvious and of higher resistance after the first few days' exposure. While average surface current densities are given in the table, the actual current distribution was probably highly nonuniform.

The weight gains of unpolarized zirconium electrodes are plotted in Figure 127, together with those of steam-resistant zirconium alloys tested in steam and in sodium at the same temperature. The behavior in the two environments is of the same order, but the somewhat lower rate of weight gain in sodium suggests the possibility of simultaneous weight loss and oxidation processes. The disturbing variability among samples of unalloyed zirconium in oxygenated sodium is also evident. The degree of correlation between various parameters from Table 55 is given in Figures 128, 129 and 130. Reduction in data scatter may be achieved through current efforts to eliminate the causes of uneven current distribution and to establish more reproducible behavior for unpolarized samples. An indication of lower weight gains and thinner films at higher

current density may be seen in the figures. The similarity of results of one cathodic polarization experiment of this group to results of the anodic polarization experiments was unexpected. There are no explanations at the present time and these observations are subject to further verification. The lack of good correlation

between weight gains and capacitive thickness index may be due in part to a film loss effect, as indicated by the slope of the upper line in Figure 128. However, the results of film stripping work in sodium-calcium solutions imply that the observed weight gains should be given credence equal to that of the capacitive results at present.

An example of the behavior of cell terminal voltage during constant-current anodic polarization of zirconium at a central sodium temperature of 540°C is given in Figure 131. Characteristically, the curves rise to levels in the 20 to 40 mV range (and occasionally higher) from an unpolarized value of about 4 mV. These voltage levels are presumably related to film thickness on at least a part of the immersed area. The cell potential frequently falls precipitously, after which, as a rule, it rises gradually to near the previous value. This type of behavior may be interpreted in terms of occasional cracking and gradual repair of the corrosion film, if not to condensate shorting in the lower region of the electrode shank.

No cathodic curves have been obtained. The EMF measured at the beginning and end of a cathodic test at an average surface current density of 21.5 mA/cm² was only slightly below that of the unpolarized value. It has also shown that momentary cathodization reduced the resistance to subsequent anodizing current to a low value.

106-8331

FIG. 127. Comparison of Corrosion Weight Gains in Oxygenated Sodium and 600 psi Steam, Both Media at 540°C., of Unalloyed Zirconium and Steam-Resistant Alloys, without Polarizing Current.

106-8345

FIG. 128. Film Thickness Index, $1/C_p$, vs. Weight Gain for Nine Samples of Zirconium after Exposure to 540°C Oxygenated Sodium. C_p is parallel capacitance for a reference area of 11.4 cm², in μf .

106-8319

FIG. 129. Weight Gain vs. Polarizing Current Zirconium Electrodes in Oxygenated Sodium at 540°C. Anodic Polarization, Except I.

106-8338

FIG. 130. Film Thickness Index, $1/C_p$ vs. Polarizing Current, Zirconium Samples after Exposure to 540°C. Oxygenated Sodium Cell. C_p is parallel capacitance for a reference area of 11.4 cm^2 , in μf .

It thus appears that the techniques of polarization are applicable to the study of zirconium corrosion in the highly oxygenated liquid-sodium environment. Additional findings, subject to further verification, are (a) phenomena such as film cracking may be observed more readily in liquid metal environments than in other media, and (b) the application of polarizing current may influence the corrosion process in the system studied.

106-8330

FIG. 131. Zirconium Electrode in Oxygenated Sodium Re Nickel-Cell Voltage vs. Time with 10 mA/cm^2 Anodic Current.

H. DEVELOPMENT OF FABRICATION METHODS

1. Fabrication of Tubing for High-Temperature Application (W. R. BURT, JR., J. E. FLINN, D. C. BRILLHART, AND R. M. MAYFIELD)

a. Primary Fabrication—Extrusion of Tungsten Tubing

While the 1963 work⁽¹⁰⁰⁾ covered various starting materials, work in the 1964 reporting period dealt almost entirely with pressed and sintered sleeves as extrusion starting material.

The technique used for extrusion of pressed and sintered sleeves measuring 3.18 cm OD x 2.54 cm ID x 10.2 cm long (1.25 in. OD x 1.00 in. ID x 4 in. long) has been previously reported in detail.⁽¹⁰⁰⁾ Basically, a core is placed in the sleeve and this assembly enclosed in a Type 304 stainless steel (304 SS) can with the overall billet diameter being 4.95 cm (1.95 in.). The billets are extruded on a 318-metric-ton vertical extrusion press at speeds ranging from 7.5 to 15 cm/sec (3 to 6 in./sec).

Sleeves from two vendors—Wah Chang and GE—have been studied. The GE sleeves exhibited a finer grain size and less porosity than did the sleeves procured from Wah Chang. The sleeves of both types had a typical hardness of about 32 Rc (320 DPH).

Extrusion parameters for the two sleeve materials are given in Table 56. Extrusion temperatures from 1000°C to 1250°C have been tried with 1100 or 1150°C apparently producing the best results. At 1000°C, the sleeve usually fractures; indicative of insufficient temperature for plastic deformation. At 1200°C and 1250°C in particular, the sleeve extrudes satisfactorily but is severely rippled along its length due to the stainless steel jacket being too soft to provide uniform deformation of the tungsten.

Reduction ratios of 4 to 16.5:1 have been used with ratios of 8:1 or higher being used initially. The high degree of deformation (8:1 representing about 85% reduction in area) was thought to abet cracking in the extruded product. Accordingly, the severity of working in the initial extrusion operation was reduced by using a 4:1 reduction ratio. Improvement in extruded tube quality resulted with cracking being greatly minimized.

Type 304 stainless steel, TZM, and molybdenum cores were tried with Mo being the only core material that resulted in acceptable extruded tube blanks. The

TZM core was too stiff at the extrusion temperature of 1100°C as both the tungsten sleeve and TZM core broke up into many segments. Uniform tubes were produced when extruding with a stainless steel core, but the tungsten tube invariably was cracked. This may be due to a lack of internal support for the sleeve by the relatively soft steel core when extruding at 1100°C.

As-extruded tubing has a high hardness and little additional work can be imparted to the material (at moderate temperatures) before serious cracking develops. Isochronal annealing studies have been conducted on as-extruded tubing to determine the hardness and structure believed to be most suitable for continued working.

For re-extrusion, sections from primary extrusions (1100 or 1150°C—4:1 reduction ratio) having a longitudinal microstructure as shown in Figure 132a were vacuum annealed for one hour at 1400°C. The resultant microstructure, for either GE or Wah Chang material, showed a uniform fine-grained recrystallized structure as illustrated in Figure 132b. After heat treating, the sections were canned in 304 SS and re-extruded at a ratio of 6.7:1 at 1100 or 1150°C. The re-extruded tubes measured approximately 0.61 cm OD x 0.06 cm wall (0.240 in. OD x 0.024 in. wall). The typical re-extruded microstructure is shown in Figure 132c.

Metallographic examination showed the re-extruded Wah Chang material to be cracked while the GE material appeared sound. X-ray radiography revealed the same results. Subsequent eddy current testing on a de-jacketed tungsten tube from Wah Chang material revealed numerous cracks to a depth of approximately 30% of the wall thickness. Unfortunately, no material from the re-extrusions of GE sleeve material was salvaged as they were severely cracked in a straightening operation at 900°C. The lack of ductility after double extrusion and at temperatures well above the transition temperature indicates the problems involved in fabricating small-diameter tubing of tungsten.

From the above results it may be tentatively concluded that starting material can make a significant difference in the quality of the extruded product as that various starting materials may require individual process development. The improved product obtained

⁽¹⁰⁰⁾ Burt, W. R., Jr., Katiyar, H. C. and Mayfield, R. M., *Development of Techniques for Fabrication of Small-Diameter, Thin-Wall Tungsten Tubing*. Interim Progress Report, July 1, 1963 through December 31, 1963. ANL-6806.

TABLE 56. SELECTED DATA ON EXTRUSION OF TUNGSTEN TUBING(*)

Ext. No.	Type of Extrusion	Material Source	Billet Components		Pre-extrusion Thermal Treatment of W Component	Extrusion Conditions			Remarks
			Can	Core		Reduction Ratio	Ext. Temp. °C	Running Extrusion Constant "K"(**) (psi) kg/cm ² (***)	
285	Primary	G.E.	304 SS	Mo	As pressed & sintered	10.3:1	1100	(60,000) 4150	Material cracked over part of the length. Some sections OK.
287	Primary	Wah Chang	304 SS	Mo	As pressed & sintered	10.3:1	1100	(59,500) 4120	Material cracked over most its length.
288	Primary	Wah Chang	304 SS	304 SS	As pressed & sintered	16.5:1	1100	(51,500) 3620	Material cracked. Very rough ID
304	Primary	Wah Chang	304 SS	Mo	As pressed & sintered	9.8:1	1100	(58,000) 4010	Material badly cracked. Rough ID.
305	Primary	Wah Chang	304 SS	Mo	As pressed & sintered	9.8:1	1150	(54,000) 3800	Material badly cracked. Rough ID.
315	Primary	GE	304 SS	Mo	As pressed & sintered	4:1	1150	(62,000) 4300	Metallographic sections indicate no cracking. Hardness on long. section is 494 DPH
316	Primary	Wah Chang	304 SS	Mo	As pressed & sintered	4:1	1150	(56,500) 3980	Some cracks near end defects. Balance OK. Hardness on long. section is 483 DPH.
321	Primary	Wah Chang	304 SS	Mo	As pressed & sintered	6.7:1	1150	(49,500) 3490	Cracked in straightening.
329	Primary	Wah Chang	304 SS	Mo	As pressed & sintered	4.1:1	1150	(71,700) 4980	Material delivered for test purposes. Not fully evaluated but OK in X-ray.
333	Primary	Wah Chang	304 SS	304 SS	As pressed & sintered	4.1:1	1150	(45,000) 3170	W tube severely cracked due to lack of support by 304 SS core.
334	Primary	Wah Chang	304 SS	TZM	As pressed & sintered	4.1:1	1150	—	Extrusion broke up in short segments.
319	Reextrusion	GE from Ext. #315	304 SS	—	Recrystallized by 1 hr. at 1400°C. Hardness ~380 DPH	6.7:1	1100	(49,000) 3450	Appeared sound in X-ray. Cracked during straightening. Hardness on long. sample is 528 DPH.
320	Reextrusion	GE from Ext. #315	304 SS	—	Recrystallized by 1 hr. at 1400°C. Hardness ~380 DPH	6.7:1	1150	(41,500) 2920	Appeared sound in X-ray. Cracked during straightening. Hardness on long. sample is 509 DPH.
322	Reextrusion	Wah Chang from Ext. #316	304 SS	—	Recrystallized by 1 hr. at 1400°C. Hardness 392 DPH	6.7:1	1150	(41,500) 2920	Cracks near lead end. Balance appears sound. Hardness on long. sample is 516 DPH.
323	Reextrusion	Wah Chang from Ext. #316	304 SS	—	Recrystallized by 1 hr. at 1400°C. Hardness 392 DPH	6.7:1	1100	(44,700) 3150	All metallographic sections show cracking. Hardness on long. sample is 502 DPH.
331	Reextrusion	GE from Ext. #315	304 SS	—	Stress-relieved 15 min. at 1100°C.	7.3:1	1100	(~40,500) ~2850	Broke into short sections in extrusion.

(*) For all primary extrusion, starting W sleeve measured 3.18 cm OD x 2.54 cm ID x 10.2 cm long (1.125 in. OD x 1 in. ID x 4 in. long).

(**) Calculated from $P = K \ln (A_0/A)$ using running extrusion pressure.

(***) Value for "K" does not reflect actual extrusion constant for W as the sleeve occupies only about 15% of billet cross-section. In Primary extrusions, however, effects of core material and extrusion temperature can be seen by comparative values of "K".

39711

150X

(a) Longitudinal Structure after Primary Extrusion (4:1 at 1150°C). Hardness: 494 DPH.

39820

150X

(b) Longitudinal Structure after Post-extrusion Anneal (1 Hour at 1400°C). Hardness: 383 DPH.

40116

150X

(c) Longitudinal Structure after Re-extrusion (6.7:1 at 1150°C). Hardness: 509 DPH.

FIG. 132. Longitudinal Microstructure of Tungsten Tubing at Various Stages of Processing. (Etchant: 5% KOH, 5% $K_2Fe(CN)_6$.)

from the GE starting material may be due to the smaller grain size of the initial pressed and sintered sleeve and/or the lower oxygen content of ≤ 100 ppm, compared with ~ 400 ppm for the Wah Chang product.

Secondary Fabrication of Tungsten Tubing

Secondary fabrication of extruded tungsten tubing has included swaging, drawing and rolling. While general observations can be made, specific criteria for secondary fabrication have not been established because a high-quality starting material was lacking.

The majority of secondary fabrication efforts were conducted on 0.63 cm (0.25 in.) diameter OD tubing procured from the Metallonics Corporation. (See the evaluation of commercial wrought tungsten tubing on page 141).

Drawing of tungsten tubing with an internal core such as molybdenum has been best accomplished to date by using an external jacket such as stainless steel or Hastelloy. Bare drawing at high temperatures has not proved feasible due to oxidation of the tungsten. The oxide builds up in the die during the draw and results in a poor surface or rupture of the tube. Bare drawing may be practical if a suitable high-temperature drawing lubricant can be found.

Pointing of the tube and core prior to drawing must be carefully controlled to prevent formation of cracks that will propagate into the main tube body during drawing. Likewise, if the draw point is reduced too far in cross-sectional area, the point will pull off in drawing.

Drawing of as-extruded tubing can only be done to a limited extent due to the high hardness of as-extruded material. A heat treatment to produce a softer, partially-recrystallized structure allows greater drawing reductions before additional annealing or stress-relieving is required. A fully-recrystallized structure with a large grain size is not suitable for drawing as the tube will immediately exhibit radial cracking of an intergranular nature. Thus, proper heat treatment of extruded tubing must be established prior to drawing.

Drawing has been tried at temperatures of 600 to 1150°C. Reductions up to 30% have been achieved. The results were somewhat inconclusive, however, owing to the earlier mentioned conditions of low-quality starting material and the crack-propagation characteristics of tungsten. Similarly, the Metallonics tubing exhibited about 0.2 mm (0.008 in.) of ovality, which made it impossible to obtain a core with a tight fit. Drawing thus required sinking until the tube seated on the core, and sinking may itself initiate cracking.

Swaging of tubing with a deformable core of molybdenum or TZM appears feasible for initial stages of

secondary fabrication. Here again, a heat treatment on as-extruded material may be necessary before high reductions can be achieved. Swaging-die design is important at high temperatures ($\sim 1000^{\circ}\text{C}$ or higher). Current cast Stellite swaging dies used at ANL feature a 32° entrance angle, a blade length two times the die diameter, and a 120° exit relief angle.

Swaging was conducted at temperatures of 750 to 1100°C . The pieces were initially swaged at the higher temperatures with the temperature being reduced gradually as additional passes were made. Close control over work piece temperature is necessary if a quality product is to be obtained. At the higher temperatures, reductions of 20% per pass were used. At the lower temperatures, reductions were limited to 10% per pass. Overall reductions of approximately 50 to 60% were achieved. Again, defective starting material made selection of specific conditions impractical, however, metallographic observations on transverse sections have indicated that sound tubing could be produced.

One problem associated with swaging was poor surface quality. After approximately 30% reductions, additional working created depressions and an uneven surface. This may be due to the large grain size of the molybdenum core and/or the tungsten grain size resulting from the preswage heat treatment. Another factor possibly contributing to poor surface quality may be bonding between the molybdenum core and tungsten tube. Should this be the case, a suitable lubricant for prevention of bonding must be found.

Rolling was also evaluated as a means of initial secondary fabrication. In general, results were similar to that obtained by swaging. Rolling appears feasible but the surface-quality problem is still present. In addition, ovality is more prevalent in rolling than in swaging or drawing.

Considering all secondary fabrication to date, it appears that tungsten tubing can be drawn or swaged (or rolled) if careful process control is maintained. Due to the crack-propagation tendency, high-quality extruded tubing should be used for starting material. Also, a suitable microstructure via heat treatment appears necessary if reasonable reductions are to be made. Careful selection of core materials and lubricants may improve surface quality. Drawn surfaces are very good, but maintaining a crack-free drawing point is a problem. In all cases, removal of the core after secondary fabrication is also a problem. Hopefully, establishment of proper drawing techniques will allow the use of plug or mandrel drawing in the smaller sizes.

Evaluation of Commercial Wrought Tungsten Tubing

Extruded tungsten tubing has been obtained from two commercial sources, Nuclear Metals, Inc., and Metallonics, Inc. Both supplied material intended for use as starting material for secondary fabrication. In addition, Metallonics, Inc. supplied a short section of finished tubing less than 2.5 mm (0.100 in.) in diameter for evaluation.

The NMI material consisted of 3.6 mm (12 ft.) of 0.95 cm OD x 0.08 cm wall (0.375 in. OD x 0.030 in. wall) with a minor amount being 1.90 cm OD x 0.15 cm wall (0.750 in. OD x 0.060 in. wall). All tubing was inspected by X-ray radiography and ultrasonic testing with metallographic sectioning used to verify some of the nondestructive indications. All material could be considered reject as numerous defects (cracks) greater than 40% of the wall thickness were located. The cracks generally originated on the ID.

The 7.6 m (25 ft.) of Metallonics tubing measuring 0.63 cm OD x 0.05 cm wall (0.250 in. OD x 0.020 in. wall) were inspected by both of these techniques as well as by eddy current inspection. This tubing can be considered reject material as defects greater than 10% of the wall were found. On the whole, however, the tubing appeared better than that obtained from NMI as defects tended to be shallower and not as numerous, but all of the tubing was oval in cross-section. Short sections were salvaged for secondary fabrication studies.

Recently, a 23 cm (9 in.) long piece of 0.95 cm OD x 1.0 cm wall (0.375 in. OD x 0.040 in. wall) extruded tungsten tube was received from NMI for evaluation. Although some defects were noted, they were less than the normal reject level of 10% of the wall thickness.

Two pieces of tungsten tubing approximately 2.0 mm OD x 0.18 mm wall x 30 cm long (0.080 in. OD x 0.007 in. wall x 12 in. long) were received from Metallonics for evaluation purposes. The first piece was improperly packaged and was severely damaged in shipment. The second piece arrived in one piece and was inspected by eddy current. Numerous serious defects were noted—some penetrating the complete wall. The tubing also showed marked ovality.

b. Tungsten-25w/oRhenium Tubing

In the last quarter of 1964, emphasis was switched from tungsten to the tungsten-25w/o rhenium alloy. The change was predicated on three major considerations. First, factors not specifically associated with tubing fabrication such as thermal expansion characteristics and ductility after recrystallization indicated that the W-Re alloy might be more suitable than pure tungsten. Secondly, difficulties in consistently produc-

The re-extruded tube appeared sound in radiography. Dejacketed sections of tubing 7.5 and 18.0 cm (3 and 7 in.) long measured approximately 0.55 cm OD x 0.055 cm wall (0.218 in. OD x 0.022 in. wall). These sections were inspected by eddy-current testing and found free of defects at a 10% defect level. Hardness measurements on the re-extruded tube were about 595 DPH.

Additional extrusions will be made to establish reproducibility and to provide stock for secondary fabrication. An annealing study is under way to determine the annealing characteristics of re-extruded tubing prior to further working.

No secondary fabrication studies on this tubing have been made during the reported period.

c. Evaluation of Commercial Wrought W-25w/oRe Tubing

Tungsten-rhenium tubing measuring 0.95 cm OD x 0.10 cm wall (0.375 in. OD x 0.040 in. wall) and approximately 2.5 mm OD x 0.25 mm wall (0.100 in. OD x 0.010 in. wall) has been received from Nuclear Metals, Inc. for evaluation.

The 0.95 cm tube was inspected by an ultrasonic technique. No cracks were observed in the tube. However, gross particles of sigma-phase W/Re (or undissolved rhenium particles with an outer layer of sigma phase) were seen at various spots. The particles were probably present in the starting material, which was a pressed and sintered sleeve. The presence of these large particles would likely eliminate the possibility of further fabrication. Interestingly enough, the triangular void spaces on the extrusion-direction sides of the particles (the hard particles were not deformed in extrusion) did not propagate cracks into the surrounding matrix metal to any significant extent. This lends some credibility to the belief that W-25w/oRe is more resistant to crack propagation than is pure tungsten.

The small-diameter tubes were evaluated by an eddy-current technique. The as-extruded tube exhibited defects greater than 30% of the wall thickness, but there were short areas free of defects. This tubing was of a higher quality than previously received tungsten tubing of approximately the same size. The two other tubes represented as-extruded tubing that had received a slight amount of secondary fabrication in the form of sink-draw operations. Both of these tubes were of poorer quality than as-extruded material, presumably because of the sink-drawing operation (no internal support).

40122

150X

(a) Longitudinal Structure after Primary Extrusion (3.2:1 at 1450°C). Hardness: 553 DPH.

40359

150X

(b) Longitudinal Structure after Post-extrusion Anneal (1 hr. at 1500°C). Hardness: 429 DPH.

40335

150X

(c) Longitudinal Structure after Re-extrusion (10.4:1 at 1150°C). Hardness: ~595 DPH.

FIG. 133. Longitudinal Microstructure of Tungsten-25w/o Rhenium Tubing at Various Stages of Processing. (Etchant: 5% KOH, 5% $K_3Fe(CN)_6$.)

2. Fabrication of Thorium-Uranium Fuel Materials (W. R. BURT, JR. AND W. C. KRAMER⁽¹⁰¹⁾,

To further evaluate irradiation behavior and permit comparison with material produced by other techniques, thorium-uranium alloys were produced in addition

fabricated from Th-20w/oU and Th-27.5w/oU alloys. Cast slugs from each alloy were extruded in the alpha or gamma phase (uranium) temperature range.

FIG. 134. Longitudinal Microstructures of 0.52 cm (0.206 in.) Diameter Extruded Th-U Alloy Rods.

tion to those described earlier.⁽¹⁰¹⁾ Specifically, specimens measuring 0.52 cm (0.206 in.) in diameter were

⁽¹⁰¹⁾ Annual Report for 1963, Metallurgy Division, ANL-6868, pp. 214-215.

The alloys were vacuum induction-melted in the crucibles and poured at temperatures of approximately 1825°C into graphite split-molds internally coated with flame-sprayed mullite. The castings measured 2.22 cm

(0.875 in.) in diameter by approximately 15 cm (6 in.) long. Extrusion billets measuring 1.9 cm (0.748 in.) in diameter by 5.1 or 6.3 cm (2.0 or 2.5 in.) long were machined from the castings. The machined slugs were "canned" in copper to prevent contamination of extrusion-press tooling and to affect adequate lubrication during extrusion. The overall extrusion billet size measured 2.5 cm (0.985 in.) in diameter by 7.6 or 8.9 cm (3.0 or 3.5 in.) long. After heating to the extrusion temperature of 500°C (α -phase) or 850°C (γ -phase), the billets were extruded at a 11.5:1 reduction ratio through a 0.75 cm (0.295 in.) die on a 150-ton vertical extrusion press. All billets extruded satisfactorily with the extrusion constant ranging from 2,700 to 3,800 kg/cm² (38,000 to 54,000 psi). As expected, the ex-

trusion constant decreased with increased extrusion temperature and increased with increasing U content in the alloy.

After extrusion, the copper jacket was removed by pickling in nitric acid. The extruded Th-U alloy rods measured approximately 0.65 cm (0.225 in.) in diameter after removal of the jackets. The rods were centerless ground to the final diameter of 0.52 cm (0.206 in.) and delivered to the Engineering Irradiation Group for sectioning into suitable test specimens. Longitudinal samples were taken from each extrusion for metallographic examination. The microstructures are shown in Figure 134. As expected, the structure shows a network of free uranium in a thorium matrix.

I. DEVELOPMENT OF NONDESTRUCTIVE METHODS

1. Correlation of the Sound Transmission Properties, Heat Transfer Properties and Strength of a Bond (R. A. DI NOVI)

The acceptance or rejection of a bonded element that has been tested by ultrasonic methods has been made on the basis of the ability of the bond to transmit or reflect ultrasonic energy, with only occasional reference to destructive evaluation of the bond. The criteria for acceptance are often poorly defined, as the tests do not provide any information about the serviceability of the element, i.e., its ability to transmit heat, because it is not known what correlation, if any, exists between the heat transfer and ultrasonic transmission properties. To make ultrasonic bond tests more significant, such a correlation is being sought.

To determine the thermal properties of the bonded elements, the thermal-pulse method for measuring thermal diffusivity and thermal conductivity developed by Parker et al.,^(102,103) is being utilized. Figure 135 is the room temperature setup.

Thermal diffusivity (α) and thermal conductivity (K) measurements have been completed on mechanical bond (brazed-bonded copper) and roll-bond (sections of BORAX fuel plates) specimens. Each specimen was scanned over its central portion in about 30 thermocouple positions. Each position gave a value for the diffusivity and conductivity in a 1 mm² area of specimen; readings were taken about 1 mm apart. Such closely spaced point-by-point measurements were necessary as poorly bonded specimens were found to exhibit great differences in thermal properties in small areas. For the copper brazed-bonded specimens values ranged from $\alpha = 1.01$ cm²/sec to $\alpha = 0.009$ cm²/sec and $K = 0.882$ cal-cm/cm²-sec-°C to $K = 0.008$ cal-cm/cm²-sec-°C. For copper $\alpha = 1.14$ cm²/sec and $K =$

0.922 cal-cm/cm²-sec-°C. For the BORAX fuel plate (Type 304 stainless steel clad and a core of UO₂ dispersed in Type 304 stainless steel) specimens values ranged from $\alpha = 0.0289$ cm²/sec to $\alpha = 0.0248$ cm²/sec and from $K = 0.0329$ cal-cm/cm²-sec-°C to $K = 0.0271$ cal-cm/cm²-sec-°C. For Type 304 stainless steel, $\alpha = 0.034$ cm²/sec and $K = 0.038$ cal-cm/cm²-sec-°C.

The ultrasonic tests were made by the through-transmission method. Both the sender and receiver transducers were collimated to a 1½ mm beam. A point-by-point ultrasonic scan was made, so that a comparison of the amplitude of the transmitted ultrasonic pulse and the thermal diffusivity and thermal conductivity can be made at each point on the specimen. Ultrasonic tests were made on all specimens at frequencies of 0.5 mc, 1.0 mc, 2.25 mc. Tests at five and ten megacycles have recently been completed and the complete analysis of the data is still in progress.

106-8039

FIG. 135. Apparatus for Measuring Thermal Diffusivity on Bonded Specimens at Room Temperature.

⁽¹⁰²⁾ Parker, W. J., Jenkins, R. J., Butler, C. P., and Abbott, G. L., *Flash Method for Determining Thermal Diffusivity, Heat Capacity and Thermal Conductivity*, A. Appl. Phys. **32** (9) 1697 (1961).

⁽¹⁰³⁾ *Annual Report for 1963, Metallurgy Division, ANL-6868*, pp. 221-222.

2. Ultrasonic Instrument and Transducer Development (R. H. SELNER)

In the past year, work has continued on the development and fabrication of transducer probes. Major emphasis has been placed on special-function probes, i.e., probes designed for a specific application. In particular, probes for the inspection of small-diameter, thin-walled tubing have been given top priority.

Initial efforts in this area have been reported.^(104,105) Ceramic materials, either lead zirconate-titanate or lead metaniobate, have been used exclusively as the piezoelectric crystal element because of their high sensitivity. It is anticipated that other materials such as quartz and barium titanate will be used in probes where sensitivity is not the primary requisite.

In the inspection of small-diameter tubing, it is desirable to have a highly concentrated or focused beam, which reduces outside diameter reflections and which

results in the maximum transfer of ultrasonic energy into the tube wall. To accomplish this focusing, tubular or hemispherical forms of the piezoelectric crystal material or lenses attached to the front face of the crystal are utilized. More often than not, formed crystals with the desired characteristics are not readily obtainable and/or are quite expensive. Thus, for most purposes, focusing must be accomplished by lenses. With this in mind, efforts have been concentrated in the development of lens-focused transducer units. Epoxy lenses have been used in preliminary models.

A Schlieren optical system was installed to evaluate the beam patterns from developmental transducers. It is planned to set up an additional facility for measuring and studying transducer characteristics.

3. Ultrasonic Imaging (H. BERGER)

The system for obtaining a television presentation of ultrasonic radiation images, as described in a previous annual report,⁽¹⁰⁶⁾ has been further studied. The most significant result of this further work is that a better understanding of the need for placing flat inspection objects in the ultrasound field at angles other than normal has been obtained. Figure 136 shows a diagram of the imaging system and indicates that flat objects should be angled with respect to the direction of the ultrasonic radiation path.

Optimum imaging results for inspecting flat objects having low or medium thickness can be obtained by placing the object in the ultrasonic radiation path at an angle, θ_i , for the generation of Lamb waves within the sample. The angles are normally great enough that ultrasonic radiation transmitted through the sample, and reflected back from the detector, is then reflected out of the imaging area. This elimination of standing wave patterns is important for clarifying the image. Equally important from the Lamb wave point of view is the increased ultrasonic transmission, and the sensitivity of Lamb waves to normally encountered internal defects.⁽¹⁰⁷⁾

⁽¹⁰⁴⁾ Annual Report for 1963, Metallurgy Division, ANL-6868, pp. 223-224.

⁽¹⁰⁵⁾ Renken, C. J., and Selner, R. H., *Refractory Metal Tubing Inspection Using Ultrasonic and Pulsed Eddy Current Methods*, Materials Evaluation (to be published).

⁽¹⁰⁶⁾ Annual Report for 1963, Metallurgy Division, ANL-6868, pp. 219-221.

⁽¹⁰⁷⁾ di Novi, R. A., *Lamb Waves: Their Use in Nondestructive Testing*, ANL-6630 (March 1963).

Figure 137 shows a series of kinescope photographs of the ultrasonic transmission image of a flat metallic sample containing a simulated flaw. The pictures represent different angles of incidence. Although the flaw image can be detected in all the photographs, optimum results are demonstrated for the first symmetrical Lamb wave mode.

106-8329

FIG. 136. Upper Diagram of Side View of Television Ultrasonic Imaging System. The camera tube, normally used with a barium titanate target and vacuum window, is continuously pumped. The lower diagram is a top view of the system showing the angle of incidence, θ_i , and the object-detector distance, x . For best results, x should be 4 cm or less.

38995

FIG. 137. Photographs of Television Presentation of a Continuous Wave Ultrasonic Inspection of a Stainless Steel Sample for an fd Product of 2.36×10^5 cm/sec (frequency was 1.9 mc, thickness was 0.124 cm). The sample contained a simulated flaw. Pictures were taken at θ_i values, left to right of 0, 12.4, 21.7 and 32.5° illustrating normal incidence and the second asymmetrical, first symmetrical and first asymmetrical Lamb wave mode images, respectively. Improved imaging at the 21.7° angle, the first symmetrical mode, is apparent. A slight image of the flaw can be observed through the standing-wave pattern at normal incidence.

Generally, best imaging results were found for first order Lamb wave modes, probably because these modes generate with higher ultrasonic radiation intensity as compared to higher order modes. In addition, there were often cases, such as the one illustrated in Figure 137, in which a clear choice between first order symmetrical or asymmetrical modes could be made. In cases in which the asymmetrical wave mode velocity approached that of Rayleigh waves, for example, the

symmetrical mode usually produced better imaging results. A more complete description of the use of Lamb waves for improving these continuous wave ultrasonic images has been reported.⁽¹⁰⁸⁾

Work presently in progress concerning the ultrasonic imaging system includes an evaluation of ultrasonic lenses for imaging purposes and a comparison between the television imaging system and other ultrasonic inspection methods.

4. Determination of Elastic Moduli of High-Temperature Materials by Ultrasonics

(R. G. PETERSON)

The object of this program is to measure the temperature dependences of the elastic moduli of materials that show promise in high-temperature reactor applications. To obtain these data a vacuum furnace has been constructed for mounting solid bar-shaped samples. Pulsed ultrasonic waves are propagated along the length of these samples, and the transit times of pulses passing a heated, indexed region in each bar are measured. The indexing is done by machining one end to a smaller diameter than the rest of the bar.

The velocity of sound in the indexed region can then be calculated from a knowledge of the length of this region and the transit time in it. Both shear-wave velocities (V_s) and longitudinal velocities (V_L) are determined. Poisson's ratio can be calculated by the formula

$$\sigma = \frac{\frac{1}{2}(V_L/V_s)^2 - 1}{(V_L/V_s)^2 - 1}$$

Young's modulus can be calculated by

$$E = \frac{V_L^2 D (1 + \sigma) (1 - 2\sigma)}{1 - \sigma},$$

and the shear modulus by

$$\mu = DV_s^2$$

where D is the density of the material.

An important problem in the operation of the vacuum furnace is the reduction of the temperature gradient in the indexed region of the specimens. Each specimen is a bar two and one-half centimeters in diameter and about 25 cm long. One end of the bar, approximately 3 cm in length, has a reduced diameter of about 1.7 cm. The large-diameter portion of the bar extends from the center of the furnace through a vacuum seal and a water-cooled jacket, and out of the furnace completely. Obviously the metal sample "leaks" heat away from its hot end at a great rate. To measure the temperature gradient, two thermocouples are resistance-welded near the two ends of the indexed region. The temperature gradient in this region depends

⁽¹⁰⁸⁾ Berger, H., and di Novi, R. A., *Angular Positioning of Thin Metallic Samples for Optimum Continuous Wave Ultrasonic Imaging*, J. Acoust. Soc. Am. **36**, pp. 2053-2058 (1964).

upon the material of the specimen, the temperature of the furnace, and the position of the sample in the furnace. Temperature differences of as high as 50°C have been measured. Considerable effort has been made to reduce this temperature difference. The most promising technique is to wind a secondary heater coil directly on the specimen above the index region; this extra heater compensates for the heat flow lost up the bar to the water jacket. To electrically insulate this winding from the metal specimen, a thin layer of alumina is plasma-sprayed on the bar over the proper region. This technique shows considerable promise, and is being further investigated.

A technique for measuring two sound velocities with one type of sound wave makes use of the waveguide effects which are present when sound is propagated in a long, narrow, bar. The transit time of 5 mc/sec longitudinal wave pulses over the index region gives V_L (see previous formulas), while the delay time between the trailing pulses generated in the index region due to the waveguide effect^(109,110) is a function of V_s . Thus, measuring the transit time and the delay time in the index region gives us V_L and V_s , if the length and diameter of the specimen are known as a function of temperature. In order to minimize trailing pulse generation in the large diameter portion of the bar, the wall is threaded with a sharp 60° Vee thread, other-

wise the pulses become confused with the trailing pulses from the indexed region.

The sound velocities and elastic moduli have been measured for stainless steel and for V-20w/oTi alloy (TV-20) from room temperature to 925 and to 1100°C, respectively. The stainless steel bar (exact type not known) was measured to compare the values obtained in this laboratory with those of Dunegan⁽¹¹⁰⁾ and with those of Leavitt and Martin;⁽¹¹¹⁾ the results were almost identical. The results on TV-20 alloy compare favorably with those given by Hill and Wilcox⁽¹¹²⁾ in the region where they overlap (they did not make measurements at as high a temperature).

In the course of the work, the following room-temperature data were determined. The error figures quoted refer to the standard deviations in the quantities based upon reproducibility of original measurements.

For tungsten:	Young's modulus: $(3.87 \pm 0.03) \times 10^{12}$ dynes/cm ²
	Shear modulus: $(1.507 \pm 0.005) \times 10^{12}$ dynes/cm ²
	Poisson's ratio: 0.2838 ± 0.0008
For TV-30:	Young's modulus: 1.13×10^{12} dynes/cm ²
	Shear modulus: 0.365×10^{12} dynes/cm ²
	Poisson's ratio: 0.537
	(Error analysis has not been completed for TV-20)

5. Development of a Neutron Image Intensification System (H. BERGER)

The value of image-intensification systems for use with penetrating radiation such as gamma or X-radiation is well established. In addition to providing a mechanism for immediate visible imaging of such radiations, an image intensification system often permits the use of lower radiation intensities thereby easing shielding requirements and creating a more favorable situation for the inspection of biological samples. Also, the radiation imaging system becomes readily adaptable for time varying studies in which the inspection sample can be subjected to variations in such things as temperature, stress, etc. Similar advantages apply to neutron imaging systems. Therefore, a program to develop a neutron image intensification system was initiated.

In the preliminary phase of this program the applicability of methods used for gamma and X-ray intensification systems was evaluated for possible use in a neutron intensification system. Following the classification system used in a review by Niklas,⁽¹¹³⁾ the X-ray image intensification systems that have been most studied and used can be grouped into three categories. These are electronic, solid-state and vacuum-tube methods.

In the X-ray field, the vacuum-tube type of image intensifier has received the greatest application use and has been developed to a relatively high degree.

⁽¹¹¹⁾ Leavitt, A. D., and Martin, A. G., *Ultrasonic Determination of Elastic Constants of Metals at Elevated Temperatures*, WAL-TR-143/34 (1959).

⁽¹¹²⁾ Hill, W. H., and Wilcox, B. A., *Elevated Temperature Dynamic Moduli of Vanadium, Titanium and V-Ti Alloys*, WADD-TR-60-245 (AD-24379) [1960].

⁽¹¹³⁾ Niklas, W. F., *X-Ray Image Intensification with a Large Diameter Image Intensifier Tube*. Am. J. Roentgenology, Radium Therapy and Nuclear Medicine **85**, 323-341 (1961).

⁽¹⁰⁹⁾ Peterson, R. G., "Mechanical Vibrations in Solid Rods," *Second Symposium on Physics and Nondestructive Testing*, NL-6515 pp. 133-161 (1961).

⁽¹¹⁰⁾ Dunegan, H. L., *Determination of Dynamic Modulus at High Temperatures by Use of Ultrasonics*, UCRL-7326 (Rev. 1) (1963).

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FIG. 138. The brightness of the output phosphor of the neutron image intensifier tube is shown as a function of the thermal neutron intensity at the tube face, and the Juggernaut reactor power used to obtain that neutron intensity. The slope of the curve is very close to 1.0. The solid portion of the curve represents measured values. The dashed extension brings the curve farther into the brightness values normally employed for low level light applications such as the brightness values encountered in X-ray fluoroscopy.

For this reason alone, the consideration of this type of intensifier for neutrons appears attractive. In addition, such use would involve a method for converting the neutron image into an electron image, either directly or through an intermediate, light-emissive step. Fortunately the method of neutron detection involving conversion from neutrons to light⁽¹¹⁴⁻¹¹⁷⁾ has received considerable attention.

It is primarily the vacuum-tube intensifier approach to neutron intensification that has been considered thus far in this study. Other possibilities would involve a material exhibiting a photoconductive type of neutron response for use in a neutron-sensitive vidicon or a solid-state type of device. Studies of both CdS⁽¹¹⁸⁾

⁽¹¹⁴⁾ Wang, S. P., Shull, C. G., and Phillips, W. C., *Photography of Neutron Diffraction Patterns*, Rev. Sci. Instr. **33**, 126-127 (1962).

⁽¹¹⁵⁾ Sun, K. H., Malmberg, P. R., and Peejak, F. A., *High Efficiency Slow-Neutron Scintillation Counters*, Nucleonics **14** (7) 46-49 (1956).

⁽¹¹⁶⁾ Bishay, A. M., *Glass Scintillator for Neutron Detection*, J. Am. Cer. Soc. **44**, 231-233 (1961).

⁽¹¹⁷⁾ Bollinger, L. M., Thomas, G. E., and Ginther, R. J., *Neutron Detection with Glass Scintillators*, Nucl. Instr. & Methods **17**, 97-117 (1962).

⁽¹¹⁸⁾ Broser, I., Kallmann, H., and Warminsky, R., *Two*

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FIG. 139. Photograph of Output Phosphor of the Neutron Intensifier Tube Showing the Neutron Image of a Flashlight.

and silicon *p-n* junctions⁽¹¹⁹⁾ have shown some promise for solid-state neutron detection. However, neither of these detection techniques presently appears as far advanced as the scintillation type. A neutron scintillator used directly with an image orthicon television camera is another fruitful possibility. Although the use of a neutron scintillator within a vacuum-tube intensifier presents some additional problems for an initial study, the large technological capability that is now available for such work and the potential advantages over the more simple approach combine to make the effort to develop a vacuum tube type of neutron image intensifier attractive.

The vacuum-tube type of image intensifier depends upon the production of an electron image signal within the intensifier tube. This can be accomplished by direct electron emission from a suitable target or a combination target consisting of a scintillator and a photoemissive surface. Both these approaches were studied for the neutron-image intensifier. Gadolinium emits internal-conversion electrons directly upon thermal neutron absorption. However, this method of obtaining an electron image within the image-intensifier tube did not appear as useful as the combination neutron scintillator-photoemissive target technique. This latter

New Methods for Counting Neutrons Using Cadmium Sulphide Crystals, Research **2**, 87-89 (1949).

⁽¹¹⁹⁾ Friedland, S. S., Mayer, J. W., and Wiggins, J. S., *The Solid State Ionization Chamber*, Hughes Aircraft Co., Tech. Memo **626** (Nov. 30, 1959).

approach was preferred because it offered the promise of improved threshold sensitivity and because of greatly simplified electron-optical problems within the intensifier tube (the electrons from the gadolinium are emitted with energies up to 70 kev).

The tube of the scintillator-photoemissive type has been prepared by the Rauland Corporation, Chicago, Illinois and subjected to preliminary tests at the Juggernaut reactor neutron radiographic facility.⁽¹²⁰⁾ Figure 138 shows the output brightness of the tube as a function of thermal neutron intensity at the tube face. The response is linear over more than three orders of neutron intensity. If one extrapolates toward lower neutron intensities, it can be seen that the tube should yield an output brightness value within the normal range used for X-ray fluoroscopy for thermal neutron intensities lower than 10^3 n/cm²-sec.

Preliminary data include a resolution capability on the order of 0.25 to 0.5 mm, a thickness sensitivity of about 8% for 2 to 4 cm of natural uranium, a speed of response such that the image of a high-contrast object moving at speeds of 1 m/min does not blur, and a high-energy gamma sensitivity such that radiation levels of 4000 R/hr yield a brightness comparable to a thermal neutron intensity of about 5×10^5 n/cm²-sec. The diameter of the input phosphor target of the tube is 22 cm. The output phosphor has a useful diameter of 2.5 cm. Figure 139 is a photograph of the output phosphor of the intensifier tube showing the neutron transmission through a flashlight.

More complete evaluation studies are now in progress. Additional intensifier tubes will be prepared and evaluated as modifications in tube design are suggested.

6. Development of Infrared Systems for Nondestructive Testing (H. BERGER)

An infrared-sensitive television system having a vidicon camera tube sensitive to radiation in the 0.8 to 2.7 μ wavelength region has been evaluated. The camera tube is a 2.54 cm diameter vidicon, available from RCA as Developmental Tube Type C74125. The vidicon tube has been used with a commercially available closed-circuit television system. Best results were found with a Kellner eyepiece lens, 37 mm OD and 28 mm focal length.

Under the best conditions tested, the system demonstrated a threshold response for objects having a surface temperature of 170°C. For most nondestructive testing applications, however, the lowest useful object temperature would be 250 to 300°C, for in that temperature range the system begins to demonstrate a capability for differentiating between similar surfaces

TABLE 58. OBJECT TEMPERATURE DIFFERENCES
DETECTABLE WITH EVALUATED INFRARED
VIDICON TELEVISION SYSTEM

Object Temperature (°C)	Temperature Difference Detectable by TV Presentation (°C)
170	Min. Temp. Observed
200	10
250	8
300	4
350 and higher	3

⁽¹²⁰⁾ Berger, H., *Characteristics of a Thermal Neutron Beam for Neutron Radiography*, Internat'l. J. Appl. Rad'n. & Isotopes 15, 407-414 (1964).

Fig. 140. The Relative Luminous Emittance of the Kinescope Presentation of the Infrared Vidicon Image of a Blackened Blade Heater is Shown as a Function of the Heater Surface Temperature in Degrees Centigrade.

having a relatively small difference in temperature. Table 58 outlines the experimentally determined values of ΔT that can be observed at various object temperatures. The overall response of the system is demonstrated in Figure 140, in which the kinescope brightness (for particular gain and brightness settings) is plotted against the surface temperature of the observed object.

Although the television system described above does not have the capability for differentiating between temperature differences as small as those which can be

detected by mechanical scanning systems, it does have the advantage of speed of response. A complete picture is presented in $\frac{1}{30}$ sec., thereby giving the television system the capability for imaging thermal transients if these have sufficient magnitude for detection.

Further efforts in this study are expected to be directed toward methods for applying heat to inspection samples in such a manner that maximum surface-temperature differences can be obtained for sound and flaw areas. The speed of response of the television technique is expected to be of advantage in such work.

7. Investigation of the Quality of Brazed Joints (A. KANNŌ*)

Although brazing is one of the important metal-joining methods, nondestructive methods of inspecting such joints have not been studied thoroughly, one reason being the wide variety of base materials, brazing alloys and brazing methods in use. Because of this variety, no single nondestructive test method appears capable of supplying all the desired inspection information. A study was undertaken to compare three different nondestructive testing methods, X-ray radiography, neutron radiography and ultrasonic testing.⁽¹²¹⁾

The strength of a brazed joint is considered to depend upon many factors such as defects inside the joint, the type of alloy formed between base metal and brazing alloy, and the clearance of the brazed parts.

Brazed joints having a thickness of 0.0254 mm were studied. The base metal was usually ASTM Type 304 stainless steel. Brazing alloys containing thermal-neutron-sensitive elements were chosen. As standard brazing faults, brazing-alloy foils with thicknesses in the range 0.0127 to 0.0762 mm and containing various holes were sandwiched between base metals with thicknesses in the range 1.59 to 6.35 mm.

X-ray and neutron radiographs were compared on these standards and on actual brazed specimens. With 0.0254 mm brazing foils, the hole diameters that could be radiographically detected were as follows: for Easy Flow foil, 0.305, 0.61 and 0.99 mm for X-radiography,

0.127, 0.152 and 0.305 mm for Gd-M direct exposure neutron radiography, and 0.457, 0.61 and 1.27 mm for indium transfer neutron radiography.

Neutron radiography showed excellent detectability when a Gd 0.127 mm-M (single) direct exposure method was applied on Easy Flow brazing alloy. The In-AA transfer method was comparable with X-radiographs for the detectability of Easy Flow faults. Both neutron methods produced poor sensitivity on BAg8 foil, which contains no neutron-sensitive element but silver.

Concerning geometrical unsharpness, the Juggernaut reactor beam facility shows an unsharpness of 2% (maximum) of distance between specimen and film. Although this value is larger than in X-radiography, the fault detectability for the Gd direct exposure method for the 12.7 mm specimen thickness was better than observed for X-radiography. This may be a result of increased scattering in the X-ray case.

The high-temperature brazing alloy with 3.5% boron content showed poorer detectability to diffusion of boron into the base metal than expected.

Ultrasonic methods have superior sensitivity to nonbonds in diffusion-bonded samples, areas that cannot be detected by radiography. Although they are very sensitive, their resolution is rather poor, so faults about 1.5 mm in diameter cannot be indicated clearly for 12.7 mm thick specimens, particularly faults near edges. Results from an ultrasonic test must usually be evaluated by reference to suitable standards. To get precise information of faults, the Gd-M direct method would be recommended for thermal-neutron-sensitive brazing alloys.

* INSE Participant from Ship Research Institute, Tokyo, Japan.

⁽¹²¹⁾ Kannō, A., *The Nondestructive Testing of Brazed Joints*, ANL-6924 (Nov. 1964).

Part II

Basic Metallurgy

A. METALLURGY OF ACTINIDE METALS

1. Preparation of High-purity Uranium and Plutonium (L. T. LLOYD AND G. B. O'KEEFFE)

We are continuing to fill requests for high-purity uranium from existing inventory. About 3.5 kgs of metal were used up in our research programs during the past year. Approximately 1.5 kgs were distributed

TABLE 59. ANALYSES OF HIGH-PURITY PLUTONIUM^(a)

Material	Chemical Analyses							Spectrographic Analyses ^(b)									Remarks
	Am ^(c)	C	H	N	O	Si	U	Al	Cr	Fe	Ga	Li	Mg	Mn	Mo	Ni	
Anode Stocks																	
3-907	547	1430	432	397	317	94	228	44	93	129	<.69	<.17	<9	<2	<1	82	Went into CM47 and CM48
3-949	325	5137	1368	829	2193	172	41	179	651	1213	<.34	<3	<9	44	75	164	Went into CM48, CM49 and CM50
Cell XI (Buttons M120 through M134)																	
CM47	7	201	<24	138	317	34	11	44	1	34	<.34	<.17	<9	<.8	75	4	MgO crucible. Held 12.9 hr. at 893°K.
CM48	12	745	98	397	30	51	22	44	13	51	<.34	2	<9	2	<.5	16	MgO crucible. Held 16.3 hr. at 893°K.
CM49	12	866	240	414	45	60	14	13	41	51	<.34	.34	<9	17	<.5	12	MgO crucible. Held 16 hr. at 903°K.
CM50	40	1370	196	846	45	172	17	143	367	242	<.34	6	<9	30	5	49	MgO crucible. Held 15.6 hr. at 893°K.
CM51			Not Determined							Not Determined							MgO crucible. Held 16.8 hr. at 893°K.
CM52			Not Determined							Not Determined							MgO crucible. Held 19 hr. at 893°K.

^(a) Values are given for the number of impurity atoms per million atoms. These were calculated from analyses, which were expressed as ppm by weight, by assuming each impurity was combined with plutonium alone.

^(b) < = less than. Other elements analyzed for, but below limits of spectrographic detection, and their lower limits of detection are: Ag-2, B-22, Ba-0.4, Be-3, Bi-1, Ca-12, Cd-2, Co-4, Cu-4, K-12, La-2, Na-20, Pb-1, Rb-3, Sb-2, Sn-4, Sr-0.003, T-i3, V-2, Zn-2 Zr-1 and W-2.

^(c) Americium content is corrected to average date of electrolysis.

TABLE 60. ANALYSES OF SOLID STATE ELECTROLYSIS SPECIMEN (PPM-ATOMIC)

Material	Chemical Analyses			Spectrographic Analyses							
	C	H	O	Al	Cr	Fe	Li	Mn	Mo	Ni	
Before Electrolysis											
CM39*	302	204	45	224	23	155	0.69	4	1	32	
	261	216	75	188	23	199	0.34	4	2	16	
Electrolyzed Specimen											
Near Anodic End	322	552	1270	358	46	129	2	17	<1	8	
Center	2276	840	1073	188	41	151	2	17	<1	28	
Near Cathodic End	322	768	710	152	32	112	2	17	<1	16	

*Analyses are for duplicate specimens after rolling to form sheet stock.

as follows: to the ANL Chemical Engineering Division for studies on compounds; to the ANL Physics Division for neutron chopper blades; and to A. E. R. E. Harwell, United Kingdom, for specific-heat and magnetic susceptibility measurements.

The preparation of high-purity plutonium by salt electrolysis has continued. A gross weight of 1.1 kgs of refined metal was obtained from 2.3 kgs of anode stock. After cropping the consolidation melts and sampling them for chemical and spectrographic analyses, 0.8 kgs of usable metal remained. This, added to 0.8 kgs of metal carried over from the previous year, gave a total of 1.6 kgs that was available for use during the year. Our own research programs consumed 1.2 kgs and 0.2 kgs have been supplied to other ANL divisions. Analytical data for the consolidation melts are given in Table 59. Analyses of some of the anode stock are included in the table for comparing the chemistry of the starting and product materials.

Lack of success in reducing the light-element impurities (carbon, hydrogen, nitrogen and oxygen) to consistently low values by various changes in operational procedures of the electrolytic process has led us to considering other methods for purifying plutonium. Solid-state electrolysis experiments, designed to move the impurity atoms in the metal by subjecting it to a DC voltage and a high temperature, were begun in 1963. In the last of these experiments a sheet 15.24 cm long, 1.43 cm wide and 0.51 mm thick was electrolyzed for approximately 350 hours with a current of 46

amps. in a vacuum (10^{-6} torr). The temperature of the thermocouple near the center of the specimen was 870°K. The analytical data for this specimen are given in Table 60, which indicate an overall increase in carbon, hydrogen and oxygen, with no evident trend of redistribution of the impurities. This was confirmed by resistance ratio measurements at 273°K and 5°K, and we have abandoned this type of experiment. We are now procuring equipment to carry-out some feasibility studies on zone refining by a floating-zone technique in vacuum with an electron beam heating source.

2. Elastic Moduli of Single Crystals of Alpha Uranium (E. S. FISHER)

Measurements of the velocities of ultrasonic waves in single crystals of alpha uranium have been confirmed so that we now have data to evaluate all of the nine principal elastic moduli in the temperature range 44° to 923°K.

Variations of the compressional and shear stiffness moduli with temperature are shown in Figures 141 and 142, respectively, and their relationships to the three principal crystallographic directions are given in Table 61. Curves showing the temperature dependence of the cross-coupling moduli, c_{ij} , the linear compressi-

bilities, $\beta_{[100]}$, $\beta_{[010]}$, and $\beta_{[001]}$ and the volume compressibility are shown in Figure 143.

The large positive slope of the c_{11} curve in the range below 200°K and the unusual dips and peaks in the curves for the other moduli and parameters near 41°K are associated with a phase transition. Although the nature of the transition is still not clear, it is probable, on the basis of neutron diffraction studies,⁽¹²²⁾ that a gradual increase in the degree of alignment of magnetic moments occurs during cooling from 300°K to 41°K.

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FIG. 141. Temperature Dependence of Compressional Stiffness Moduli for Alpha Uranium.

TABLE 61. RELATIONSHIPS BETWEEN STIFFNESS MODULI AND MODES OF WAVE PROPAGATION IN ALPHA URANIUM

Direction of Wave Propagation	Type of Mode (Shear Polarization)	Stiffness Modulus
[100]	Longitudinal	c_{11}
	shear [010]	c_{66}
	shear [001]	c_{55}
[010]	Longitudinal	c_{22}
	shear [100]	c_{66}
	shear [001]	c_{44}
[001]	Longitudinal	c_{33}
	shear [100]	c_{55}
	shear [010]	c_{44}
45.5° to [001], 90° to [010]	quasi-long. quasi-shear [hol]	ρV_D^2 ρV_{DS}^2
~38° to [001], 90° to [100]	quasi-long. quasi-shear [okl]	ρV^2 ρV_{ES}^2
44.5° to [100], 90° to [001]	quasi-long. quasi-shear [hko]	ρV_F^2 ρV_{FS}^2

⁽¹²²⁾ Barrett, C. S., Mueller, M. H., Hitterman, R. L., *Crystal Structure Variation in Alpha Uranium at Low Temperatures*, Phys. Rev. **129**, 625 (1963).

All of the stiffness moduli show effects of the alignment in the 44° to 60°K range; in the 60° to 400°K range, c_{22} , c_{33} and the three shear moduli, c_{44} , c_{55} , and c_{66} , have normal, close to linear, temperature dependence,

40058

FIG. 142. Temperature Dependence of Shear Stiffness Moduli for Alpha Uranium.

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FIG. 143. Temperature Dependence of Cross-Coupling Stiffness Moduli and the Adiabatic Compressibilities for Alpha Uranium.

whereas the c_{11} curve deviates markedly from linearity. The linear compressibility, $\beta_{[100]}$, has a negative slope in this temperature range.

Significant changes in the temperature dependence of the shear and cross-coupling moduli are observed above 400°K. The shear modulus c_{55} , which has a very large negative but linear temperature dependence in the 200° to 400°K range, changes to a still higher negative slope, with a region of relatively large curvature between 400° and 425°K. Similar changes occur in the c_{44} and c_{66} curves, but at higher temperatures.

The curves for Young's moduli, E , (Figure 144) are especially interesting. At temperatures below 575°K, $E_{[010]}$ and $E_{[001]}$ vary almost linearly down to 100°K. At $575 \pm 5^\circ\text{K}$ both curves have large negative curvatures, which reflect, primarily, the large decrease in c_{23} in this temperature range. The relative values of Young's moduli in different directions of the crystal structure also change significantly upon heating above 300°K. $E_{[100]}$ becomes the largest of the three principal axes, although E_{max} remains in the (100) plane, approximately 37° to [001]. The minimum value of E changes at 575°K from [010] to the directions in the (010) plane that are 45° to [001] and [100]. The temperature dependence of this modulus, E_{45° , is shown

40054

FIG. 144. Temperature Dependence between 300° and 923°K of Young's Moduli, E , for the [100], [010] and [001] Directions and for the Directions of the Maximum and Minimum E in Alpha Uranium.

40056

FIG. 145. Young's Modulus in Directions 90° to [010] in Alpha Uranium at Various Temperatures. Circles at top indicate atomic arrangement in (010) plane, dashed circles are below plane of full circles.

in Figure 144, and the large effect of temperature on the anisotropy of E in the (010) plane is shown in Figure 145. At 923°K, E_{45° is about $\frac{1}{2}$ that of $E_{[100]}$ or $E_{[001]}$, whereas at 298°K it is approximately 0.8.

The temperature dependence of the Poisson's ratios, σ_{ij} , are shown in Figure 146. The first subscript, i , denotes the direction of the uniaxial stress and the second subscript, j , denotes the direction of the coupled strain, i.e. σ_{12} is the ratio of $e_{[010]}/e_{[100]}$ for $T_{[100]}$ where e and T are the directional strain and stress, respectively.

40052

Fig. 146. Temperature Dependence Between 300° and 923°K of Poisson's Ratios, $\sigma_{ij} = -e_{ij}/s_{ij}$, for Alpha Uranium.

These ratios are extremely anisotropic over the range of 50° to 923°K. σ_{13} and σ_{31} are very near zero throughout the temperature range, whereas the ratios that involve the [010] direction are in the range of 0.2 to 0.5 at low temperature, increase linearly with temperature between 50° and 400°K and increase with significant positive curvature above 400°K.

Figure 147 is a comparison of the temperature dependence of the stiffness moduli for uranium with those for Zr. The fractions of the maximum values of the moduli, M_0 , are plotted against temperature. There are two points to be noted: (1) the relatively large temperature dependence of the shear moduli and c_{33} for uranium, and (2) the remarkable coincidence of the curves for c_{55} of uranium and c_{66} of zirconium in the 50° to 400°K range.

Correlation of Elastic Moduli with Thermal Expansion

Between 50°K and the temperature of the $\alpha \rightarrow \beta$ phase transformation (935°K) the three linear expansion coefficients α_1 , α_2 and α_3 (subscripts 1, 2 and 3 refer to the [100], [010] and [001], respectively) are abnormally affected by temperature changes.^(122,123) α_1 decreases with increasing temperature to a minimum in the 100°K range and then increases continuously between 100° and 935°K. α_2 has a small positive value at 50°K, decreases continuously to zero at approximately 350°K, and has an increasingly negative temperature dependence at higher temperatures. α_3 has a very large positive temperature dependence,

⁽¹²²⁾ Lloyd, L. T., *Thermal Expansion of Alpha Uranium Single Crystals*, J. Nucl. Mat. **3**, 67 (1961).

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FIG. 147. Comparison of the Temperature Dependence of the Principal Stiffness Moduli for Alpha Uranium and Alpha Zirconium. Ordinate is the ratio of each modulus at temperature with respect to the maximum value of each modulus.

increasing by a factor of almost 5 between 50° and 923°K.

The relation between elastic moduli and thermal expansion coefficients is given by the Grüneisen relation:⁽¹²⁴⁾

$$\alpha_v = \frac{C_p \beta_v \Gamma}{V},$$

where α_v is the volume expansion coefficient, C_p is the lattice specific heat at constant pressure, V is the specific volume, β_v is the adiabatic compressibility (Figure 143), and

$$\Gamma = -\frac{1}{3N} \sum_{i=1}^{3N} \frac{\partial \ln \nu_i}{\partial \ln V}.$$

ν_i is the frequency of the i^{th} normal mode of thermal vibration and $3N$ is the total number of normal modes. For most solids Γ at high temperatures has a value of 1.5 to 3, with some temperature dependence, thus indicating a significant effect of Γ on α_v . For metals, an additional contribution to α_v arises through the electronic specific heat and an electronic Grüneisen Γ_e , which denotes the volume dependence of the density of electronic energy states. The origin of the negative α_2 in uranium might then be ascribed to a negative Γ_e , since such contributions may exist in metals with complex electronic configurations, but by expressing the components of the Grüneisen relation in tensor form, it can be shown that negative Γ 's need not be a requirement for a negative linear thermal expansion coefficient in an anisotropic crystal when certain of the elastic compliance moduli, s_{ij} , are

⁽¹²⁴⁾ Grüneisen, E., and Goens, E., *Thermisch Ausdehnung von Zinc und Cadmium*, *Zeits. für Phys.* **29**, 141 (1924).

sufficiently large and of the normal negative algebraic sign.⁽¹²⁴⁾ For alpha uranium the following relations apply:

$$\frac{V}{C_p} \alpha_1 = s_{11}\Gamma_1 + s_{12}\Gamma_2 + s_{13}\Gamma_3 = \frac{\Gamma_1}{E_1} - \frac{\sigma_{21}}{E_2}\Gamma_2 - \frac{\sigma_{31}}{E_3}\Gamma_3$$

$$\frac{V}{C_p} \alpha_2 = s_{12}\Gamma_1 + s_{22}\Gamma_2 + s_{23}\Gamma_3 = -\frac{\sigma_{12}}{E_1}\Gamma_1 + \frac{\Gamma_2}{E_2} - \frac{\sigma_{32}}{E_3}\Gamma_3$$

$$\frac{V}{C_p} \alpha_3 = s_{13}\Gamma_1 + s_{23}\Gamma_2 + s_{33}\Gamma_3 = -\frac{\sigma_{13}}{E_1}\Gamma_1 - \frac{\sigma_{23}}{E_2}\Gamma_2 + \frac{\Gamma_3}{E_3},$$

which reduces to,

$$\alpha_v = \frac{C_p}{V} (\beta_{[100]}\Gamma_1 + \beta_{[010]}\Gamma_2 + \beta_{[001]}\Gamma_3).$$

In the above Γ_1 , Γ_2 , and Γ_3 refer to the dependence of the average frequency of vibration on dilatation strains in the [100], [010], and [001] directions, respectively, and E_1 , E_2 , and $E_3 = E_{[100]}$, $E_{[010]}$, and $E_{[001]}$, respectively. From the right hand set of equations it can be seen immediately that combinations of large Poisson's ratio σ_{ij} and small Young's moduli, E_i , can in fact lead to negative linear α 's with normal values of Γ_j . The solutions obtained at various temperatures between 70° to 900°K by using the most accurate values for the α 's^(122,123) and the lattice C_p (see below), show that Γ_1 varies between 3 and 3.5, Γ_2 varies from 1.8 to 1.5 and Γ_3 from 2.6 to 3.6, with a weighted average volume Γ varying from 2.5 to 2.9. The negative α_2 arises then primarily from the abnormally large Poisson's ratio σ_{32} and the large negative temperature dependence of E_3 . The positive values of σ_{13} and σ_{31} are evidently primary contributing factors to the abnormally large positive temperature dependence of α_3 and α_1 above 300°K. Similarly, the increase in α_1 on cooling from 100° to 50°K can be attributed to the 15% decrease in E_1 .

Correlation of Elastic Moduli with Specific Heat

The temperature dependencies of various contributions to the total specific heat for alpha uranium, including among others, the C_p curve between 0° and 300°K as given by Flotow and Lohr⁽¹²⁵⁾, and, at that higher temperatures by Ginnings and Corruccini⁽¹²⁶⁾, and the specific heat at constant volume, C_v , are shown in Figure 148. C_v is given by the thermodynamic relation

⁽¹²⁵⁾ Flotow, H. E. and Lohr, H. R., *The Heat Capacity and Thermodynamic Functions of Uranium from 5° to 350°K*, *J. Phys. Chem.* **64**, 904 (1960).

⁽¹²⁶⁾ Ginnings, O. C. and Corruccini, R. J., *Heat Capacities at High Temperatures of Uranium, UCl₃ and UCl₄*, *J. Research Natl. Bur. Standards*, **39**, 309 (1947).

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FIG. 148. Temperature Dependence of the Specific Heat Functions Derived from C_p Data Given in References 125, 126, and 127. C_p is the specific heat at constant pressure, $C_v(V_0, T) - \gamma_0 T$ is obtained from C_p by subtracting electronic specific heat and specific heat due to volume change, and C_D is obtained from Debye approximation using Debye θ of 200°K. γ is the electronic specific heat coefficient assuming that C_D is the true lattice specific heat at temperatures above 50°K.

$$C_v = \left(\frac{\beta_v}{\alpha_v^2 V T + \beta_v C_p} \right) C_p^2,$$

at temperature T . The lattice specific heat calculated from the Debye model by using θ_D of 200°K⁽¹²⁷⁾ is noted as the dashed line, C_D . The experimental lattice specific heat due to temperature change only, $C_v(V_0, T) - \gamma_0 T$, was computed from the C_p data by assuming a temperature independent electronic specific heat coefficient, $\gamma_0 = 26 \times 10^{-4}$ cal/mol-deg²⁽¹²⁷⁾ and then correcting for the change in C_p with volume with the aid of the relation

$$\left(\frac{\partial C_v}{\partial V} \right)_T = T \frac{\left(\beta_v \frac{d\alpha_v}{dT} - \alpha_v \frac{d\beta_v}{dT} \right) C_p}{v^2}.$$

⁽¹²⁷⁾ Smith, P. L. and Wolcott, N. M., *Conference de Physique des Basses Températures*, Paris, 2-8 September, 1955, Annexe 1955-3, Supplement au Bulletin de l'Institut Int. du Froid, pp. 283-286.

The resulting curve approaches the C_D curve in the range of 100° to 120°K. Below 100°K the specific heat in excess of C_D increases with decreasing temperature; this reflects either a decreasing θ_D or an increasing contribution from the free electrons, or from a magnetic moment. Above 120°K the $C_v(V_0, T) - \gamma_0 T$ curve follows the Debye function reasonably well, allowing for experimental error, up to approximately 400°K where it has a significant positive curvature and increases above $3R$ at higher temperatures.

The temperature region where the positive curvature in the $C_v(V_0, T) - \gamma_0 T$ curve begins corresponds closely to the beginning of accelerated temperature dependence of the thermal expansion coefficients and of the c_{55} elastic modulus. This coincidence suggests that the electronic specific heat coefficient does remain temperature independent, as assumed, and that an unusually large temperature dependence of the vibrational frequency spectrum exists in the 400° to 900°K range, which drastically reduces the effective Debye θ . This conclusion would be consistent with the measurements of the Debye-Waller temperature factor by Mueller et al., reported in ANL-6516 (Annual Report 1961).

There is, however, some evidence to suggest that the excess in C_v is due, at least partially, to a positive temperature dependence of the electronic specific heat coefficient, γ . The evidence, which is based on the temperature dependence of paramagnetic susceptibility, specific heat and electrical resistivity, has been reviewed by Friedel in terms of the band approximation to the electron energy states.⁽¹²⁸⁾ In principle, this approach also can be applied to the temperature dependence of elastic moduli through the change in electronic energy with strains that distort the Fermi surface. Calculations of these contributions to the elastic moduli of uranium, however, would require considerably more information about the shape of the Fermi surface than is now available.

The curve marked $\gamma = (C_v - C_D)/T$ of Figure 148 represents the temperature dependence of the electronic specific heat coefficient on the assumption that all of the deviation of C_v from C_D is due to a temperature dependent γ . At the present time there is little basis for deciding between the two possible causes of $C_v - C_D$. As stated above, the Debye-Waller data tend to support the concept of a decreasing Debye θ ; the anomalous negative curvature in the electrical resistivity, however, would not be consistent with this concept.

⁽¹²⁸⁾ Friedel, J., *The Structure of Metallic Uranium*, J. Phys. Chem. Solids 1, 175 (1956).

The 41°K Transition

Although the nature of the phase transition at 41°K is not established, neutron diffraction evidence suggests that some sort of superstructure of magnetic moments is involved and that the alignment of moments increases gradually upon cooling from 300°K.⁽¹²²⁾ The broad temperature range of the anomalous c_{11} temperature dependence may be assumed as further evidence of a continuous change from the disordered to the fully ordered state. The full meaning of the term "order" must await further neutron diffraction and magnetic susceptibility studies. There is no obvious reason for assuming that the magnetic or exchange interactions do not exist at temperatures higher than 300°K. The unusual changes in the temperature dependence of the thermal properties upon heating above 300°K may then be due to the disappearance of these interactions. The onset of magnetic ordering may occur at different temperatures between the different inter-atomic bonds. This conclusion is suggested by the different temperatures, between 350° and 700°K, at which the different

elastic moduli undergo changes in degree of temperature dependence. It also is supported by the fact that the attenuation of the ultrasonic waves by the crystals was extremely temperature dependent for only certain of the modes of wave propagation. These high acoustic losses occurred at discrete, but different, temperature ranges that varied in extent. In some cases these losses occurred at temperatures above 900°K, indicating that the interactions may extend to the $\alpha \rightleftharpoons \beta$ structural transformation temperature. Since cooperative phenomena involved in higher order phase transitions are well known to cause acoustic attenuation, these observations add further support to the proposal that the manifestations are due to a magnetic ordering process.

This evidence is much too inadequate for proof. Nevertheless, further investigation of the possible occurrence of a magnetic structure in alpha uranium at high temperatures seems advisable in view of the present difficulties in understanding the existence of the complicated crystal structures and physical properties of the actinide metals.

3. Crystallographic Structure of Alpha Uranium (M. H. MUELLER, L. HEATON, AND R. L. HITTERMAN)

Alpha uranium shows unusual temperature dependence of its elastic moduli and other physical properties near 43°K that we previously correlated with the atomic position parameter and with the cell dimensions.⁽¹²⁹⁾ Neutron diffraction had also disclosed the existence of additional reflections, especially at the lower temperatures, which could possibly be due to a magnetic contribution. This we intend to investigate as soon as the cryostat becomes operative.

In the meantime we have taken a careful look at the room-temperature neutron diffraction data. A summary of the least squares results for the various parameters is given below as obtained from 137 reflections:

	Isotropic Refinement		
	Input	1st Cycle	2nd Cycle
Overall B	0.35	0.14	0.16
y^*	0.1024	0.10235	0.10236
R	0.108	0.060	0.061

⁽¹²⁹⁾ Barrett, C. S., Mueller, M. H., and Hitterman, R. L., *Crystal Structure Variation in Alpha Uranium at Low Temperatures*, Phys. Rev. **129**, 625-629 (1963).

	Anisotropic Refinement		
	Input	1st Cycle	2nd Cycle
y	0.10236	0.10236	0.10236
β_{11}	0.004923	0.008835	0.008956
β_{22}	0.001164	0.000444	0.000469
β_{33}	0.001633	0.001703	0.001705
R	0.061	0.054	0.054

*uranium at 0, y , 1/4.

The RMS thermal displacement along the three principal axes from the above data is: 0.0286, 0.0461 and 0.0608Å. Orientation of this ellipsoid within the unit cell of uranium shows the least displacement, 0.0286Å, along the "b" axis, the largest, 0.0608Å, along the "a" and an in-between value, 0.0461Å, along the "c" axis. Correlation of this thermal motion with temperature and other physical data will be of interest.

We have also collected preliminary intensity data for the (001) reflection as a function of sample rotation about an axis perpendicular to the diffraction plane. It appears that there is a somewhat higher background intensity between the peaks from the double scattered

reflections on this pattern than is observed from a 2θ , χ , φ or ω scan through this same reciprocal lattice point. This may indicate that there is some real diffracted intensity at room temperature, although very weak,

for such reflections as (001). An explanation of the existence may well have a bearing on the explanation of the structure changes and physical properties at low temperatures.

4. Self-diffusion in Alpha Uranium (S. J. ROTHMAN, R. A. BASTAR, J. J. HINES,* AND A. L. HARKNESS*)

Although diffusion in metals with a non-cubic structure can be anisotropic, very strong anisotropy has been found only for self-diffusion in bismuth.⁽¹³⁰⁾ Because many of the physical properties of uranium are very anisotropic, it seemed likely that diffusion in uranium also would be anisotropic, and so a study of self-diffusion in alpha uranium was undertaken.

The first results (Annual Report for 1961, ANL-6516) showed that self-diffusion in alpha uranium was indeed highly anisotropic, with $D_{[001]} \approx D_{[100]} \gg D_{[010]}$. Two questions, however, were left unanswered: is the temperature dependence of the diffusion coefficients also anisotropic, and is the anisotropy representative of volume diffusion or of diffusion along dislocations? The second question is especially important because the single crystals used in the experiment reported in ANL-6516, which were grown by a phase-transformation technique, had extensive mosaic structure. (Each Laue spot was spread over 5–6° arc.) This year's work has been directed towards answering these questions.

We have attempted to answer the first question by annealing three mosaic structured single crystals, one for each principal crystallographic direction, at 925.9°K, and another three at 860.4°K. In order to assess the influence of the mosaic structure on the diffusion, three single crystals grown by the grain coarsening technique, and therefore containing relatively little mosaic structure, were annealed at 860.4°K together with the mosaic-structured ones. Analyses of crystals annealed at 860.4°K have not been completed yet.

The diffusion anneal at $925.9 \pm 2^\circ\text{K}$ lasted for 59 days, 10.5 hours. The thin layer geometry was used, and U^{235} was the diffusing isotope. The samples were sectioned on a lathe, and the turnings were analyzed

for U^{235} by fission counting. The penetration plots (plots of $\log C$ vs x^2 , where C is the concentration of in-diffused U^{235} in a section, and x is the distance of the center of that section from the original interface), are shown in Figure 149. The scatter in the points is due to errors in sectioning, especially to the uncertainty in the section weights. The plots are very similar to the penetration plots shown in ANL-6516; the [100] and [001] directions exhibit a straight-line dependence of $\log C$ on x^2 , whilst for the [010] direction $\log C$ drops very rapidly, then the curve flattens out. These similarities support, but do not confirm, our hypothesis that the dislocation structure of the crystals does not affect the diffusion profoundly, since the dislocation structures of two different sets of single crystals can be expected to differ.

40295

FIG. 149. Penetration Plots for Self-diffusion in Alpha Uranium at 925.9°K.

* Chemistry Division.

⁽¹³⁰⁾ Seith, W. and Keil, A., *Abhängigkeit der electrolytischen Leitfähigkeit und der Selbstdiffusion in Kristallen von der Kristallographischen Richtung*, Zeits. f. Electrochem. **33**, 538 (1933).

5. Tracer Element Diffusion in Gamma Uranium (S. J. ROTHMAN AND N. L. PETERSON)

Publication

N. L. Peterson and S. J. Rothman, *Diffusion in Gamma Uranium*, Phys. Rev. **136** A842-A848 (1964).

As part of the diffusion studies on uranium, we have measured the diffusion of a number of impurities in gamma uranium. The results are summarized in the above publication. Our conclusions are:

1. Diffusion in gamma uranium takes place by a

defect mechanism, and the defects are probably lattice vacancies.

2. It is unlikely that either dislocations or nonequilibrium defects, which might be introduced by the $\beta \rightarrow \gamma$ phase transformation, play an important role in diffusion in gamma uranium.

3. The impurities are bonded to the vacancies, and the motion of the vacancies is highly correlated.

No further studies are planned on this program.

6. Metallography of Plutonium (M. D. ODIE AND L. T. LLOYD)

The mechanical preparation and electropolishing methods described in last year's Annual Report (ANL-6868) have been shown to reproduce consistently the microstructures of alpha plutonium. An example of this reproducibility is shown in the series of photomicrographs in Figure 150 which were obtained from the same area of a sample of as-cast, high-purity plutonium (CM-45). The details of the microstructures are not exactly the same because each represents a slightly different level in the sample, but it is obvious that the electropolishing procedure reveals reproducible structures over a range of current densities (the optimum current density is 0.7 to 0.8 A/cm²). Similar results were obtained even with more drastic mechanical repolishing treatments, i.e. coarser abrasives and more laps.

Significant features of the microstructure in Figure 150 that are worth noting are: (1) large difference in grain size, with fine grains occurring in clusters (note the area in the lower right hand portion of Figure 150b); (2) some of the larger grains show substructure, some do not; (3) grain boundaries are very irregular for the most part and show nonequilibrium configurations, i.e. the angles between grain boundaries at triple points, when triple points exist, are seldom near 120°, (4) some coarse grains are partially, or wholly, speckled as if etched, while the remainder of the grain surface and surrounding grains are smooth faced (Figure 150 does not show a good example of this, but again the lower right hand corner of the photographs gives an indication of such an area) and (5) some grains are completely surrounded by another grain (two such grains are located near the center of the photographs in Figure 150). The first three features can be rationalized in terms of what is known about the kinetics of the beta-to-alpha phase transformation and the accompanying

volume changes. The interpretation of the last two is complicated by the fact that they may be artifacts created by local heating during metallographic preparation, resulting in partial $\alpha \rightleftharpoons \beta$ transformation, for the reasons discussed below.

Evidence for the existence of heating effects during metallographic preparation was obtained when an abrupt increase in the current reading across an electropolishing cell was observed while making a determination of the voltage-amperage relationship for the 3B electrolyte. The sudden increase in current corresponded to the decrease in resistance, ~30%, which is associated with the $\alpha \rightarrow \beta$ phase transformation. Also, the thermo-setting plastic mount was softened, and the polished surface of the sample was roughened. One or more of these observations have been repeated several times when samples were electropolished at current densities of 1.5 A/cm² or above.

Samples that were subjected to current densities of 1.5 A/cm², or greater, showed a layer of fine grains along the edges. The thickness of the layer increased cumulatively as the current density was increased and eventually, fine grains were observed throughout the sample. The effect of the heating on the microstructure is illustrated in Figure 151. When a sample of high-purity plutonium (CM-41) with a typical as-cast microstructure (Figure 151a) was electropolished at a current density of 1.5 A/cm², mechanically repolished to remove the roughened surface and electropolished again at 0.7 A/cm², it had the microstructure shown in Figure 151b. The two microstructures bear little resemblance to each other. Areas having a speckled appearance consist of very small grains as viewed at higher magnification (Figure 151c); they seem to be crystallographically oriented. The similarity in orientation of the small isolated grains is illustrated more

39029

250X

a. Current density 0.7 A/cm^2 .

39035

250X

b. Same area as a., repolished on 1μ diamond lap and electropolished at 0.8 A/cm^2 .

39041

250X

c. Same area as b, repolished on 1μ diamond lap and electropolished at 1.0 A/cm^2 .

FIG. 150. Microstructures of As-cast, High-purity Plutonium (CM-45) Revealed by Electropolishing for 2 Minutes in the 3B solution. Polarized light illumination.

clearly in the series of photographs in Figure 152. These were taken from the same area of a sample at different angles of rotation with respect to the plane of polarization of the illuminating light. All of the isolated grains in the lower left two thirds of the photo-

graphs have the same coloration at the different angles and, therefore, have the same crystallographic orientation.

The fact that isolated grains can be created by heating effects during electropolishing makes one

38051

250×

a. As-cast, electropolished 2 minutes at a current density of 0.7 A/cm².

38477

250×

b. Electroplished 2 minutes at a current density of 1.5 A/cm², repolished mechanically and electropolished 2 minutes at 0.7 A/cm².

38478

1000×

c. Selected area from b.

FIG. 151. Microstructures of High-purity Plutonium (CM-41) in As-cast Condition and after Electropolishing in 3B Solution at High Current Density. Polarized light illumination.

suspicious that they are always artifacts, even when there are no obvious sources of their creation during the metallographic preparation. In this respect, effects similar to those caused by heating during electropolish-

ing have been observed at a surface that was formed by cutting with a hacksaw. Thus we still do not know if the isolated grains, and possibly the speckled areas, are artifacts or not.

FIG. 152. Microstructure of High-Purity Plutonium (CM-45) after Electropolishing in 3B Solution at a Current Density of 1.6 A/cm², Mechanically Repolishing, and Electropolishing 2 Minutes at 0.7 A/cm². Photographs were taken at various angle settings of the metallograph stage. Polarized light illumination.

7. Preferred Orientation in a Sheet of Rolled Alpha Plutonium (A. F. BERNDT AND L. T. LLOYD)

In the course of work directed towards attempts at introducing sufficient strain into the monoclinic lattice of alpha plutonium to provide a driving force for recrystallization (see the Annual Reports for 1962 and

1963, ANL-6677 and ANL-6868), a technique was developed whereby large reductions in thickness, more than 90 %, were achieved by flat rolling at room temperature without intermediate heat treatments,

even though alpha plutonium heretofore had been considered to be quite brittle, since it has less than 0.1 % tensile elongation at room temperature.⁽¹³¹⁾ Evidence for preferred orientation in such rolled sheets of alpha plutonium, was noted by Ianniello.⁽¹³²⁾

X-ray patterns for preferred orientation studies can be made from either high angle reflections in the back-reflection region or from low angle reflections in the front-reflection region. The latter method was chosen, even though extremely thin samples are required in the case of plutonium due to its large x-ray absorption coefficient, because: (1) arcing of the Debye rings, which is indicative of preferred orientation, is more noticeable for reflections with a low value of θ than for reflections with a high value of θ ; and (2) the complete diffraction pattern of alpha plutonium consists of a large number of reflections due to the relatively large unit cell and low symmetry. For $\text{CuK}\alpha$ radiation, 806 planes lie within the sphere of reflection.⁽¹³³⁾ In the back-reflection region it is practically impossible to find lines of sufficient intensity that are far enough separated from their neighbors to be unambiguously indexed. In the front-reflection region, however, four suitable reflections can be found; these are the (013), (004), (20 $\bar{3}$), and (21 $\bar{3}$), which occur at $\theta = 15.6^\circ$, 16.7° , 17.3° , and 19.8° , respectively, for $\text{CuK}\alpha$ radiation.⁽¹³³⁾

In order to prepare specimens of rolled alpha plutonium, a cylindrical shaped piece 1.52 mm high by 12.7 mm diameter was cut with a hacksaw from an ingot of high-purity plutonium (CM-40). The specimen was rolled initially in the beta phase at 428°K , and the rolling was continued as the temperature was lowered through the temperature range of the $\beta \rightarrow \alpha$ transformation down to approximately 323°K . After this treatment, the thickness of the sheet at room temperature was about 0.60 mm. The specimen was then cut in half, and each piece was rolled separately at room temperature, $\sim 300^\circ\text{K}$, to a final thickness of about 7.6×10^{-3} mm (98.7 % reduction in thickness). The roll speed was maintained at 1.5 cm/sec throughout the rolling operations, and the direction of rolling was reversed for each successive pass.

An area about 5 by 10 mm was cut from each sheet and cleaned by electropolishing in a 3B solution. The specimens were coated with collodion, glued with collodion to a 8.9×10^{-3} mm thick nickel foil for

⁽¹³¹⁾ Gardner, H. R. and Mann, I. B., "Mechanical Property and Formability Studies on Unalloyed Plutonium," *Plutonium, 1960*, edited by E. Grison, W. B. H. Lord and R. D. Fowler Cleaver-Hume Press Ltd. London, p. 522 (1961).

⁽¹³²⁾ Ianniello, L., *The Recrystallization of Alpha-Plutonium*, Trans. ASM **57**, 768 (1964).

⁽¹³³⁾ Berndt, A. F. and Lloyd, L. T., *Tabulations of Calculated Crystallographic Data for Alpha Plutonium*, ANL-6676 (1963).

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FIG. 153. Composite Pole Figure of High-purity Plutonium Sheet Rolled to 98.7% Reduction in Thickness at Room Temperature.

rigidity and mounted in a closed container on a goniometer for x-ray examination. The diffraction pattern of the nickel foil, which also served as an x-ray filter, was superimposed upon that of alpha plutonium, but, since the innermost line of the nickel pattern occurred at $\theta = 22.3^\circ$, there was no interference with the alpha plutonium reflections of interest. Mylar films 1.3×10^{-2} mm thick were used as x-ray windows, and a desiccant to retard corrosion was enclosed inside the sample chamber.

Transmission x-ray patterns were made in a Laue Camera (specimen to film distance 6.75 cm) with $\text{CuK}\alpha$ radiation (35 KV, 20 ma). The angle, α , between the normal to the plutonium sheet and the x-ray beam was varied between exposures; patterns were prepared for $\alpha = 0^\circ, 10^\circ, 20^\circ, 30^\circ, 40^\circ$, and 50° with the rolling direction (R.D.) vertical to the x-ray beam, and for $\alpha = 10^\circ, 20^\circ, 30^\circ, 40^\circ$, and 50° with the cross direction (C.D.) vertical. Intensities on the Debye rings were estimated visually by use of a calibrated intensity strip and the multiple film technique, and they were corrected for absorption.⁽¹³⁴⁾ The corrected intensities for the various values of α were placed on a comparable basis by dividing by the time of exposure, which varied from 6 hours to $\alpha = 0^\circ$ to 16.5 hours for $\alpha = 50^\circ$.

The integrity of the specimens was monitored by examining the x-ray patterns for the appearance of the

⁽¹³⁴⁾ Smoluchowski, R. and Turner, R. W., *Absorption Corrections in X-Ray Studies of Preferred Orientation*, Rev. Sci. Inst. **20**, 173 (1949).

strongest line of the PuO_2 pattern at $\theta = 14.5^\circ$. The samples remained essentially unoxidized for about one week, but after that time the intensity of the oxide line became appreciable. Therefore, it was impossible to obtain the entire set of x-ray patterns from one specimen, thus necessitating the use of the two samples. There was no evidence of nonreproducibility of the x-ray patterns for the two rollings.

The pole figures for the four reflections (013), (004), (20 $\bar{3}$) and (21 $\bar{3}$) are shown in Figure 153. The appearance of horizontal mirror planes on all the x-ray patterns proved that the preferred orientation had

mm symmetry with the R.D. and C.D. lying in the mirror planes. The blind spot near the center of the diagram results from the fact that data for $\alpha > 50^\circ$ could not be taken, because the scattered x-rays were intercepted by the sample holder.

The (20 $\bar{3}$) and (21 $\bar{3}$) poles show maxima at directions inclined about $40\text{--}70^\circ$ to the normal to the sheet. The (004) pole appears to be oriented approximately normal to the sheet, and the (013) pole is in this same general direction, although inclined slightly toward the rolling direction. We are attempting to interpret these pole figures in terms of ideal orientations.

8. Preparation of Single Crystals of Alpha Plutonium (A. F. BERNDT AND L. T. LLOYD)

Publications

Alan F. Berndt, *Attempted Preparation of Single Crystals of Alpha Plutonium—A Progress Report*, ANL-6757 (May, 1964).

A. F. Berndt, *Single Crystal Study of an Alpha-Plutonium-Neptunium Alloy*, J. Nucl. Mat. **11**, 352 (1964). [letter to editor]

The problem of preparing single crystals of alpha plutonium has been attacked from a number of experimental approaches. The first of the above publications describes the work in detail. The experiments have included attempts at growing crystals by: (1) reduction of plutonium halides by lithium in nonaqueous solvents, (2) electrolytic reduction of plutonium halides in various solvents, (3) precipitation from a liquid metal in convection cells, i.e. mass transfer, and (4) solid-state reactions involving slow cooling through the $\beta \rightarrow \alpha$ transformation. None of these approaches have been encouraging, with the exception of the last method under special conditions. Slow cooling of pure plutonium through its five solid-state transformations did not result in a significant increase in the grain size of the alpha phase over that of as-cast material, but large grains with the crystal structure of alpha plutonium were obtained when the number of transformations was decreased to two and the temperature of the $\beta \rightarrow \alpha$ transformation was increased to about 543°K by alloying plutonium with 56.4% neptunium. The second of the above publications describes a verifi-

cation of the crystal structure of alpha plutonium that was obtained from an x-ray study on a single crystal of the Pu-Np alloy.

Success in preparing large grains of the Pu-Np alloys, however, has not provided a solution to the problem of growing single crystals of unalloyed plutonium, but it has demonstrated that another approach, which involves the same principles, may be successful. Stephens⁽¹³⁵⁾ study of the pressure-temperature phase diagram for plutonium showed that the number of phase transformations was decreased and the temperature of the $\alpha \rightleftharpoons \beta$ transformation was increased by increasing hydrostatic pressure. Extrapolation of his data suggests that at pressures above 55 kilobars (kb) the alpha phase may be in equilibrium with the liquid, thereby providing a method of growing single crystals of alpha plutonium by solidification from the melt. Recently, Fischer⁽¹³⁶⁾ has demonstrated that large-grained alpha plutonium can be obtained when melts are slowly cooled under a pressure of about 60 kb. It is believed that experiments at high pressures offer the best means of producing single crystals of alpha plutonium, and studies of this type will be carried out with a piston-cylinder, high-pressure apparatus currently under construction.

⁽¹³⁵⁾ Stephens, D. R., *The Phase Diagram of Plutonium*, J. Phys. Chem. of Solids **24**, 1197–1202 (1963).

⁽¹³⁶⁾ Fischer, R. B., *Growth of Alpha Plutonium Crystals from Melts Under Extreme Pressure*, RFP-421 (Sept., 1964).

9. Preparation of Single Crystals of Stabilized Delta Plutonium Alloys (A. F. BERNDT AND L. T. LLOYD)

We would like to have single crystals of delta plutonium in order to study the properties of this phase, which, although it has a f.c.c. crystal structure, has a negative coefficient of thermal expansion. Delta plutonium, unfortunately, is stable only in the temperature range 592° to 724°K, but the delta phase may be stabilized to room temperature by the addition of various alloying elements and still retain some of the anomalous thermal expansion. A program with the goal of preparing single crystals of a stabilized delta plutonium alloy has been initiated during this year.

Gallium seems to be an attractive alloying element since stabilization to room temperature may be accomplished with a relatively small amount of solute, ~2.5 to 8a/o, and since data are available concerning

the preparation and homogenization of these alloys.^(137, 138)

Although no data are available on the thermal expansion of gallium-plutonium alloys, Gschneidner, et al.⁽¹³⁹⁾ have shown that a delta-stabilized plutonium alloy having an electron to atom ratio greater than 4.74 ± 0.02 (assumed valence of delta plutonium was 4.82) will retain the negative coefficient of expansion. In the case of gallium, valence 3, this means that the solute concentration must be less than $4.4 \pm 1.1a/o$.

A melt containing 3a/o gallium in plutonium has been prepared and is being homogenized by annealing. Tensile specimens will be prepared and used to determine the critical strain in order to attempt growth of crystals by the strain-anneal technique.

10. The Effects of Pressure on Transformation Behavior (R. G. LIPTAI AND L. T. LLOYD)

The general objectives of the program to study the effects of pressure on transformation behavior in actinide elements, initially plutonium, were discussed in last year's Annual Report (ANL-6868). During the past year, two different types of experimental equipment have been designed for glovebox operation. One of these, an opposed anvil device, or simple squeezer, has been constructed, and recently it has been put into operation for measurements on plutonium. Acquisitions of the components for the second apparatus, a piston-cylinder device, have been completed, and it is being assembled for preliminary testing.

The piston-cylinder apparatus is the more versatile of the two systems. It is adaptable to many high pressure, high temperature measurements such as differential thermal analysis, compressibility, electrical resistance, thermo-electric power and transformation volume change. The system we are using is capable of repeated loadings to 45 kilobars (kb) and 1273°K with an unsupported piston arrangement, and to 80 kb and 1273°K with a supported piston. Heating of the test specimen is achieved by a tubular furnace of graphite inside the pressure cell. Test samples can be reasonably large, cylinders up to approximately 6 mm in diameter by 1 cm high, and they are subject to nearly hydrostatic conditions.

The opposed anvil device is capable of producing pressures up to 80 kb at temperatures to 873°K, and pressures in excess of 120 kb at room temperature, but the type of experimental measurements that can be

made is limited to electrical resistance. Specimen shape is restricted to foils approximately 0.02 to 0.07 mm thick, and they are heated by heating the entire assembly with an electrical furnace. Because there is a significant pressure gradient across the faces of the anvils, the samples are not subject to true hydrostatic conditions. Therefore, measurements with this equipment are primarily qualitative in nature, but, because these tests are relatively simple to perform, they are very useful in pin-pointing critical test conditions for studies with the piston-cylinder apparatus.

The opposed anvil device is being used to make the preliminary measurements of the effects of pressure and temperature upon the phase transformations in plutonium. High-purity plutonium (CM-47) was rolled at 433°K to form sheet material about 0.05 mm thick. The electrical resistance of specimens, 1 mm by 4 mm, is being measured by a procedure similar to that of Bridgman⁽¹⁴⁰⁾ and Montgomery, et al.,⁽¹⁴¹⁾ using a

⁽¹³⁷⁾ Ellinger, F. H., Land, C. C. and Struebing, V. O., *The Plutonium-Gallium System*, J. Nucl. Mat. **12**, 226 (1964).

⁽¹³⁸⁾ Johnson, K. A., *Homogenization of Gallium-Stabilized Delta-Phase Plutonium*, LA-2989 (1964).

⁽¹³⁹⁾ Gschneidner, Jr., K. A., Elliott, R. O., and Waber, J. T., *Influence of Alloying on the Negative Thermal Expansion of Delta Plutonium*, Acta Met. **11**, 947 (1963).

⁽¹⁴⁰⁾ Bridgman, P. W., *The Resistance of 72 Elements, Alloys, and Compounds to 100,000 kg/cm²*, Proc. Am. Acad. Arts Sci. **81**, 169 (1952).

⁽¹⁴¹⁾ Montgomery, P. W., Stromberg, H. D. Jura, G. H. and Jura, G., "Calibration of Bridgman Anvils, A Pressure Scale

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FIG. 154. Effect of Pressure on the Resistance of Alpha Plutonium at Room Temperature.

pyrophyllite retaining ring and silver chloride pressure transmitting media between the tungsten carbide anvils.

Figure 154 shows a normalized curve of resistance at room temperature and up to 90 kbs pressure. Its general shape was normal, a decreasing resistance with upward curvature; however, the value of the decrease in resistance with increase in pressure was very small,

being less than 2 per cent. Neodymium exhibits a similar behavior.⁽¹⁴⁰⁾

A few tests have been run at various constant pressures up to 40 kb while heating up to temperatures of about 873°K. The observed pressures and temperatures associated with the changes in resistance, i.e. phase transformations, agreed well with the results obtained by Stephens.⁽¹³⁵⁾ This work is being continued to extend the pressure-temperature phase diagram for plutonium up to at least 80 kb and 873°K.

A very interesting aspect of the deformation characteristics of plutonium has been demonstrated by "blow-outs" of the silver chloride through the retaining ring. When "blowouts" occurred at pressures over 30 kb and at temperatures where the plutonium was within the alpha phase range, portions of the plutonium samples were extruded along with the silver chloride to form fine "wires," demonstrating that alpha plutonium deforms in a ductile manner when subjected to high pressure and/or high-velocity deformation conditions.

11. Electronic Structure of Plutonium (M. B. BRODSKY)

Publications

M. B. Brodsky, *Hall Effect in Beta Plutonium*, Bull. Am. Phys. Soc. **9**, 59 (1964) [Abstract].

M. B. Brodsky, *Electrical Resistivity in Cold-Rolled Alpha Plutonium*, J. Metals **16**, 129 (1964) [Abstract].

M. B. Brodsky, *Hall Effect in Alpha, Beta and Delta Plutonium*, Bull. Am. Phys. Soc. **9**, 633 (1964) [Abstract].

Measurements of electron transport properties are being made to help gain an understanding of the electronic structure of the actinide elements. In previous reports (1962—ANL-6677 and 1963—ANL-6868), results were given for Hall coefficient, R_0 , and electrical resistivity measurements, which were made on make-shift equipment while adequate apparatus was being assembled. Those results were given in the first two publications listed above, as well as in Reference 142. During the past year, the new apparatus was completed, and measurements of the Hall effect and electrical resistivity can now be made routinely between 5° and 438°K, on alpha active samples, at magnetic fields up to 21,000 gauss. Publication number 3, above,

presented results obtained thus far on plutonium allotropes and these are given below.

Alpha Plutonium

Figure 155 summarizes the Hall data for alpha plutonium. The newer results were about 50 % larger, in absolute value, than those presented before⁽¹⁴²⁾ because a better method was used to attach the potential leads to the specimens. The outstanding result upon extending the measurements to lower temperatures was the minimum at 23°K. Agreement with Loasby and Taylor's⁽¹⁴³⁾ results was as before; i.e., same change in sign, but once more the reported dependence of Hall coefficient on time was not found.

Plots of Hall voltage versus applied field were linear, even in the region of the minimum. Values of the Hall coefficient calculated from these plots are shown in Figure 155, also, and it is seen that these isothermal data were in good agreement with results obtained with slow heating or cooling. The two samples used for the study, Pu 1 (CM-17) and Pu 2 (CM-47), were both purified by fused salt electrorefining prior to being cross-rolled in the alpha phase. Pu 1 was elec-

⁽¹⁴²⁾ Brodsky, M. B., *Hall Coefficient of Alpha Plutonium*, Phys. Rev. **131**, 137 (1963).

⁽¹⁴³⁾ Loasby, R. G. and Taylor, J. C., *Hall Effect in Plutonium*, Proc. Phys. Soc. London **78**, 776 (1961).

to 125 kb," *High Pressure Measurement*, Butterworths, Washington, p. 1 (1963).

39879

FIG. 155. Hall Coefficient of Alpha Plutonium ("I" refers to reference 142).

trorefined more than a year before Pu 2, and the agreement between the two sets of data is quite good, despite the differences in amounts of inbred impurities.

Beta Plutonium

The Hall data for pure beta plutonium are shown in Figure 156. Once again, the Hall coefficient changed slowly in the higher temperature range, but it had a large temperature dependence at low temperatures. Data at low temperatures were taken on samples that had been quenched in liquid argon from the stable beta region. Retention of the beta phase was verified by electrical resistivity measurements.⁽¹⁴⁴⁾ The temperature of the maximum 29°K, was close to the temperature of a resistivity maximum, 22°K.

Field dependence data were obtained at the indicated "isothermal temperatures" in Figure 156. As in the case for alpha plutonium, the Hall voltages were linear with applied field and extrapolated to zero potential at zero field. Good agreement was obtained, once more, between isothermal and dynamic results. The start of the beta to alpha transformation upon heating above 160°K is seen in the data.

Delta Plutonium

The Hall results for a delta plutonium alloy (stabilized with 3.4a/oAl), shown in Figure 157, also ex-

⁽¹⁴⁴⁾ King, E. and Lee, J. A., *The Low Temperature Resistivity of Beta-phase Plutonium*, *Cryogenics* **3**, 177 (1963).

hibited a small temperature dependence at higher temperatures and a large dependence at low temperatures. Unlike the results for the alpha and beta phases, the Hall coefficient remained positive throughout the temperature range studied here. Agreement with Loasby and Taylor's⁽¹⁴³⁾ results was as with alpha

40445

FIG. 156. Hall Coefficient of Beta Plutonium.

39880

FIG. 157. Hall Coefficient of Delta Plutonium Stabilized by Alloying Plutonium with 3.4a/o Aluminum.

plutonium; i.e., the Hall coefficient had the same sign and same order of magnitude. Once again, the Hall potentials were linear with applied field, and the isothermal results agreed well with the dynamic data.

Relationship Between the Electrical Resistivity and the Hall Coefficient

Much effort has been directed towards understanding the "electrical resistivity anomaly" in pure, alpha plutonium, i.e. large positive $d\rho/dT$ at low temperatures, a maximum near 100°K, and a negative $d\rho/dT$ between 100°K and the alpha-beta transformation (see ANL-6868). Explanations of this behavior have been based on antiferromagnetic ordering^(145,146,147) or interband scattering.^(148,149) Similar resistivity behavior is found in beta and delta plutonium.

Strong similarities between the electrical resistivities of alpha plutonium and alpha manganese led to the conclusion that alpha plutonium also undergoes a paramagnetic to antiferromagnetic transition near the temperature of the resistivity maximum, or about 100°K.^(145,148) A different approach, which analyzed magnetic-disorder contributions to the resistivity, led to an assumed Néel point near the intersection of the high and low temperature portions of the resistivity-temperature curve, or around 60°K.⁽¹⁴⁶⁾ Smoluchowski showed, however, that the large slope at low temperatures could be due to interband scattering. The interband scattering reaches its maximum at two to five times θ' , where $k\theta'$, which is much less than $k\theta_D$, is the energy of the lowest lattice frequency that can cause the interband scatter (k is Boltzmann's constant and θ_D is the Debye temperature). He showed, further, that the negative $d\rho/dT$ at high temperatures could occur in a band structure having a very high density of states at the Fermi surface (see below). Definitive experiments seeking to establish the existence of antiferromagnetic ordering at 60° or 100°K by neutron

diffraction⁽¹⁵⁰⁾ or by magnetic susceptibility⁽¹⁵¹⁾ studies were unsuccessful.

In the absence of direct evidence for a Néel point in plutonium, it becomes necessary to draw inferences from Hall data of other materials to explain the low temperature behavior shown in Figures 155–157. All Hall data for the rare earth metals, which have Néel points, exhibit maxima, or minima, or other strongly temperature dependent behavior near their Néel points.^(152,153,154) Conversely, the non-magnetic rare earths have the usual, low temperature dependence of the Hall coefficient.^(152,153) Thus, it is likely that the three plutonium allotropes studies here undergo antiferromagnetic ordering at the following temperatures: alpha, 23°K; beta, 29°K; and delta, below 120°K. It should be noted that the Néel temperature for alpha plutonium is close to a very small maximum found in the magnetic susceptibility at 15–20°K.⁽¹⁵¹⁾ It should be noted, further, that, of the above assumed Néel temperatures, only the one for beta Pu is close to the Néel temperature estimated from resistivity data (60–100°, 22° and 165°K for alpha, beta and delta, respectively).

Following Smoluchowski's treatment, calculated values of θ' are 55° for alpha, 10–15° for beta and 30°K for delta plutonium. Thus the interband scattering is very temperature dependent at the 23°K Néel temperature of alpha plutonium, but has already achieved its maximum value slightly below the beta-plutonium Néel temperature. Therefore, no discontinuous change is seen in the resistivity of alpha plutonium at its Néel temperature, and the resistivity maximum of beta is very sharp because its Néel temperature is about the same temperature at which the interband scattering saturates. The case for delta plutonium is probably similar to that of alpha, but the uncertainty as to its Néel temperature from the Hall data makes any definite conclusion highly speculative.

Two-Band Calculations

As before (ANL-6677, ANL-6868), the data were tested against several two-band models in which the

⁽¹⁴⁵⁾ Sandenaw, T. A. and Gibney, R. B., *The Electrical Resistivity and Thermal Conductivity of Plutonium Metal*, J. Phys. Chem. Solids **6**, 81 (1958).

⁽¹⁴⁶⁾ Rocher, Y. A. and Friedel, J., *Aspect Phenomenologique de Quelques Propriétés du Plutonium et des Solutions Solides Plutonium-Aluminium Delta*, J. Phys. Chem. Solids **18**, 196 (1961).

⁽¹⁴⁷⁾ Meaden, G. T., *Low Temperature Properties of Trans-uranic and other Heavy Metals*, thesis, University of Oxford, 1961.

⁽¹⁴⁸⁾ Lee, J. A., Hall, R. O. A., King, E. and Meaden, G. T., "Some Properties of Plutonium and Plutonium-Rich Alloys," *Plutonium 1960*, edited by E. Grison, W. B. H. Lord and R. D. Fowler, Cleaver-Hume Press, London, p. 39 (1961).

⁽¹⁴⁹⁾ Smoluchowski, R., *Problem of Anomalous Resistivity in Plutonium*, Phys. Rev. **125**, 1577 (1962).

⁽¹⁵⁰⁾ Roof, R. B., *A Neutron Diffraction Examination of Alpha Plutonium at 23°K*, LA-2912 (1963).

⁽¹⁵¹⁾ Weil, L., Quézel, G., Cohen, J. and Pascard, R., Discussion presented at session on Propriétés Physiques, *Plutonium 1960*, op. cit., p. 104.

⁽¹⁵²⁾ Kevane, C. J., Legvold, S. and Spedding, F. H., *The Hall Effect in Yttrium, Lanthanum, Cerium, Praseodymium, Neodymium, Gadolinium, Dysprosium, and Erbium*, Phys. Rev. **91**, 1372 (1953).

⁽¹⁵³⁾ Anderson, G. S., Legvold, S. and Spedding, F. H., *Hall Effect in Lu, Yb, Tm and Sm*, Phys. Rev. **111**, 1257 (1958).

⁽¹⁵⁴⁾ Volkenshtein, N. V. and Fedorov, G. V., *Temperature Dependence of the Electrical Conductivity and Hall Effect of Dysprosium and Erbium*, Soviet Physics JETP **44**, 825 (1963).

number of electrons or holes in a given band is calculated as a function of μ_e/μ_h , the ratios of the mobilities of electrons and holes. Since it was concluded that the low-temperature results were strongly influenced by magnetic ordering effects, only the data at high temperatures are of use for these calculations.

The following four cases for the distribution of the eight electrons beyond the radon core, to achieve positive Hall coefficients, were considered:

1. There is a nearly full 7s conduction band, which causes the net hole conduction, and a narrow, mostly empty 5f, 6d or hybrid 5f-6d band. Solutions of interest are at $\mu_e/\mu_h \leq 1$.
2. Hole conduction takes place in a nearly full 6d band and electronic conduction in the 5f band, and solutions of interest are at $\mu_e/\mu_h \leq 1$.
3. Hole conduction in the 6d band is coupled with electronic conduction in a nearly empty 7s band. In this case, pertinent solutions are at $\mu_e/\mu_h \geq 1$.
4. Splitting of the 5f band due to spin-orbit coupling causes a nearly full 5f' band with a 7s, 6d or f5'' nearly empty band. For this case, $\mu_e/\mu_h \geq 1$ is of interest.

Solutions for all three phases were very similar in each model. In general, the results were double valued, but one branch of the solution often led to more reasonable results than did the other. Solutions near room temperature for cases 1 and 3 were found to be very reasonable for both n_e and n_h , (numbers of electrons and holes per atom) for all three allotropes. Neither branch of the double-valued solutions for case 2 was useful for both n_e and n_h , while case 4 always led to imaginary or negative solutions. Typical results for cases 1 and 3 at 393°K are presented in Table 62. If the basic assumption of case 3 is accepted; i.e., a 6d band with eight electrons can have hole conduction,

TABLE 62. CALCULATED VALUES FOR n_e AND n_h AT 393°K

Case	μ_e/μ_h	Allotrope	n_e	n_h
1	0.04	Alpha	6.035	0.035
		Beta	6.020	0.020
		Delta	6.018	0.018
1	0.10	Alpha	6.501	0.501
		Beta	6.155	0.155
		Delta	6.134	0.134
3	2.0	Alpha	0.127	2.127
		Beta	0.311	2.311
		Delta	0.352	2.352
3	10.0	Alpha	0.006	2.006
		Beta	0.013	2.013
		Delta	0.014	2.014

39881

FIG. 158. Two-band Models Proposed for the Electronic Structure of Plutonium.

then the results at $\mu_e/\mu_h = 10$, for example, are seen to be reasonable. As might be assumed from the low temperature data presented above, inconsistencies were found for cases 1 and 3, also, where the R_0 's were negative.

The band pictures for cases 1 and 3 are sketched, qualitatively, in Figure 158. If the mobility ratios in the three phases are assumed to be the same, then the number of holes/atom decreases in the order alpha, beta, delta for case 1, and increases in the order alpha, beta, delta for case 3 (beta and delta have nearly the same n_h in both cases). The large, positive thermoelectric power of all plutonium phases is generally taken to be the result of a high density of states at the Fermi level. This result, which is borne out by specific heat studies,^(149,155) is consistent with each sketch in Figure 158. The thermoelectric power, however, decreases in

⁽¹⁵⁵⁾ Lehman, G. W., *Electronic Properties of Th, U and Pu, II. Energy Band Structure of Metallic Phases*, NAA-SR-1839 (1957).

the order alpha, beta, delta,⁽¹⁴⁸⁾ which is consistent with Figure 158a (case 1) but not 158b or 158c in a rigid band approximation. This substantiates the earlier conclusion⁽¹⁴²⁾ that a $7s^{2-x}5f^{6+x}$ configuration is likely in plutonium. This assumption of the same band

picture for all three allotropes may be in error. The use of this approach, however, is made reasonable by the strong similarities found in the two-band model calculations for all phases under the conditions of the four assumed cases.

12. Electronic Structure of Neptunium (M. B. BRODSKY)

Studies of the electron-transport properties of the actinide-metals have been extended to alpha neptunium. Calcium-reduced metal has been received from Oak Ridge National Laboratory for this work. Analyzed impurities were: Al—50 ppm, Ca—190 ppm, Fe < 290 ppm, Mg < 7 ppm, Mn < 30 ppm, Mo < 90 ppm, Ni—350 ppm, Si < 60 ppm, Ti < 15 ppm, V < 60 ppm, Zr < 60 ppm, and Pu—40 ppm (all in parts per million, by weight). These impurity levels were lower than those in the metal used for earlier neptunium studies at Harwell,^(147,156,157) which were: Al—200 ppm, Ca—3400 ppm, Mg—300 ppm, Mo < 500 ppm, Ni—600 ppm, V < 600 ppm, U—2200 ppm, and Pu—300 ppm.

Despite the lower purity of the Harwell neptunium, the as-cast density of that metal was 20.14 to 20.25, compared to an x-ray density of 20.45 g/cm³, while the metal obtained from Oak Ridge had an as-received density of 19.9 to 20.0 g/cm³. Cooling samples from the beta to the alpha phase under about 6 kilobars uniaxial pressure did not increase the density of the metal used here. Metallographic examination of the Oak Ridge neptunium revealed a dispersed second phase of bright, equiaxed particles about 20 μ in diameter. If the dispersed phase is NpO₂, then 5% NpO₂, by volume, in the material would account for the observed lower density. Approximately that amount of second phase was seen by metallographic examination. Second phase was found in the Harwell neptunium also,⁽¹⁵⁷⁾ and was said to make up about 3% of the sample.

In view of the doubtful purity of the metal used, the results presented below must be considered as preliminary, and any definitive property measurements must await the use of purer and more fully analyzed metal.

⁽¹⁵⁶⁾ McKay, N. A. C., Nairn, J. S. and Waldron, M. B., *The Chemistry and Metallurgy of Neptunium*, Proc. of the 2nd Int. Conf. on Peaceful Uses of Atomic Energy, Geneva Paper P/304 (1958).

⁽¹⁵⁷⁾ Lee, J. A., "A Review of the Physical Metallurgy of Neptunium," *Prog. in Nucl. Energy, Ser. V, Metallurgy and Fuels, III*, edited by H. M. Finnieston and J. P. Howe, Pergamon Press, London, 1961 p. 453.

Electrical Resistivity

Figure 159 shows the electrical resistivity of alpha neptunium. The curves for the Harwell data and the data obtained here are in good agreement. Resistivity ratios ($\rho_{293^\circ}/\rho_{8^\circ}$) are 34 and 52 for the Harwell and

40442

FIG. 159. Electrical Resistivity of Alpha Neptunium.

40444

FIG. 160. Electrical Resistivity of Alpha Neptunium near 273°K.

ANL data, respectively. This is in agreement with the lower metallic impurity content of the metal used here, and implies that the low density second phase might not enter into the electron transport processes of the matrix, i.e., may be an insulator.

Figure 160 shows a change in slope, or break, found near 273°K in the resistivity of cast Harwell metal.⁽¹⁴⁷⁾ This break was not found when the neptunium was

40443

FIG. 161. Hall Coefficient of Alpha Neptunium.

40440

FIG. 162. Hysteresis in the Hall Coefficient of Alpha Neptunium at 78°K. Increase and decrease of the applied field are shown by arrows.

40441

FIG. 163. Remanent Potential of Neptunium after Application of 20,000 Gauss.

extruded to form the specimens (density—20.5 g/cm³), and it was concluded that the break was due to an impurity from the casting. It is seen that no such break occurred in the results of the present study, even though low-density samples were used.

Hall Effect

The Hall coefficient of neptunium from 5° to 420°K is shown in Figure 161. The results were relatively insensitive to temperature at higher temperatures, as is the case with plutonium. At 254°K, however, there was a change in slope, and the data below this temperature became highly temperature dependent. Plots of Hall voltage versus applied field above 254°K were linear and extrapolated to zero potential at zero field. Below 254°K these plots were nonlinear, indicative of magnetic ordering. Furthermore, hysteresis was found in the results below 254°K. A typical hysteresis curve is shown in Figure 162 for the data at 78°K. The hysteresis was determined as a function of temperature and is shown in Figure 163. The disappearance of the remanent potential at low temperatures is indicative of anti-ferromagnetic ordering, and it is assumed, therefore, that there was a Néel point at 254°K.

Because of the uncertain impurity content of the metal used, and because of complicated behavior found in impure neptunium,⁽¹⁴⁷⁾ further discussion of these results must await measurements on pure specimens.

B. METALLURGY OF HCP METALS

1. Effects of Hydrogen and Oxygen on Plastic Behavior of Zirconium (D. G. WESTLAKE)

Publication

D. G. Westlake, *Precipitation Strengthening in Crystals of Zirconium-Hydrogen Alloys Containing Oxygen as an Impurity*, Acta Met. **12**, 1373-1380 (1964).

Investigations to determine the mechanisms whereby additions of hydrogen alter the plastic behavior of zirconium have been concluded during the past year. Earlier work⁽¹⁵⁸⁾ has shown that large precipitates of zirconium hydride were formed when alloys with hydrogen in interstitial solution at elevated temperatures were slowly cooled to room temperature, and that plastic deformation caused these precipitates to crack thus making the alloys brittle even though the metal phase was ductile. The following sections deal with the final results of these studies obtained during the past year.

Yield Stress, Cross-Glide, and Twinning in Single Crystals of Quenched Zr-H Alloys

The studies of the effect of hydrogen on the critical resolved shear stress (CRSS) for glide on $\{10\bar{1}0\}$ prism planes in single crystals of quenched Zr-H alloys in the temperature range 77° to 298°K are described in detail in the above publication. Hydrogen, in the form of finely dispersed hydride needles, increased the CRSS by as much as 500 per cent over that for unalloyed zirconium. Some additional strengthening was due to oxygen, an impurity in all the specimens. The combined strength increment, $\Delta\tau$, was related to that due to hydrogen, τ_H , and to oxygen, τ_O , by the expression

$$\Delta\tau = (\tau_H^2 + \tau_O^2)^{1/2}, \quad (1)$$

where,

$$\begin{aligned} \tau_H &\simeq KG, \\ \tau_O &\simeq (A - BT^{2/3})^{3/2}, \end{aligned}$$

A , B and K are constants, G is the shear modulus and T is the absolute temperature. Thus, the overcoming of oxygen barriers by glide dislocations can be thermally activated, but the overcoming of hydride barriers cannot.

The investigation has demonstrated that finely dispersed hydride needles are effective deterrents to prism glide. One mechanism by which dislocations may over-

come barriers is cross-glide. Two phenomena, which were observed, suggested that cross-glide on the basal plane did play a role in the deformation: (1) kink bands, and (2) wavy slip lines that could arise from double cross-glide on planes of the $\langle 2\bar{1}\bar{1}0 \rangle$ zone. The fact that the kink bands were within 8° of being perpendicular to the direction of prism slip can be explained best on the basis of cross-glide from prism to basal planes, as has been discussed by Martin and Reed-Hill.⁽¹⁵⁹⁾

Another mode of deformation observed in some of these quenched Zr-H crystals was twinning. Two samples, which were tested in tension at room temperature, twinned before the stress-strain curve gave any indication of plastic deformation. One of these crystals contained no hydrogen, and its Schmid factor* for prism slip was only 0.132. It twinned when the resolved shear stress for slip on the $(01\bar{1}0)$ plane was 0.81 kg/mm², which is comparable to the CRSS for prism slip obtained on a crystal with the same history but oriented favorably for prism slip. Subsequent examination revealed that all of the twins were of the $\{11\bar{2}1\}$ family and that the frequency of the occurrence of each was in the same order as the magnitudes of their Schmid factors. Only four of the $\{11\bar{2}1\}$ planes could be active twin planes in tension because of the orientation of the crystal. The maximum resolved shear stress on each system was: $(11\bar{2}1)$ —2.98; $(2\bar{1}\bar{1}1)$ —2.75; $(\bar{1}2\bar{1}1)$ —1.57; and $(1\bar{2}11)$ —0.94, all in kg/mm². Prism slip traces were very rare, but a few were detected at 1000×.

Twinning occurred in the second crystal, which had been precipitation strengthened by 0.58 a/o H, when the shear stress on the $(01\bar{1}0)$ — $[2\bar{1}\bar{1}0]$ slip system reached 6.37 kg/mm². The CRSS for a hydrogenated crystal with the same history, but oriented favorably for slip, was 6.05 kg/mm². The maximum resolved shear stresses on the three operative $\{11\bar{2}1\}$ twin planes were 8.38, 7.30 and 5.50 kg/mm². Again, only a few $(01\bar{1}0)$ slip traces were detected. Thus, in each crystal, twinning occurred when the resolved shear stress on the $(01\bar{1}0)$ — $[2\bar{1}\bar{1}0]$ system reached the level at which one would expect slip to be initiated.

The existence of a CRSS for twinning has been de-

⁽¹⁵⁹⁾ Martin, J. L., and Reed-Hill, R. E., *A Study of Basal Slip Kink Bands in Polycrystalline Zirconium*, Trans. A.I.M. **230**, 780-785 (1964).

* Schmid factor = $\cos \theta \cos \phi$, where θ is the angle between the tensile axis and the pole of the glide plane, and ϕ is the angle between the tensile axis and the glide direction.

⁽¹⁵⁸⁾ Westlake, D. G., *Initiation and Propagation of Microcracks in Crystals of Zirconium-Hydrogen Alloys*, Trans. ASM **56**, 1-10 (1963).

...ed for a long time. While results reported here do not yield conclusive proof, they are consistent with the following hypothesis. Nucleation of a twin requires a CRSS, but only in the immediate vicinity of the nucleation site. Prior slip leads to stress concentrations at the head of dislocation pile-ups; these, added to the applied stress, may exceed the CRSS for twinning on a given plane. Thus, twinning is initiated in zirconium at the load required to pile slip dislocations against an obstacle.^(160,161) The probability that the sum of the applied stress (resolved in the twinning direction) and the stress due to pile-ups of dislocations will exceed the CRSS increases with increasing values of the Schmidt factor. Therefore, the frequency of occurrence of twins on a particular member of a family of planes also increases with the Schmid factor.

Disposition of the Hydrogen in Quenched Polycrystalline Zr-H Alloys

Observations on quenched Zr-H alloys by transmission electron microscopy have shown that these alloys consisted of very fine dispersions of zirconium hydride in the zirconium matrix (ANL-6868). Subsequent work has confirmed the preliminary conclusions and also provided the following additional results:

- Tilting experiments indicated that the smaller particles were visible due to strain contrast, for which the theory is discussed in Reference 162, but that larger non-coherent particles could be imaged by diffraction from their own planes. The latter phenomenon was manifested sometimes as moiré-fringe patterns.
- As reported previously, the second phase appeared to be needles lying parallel to $\langle 11\bar{2}0 \rangle$ directions, but there was the possibility that they were plates parallel to prism planes,^(163,164) and appeared as needles only because the foil was very thin or because the foil was parallel to the basal plane. The needle-like configuration was definitely established by observation of two grains in the same

sample, one having its basal plane parallel to the foil and the other having its basal plane perpendicular to the foil.

- To confirm that the precipitates were indeed the hydride, some of the zirconium-hydrogen alloys were observed at $20,000\times$ while the temperature of the sample was varied between 300° and 573°K on a "hot stage." Dissolution of the particles began to occur at an observable rate when the temperature reached 473°K and was complete at 573°K . The precipitates reappeared upon cooling. This was the same behavior that Bailey⁽¹⁶⁵⁾ reported for precipitates that he confirmed to be γ' -zirconium hydride.
- Dislocations were generated by the growth of large hydride needles, but this was not an important phenomenon for the smaller precipitates. This is in agreement with Bailey's⁽¹⁶⁵⁾ conclusion that the hydride and metal phases are highly coherent.

The Combined Effects of Oxygen and Hydrogen on the Mechanical Properties of Polycrystalline Zirconium

The study of the combined effects of oxygen and hydrogen on the CRSS of zirconium single crystals was limited in several ways.

- The single crystals could not be quenched from temperatures higher than 573°K without causing them to deform by twinning. This set the maximum hydrogen concentration of the alloys at only about $0.6a/o$.
- Oxygen concentrations were limited to the impurity level, less than $0.14a/o$.
- Equation (1), expressing the combined strengthening of oxygen and hydrogen, was obtained by indirect means; a more direct approach would be desirable.

For these reasons, an investigation was made of the combined effects of oxygen and hydrogen on the mechanical properties of polycrystalline zirconium alloys with oxygen concentrations up to $3.7a/o$, and hydrogen concentrations up to $3.6a/o$.

Yield Stress at 298°K

A plot of the yield stresses at 0.2% strain, $\sigma_{0.2}$, of the oxygen alloys with $0.0a/o\text{H}$, indicated that $\sigma_{0.2}$ varies linearly with $C_o^{1/2}$, where C_o is the oxygen concentration (Figure 164). It appeared that if one could prepare some oxygen-free zirconium its yield stress would be very low. Therefore, $\sigma_{0.2}$ for the oxygen alloys was nearly equal to σ_o , the strength increment contributed by the

⁽¹⁶⁰⁾ Westlake, D. G., *Twinning in Zirconium*, Acta Met. **9**, 327-331 (1961).

⁽¹⁶¹⁾ Westlake, D. G., *Some Dislocation Models of Twinning Modes*, Conference on Deformation Twinning, Gainesville, Florida, March 21-22, 1963, to be published by Gordon and Breach for the Metallurgical Society of A.I.M.E.

⁽¹⁶²⁾ Ashby, M. F., and Brown, L. M., *On Diffraction Contrast from Inclusions*, Phil. Mag. **8**, 1649-1676 (1963).

⁽¹⁶³⁾ Langeron, J. P., and Lehr, P., *On the Preparation of Large Crystals of Zirconium and the Determination of the Orientation of the Hydride of Zirconium*, Comp. Rend. **243**, 151-154 (1963).

⁽¹⁶⁴⁾ Westlake, D. G., and Fisher, E. S., *Precipitation of Zirconium Hydride in Alpha Zirconium Crystals*, Trans. A.I.M.E. **224**, 254-258 (1962).

⁽¹⁶⁵⁾ Bailey, J. E., *Electron Microscope Observations on the Precipitation of Zirconium Hydride in Zirconium*, Acta Met. **11**, 267-280 (1963).

presence of oxygen. The relationship between $\sigma_{0.2}$ and C_O was expressed by $\sigma_{0.2} = 31.3 C_O^{1/2}$, with the yield stress in kg/mm² and the concentration in a/o .

Each of the series of hydrogen alloys that were not intentionally alloyed with oxygen contained 0.081 a/o O as an impurity. From Figure 164, this small amount of oxygen made a significant contribution to the strength of these alloys, which could not be ignored when we evaluated the contribution of the finely dispersed hydride, σ_H . If one assumes the validity of the following equation:

$$\sigma_{0.2} = (\sigma_O^2 + \sigma_H^2)^{1/2}, \quad (2)$$

which is analogous to equation (1) for single crystals, and calculates values of σ_H by using the experimental values of $\sigma_{0.2}$ and $\sigma_O(0.081a/o) = 8.9 \text{ kg/mm}^2$, one obtains the plot shown in Figure 165. The plot suggests the following:

- Very small amounts of hydrogen may be quenched into solution, thereby making little strength contribution.
- At intermediate hydrogen concentrations, the linear increase of σ_H with $C_H^{1/2}$ may mean that additions of hydrogen decrease the free lengths of dislocations only by increasing the number of hydride precipitates.
- The fact that this high rate of strengthening did not continue at the higher hydrogen concentrations could indicate that hydrogen additions caused larger particles to form, which, of course, would have less effect on the lengths of dislocation loops than an increase in the number of precipitates. Observations by transmission electron

39313

FIG. 164. Variation with Oxygen Concentration of the 0.2% Yield Stress for Zr-O Alloys.

39312

FIG. 165. Variation with Hydrogen Concentration of the Strength Contribution due to Dispersed Hydride Precipitates.

microscopy have established that the precipitates in a 3.6 a/o H alloy are much larger than those in a 0.36 a/o H alloy.

A number of Zr-O-H alloys with oxygen varying between 0.32 and 3.7 a/o and hydrogen between 0.36 and 3.6 a/o were prepared and tested in tension at 298°K. The experimental values of $\sigma_{0.2}$ were compared with values calculated by substitution of appropriate values of σ_O from the above oxygen alloys (Figure 164) and σ_H from the hydrogen alloys (Figure 165) into equation (2). The very close agreement between the observed and calculated values justified the use of equation (2) to describe the combined effect of oxygen and hydrogen on the yield stress.

Tensile Strength

The tensile strength of the Zr-O-H alloys was increased by oxygen and finely dispersed hydrides along with the 0.2% yield stress; in fact, the difference between the tensile strength and 0.2% yield stress appeared to remain nearly constant for all the alloys tested at room temperature. The average difference was 10.4 kg/mm², and the mean deviation from the average was 1.1 kg/mm². Thus, the amount of strain hardening, which occurred before necking of the specimens, seemed to be independent of the amount of oxygen in solution or the amount of precipitated hydride.

Ductility

In light of the observed strengthening due to addition of oxygen or finely dispersed hydride (or both), one might predict that the ductility would be reduced be-

use the stress necessary for dislocation glide is raised, thereby increasing the probability of crack propagation. Figure 166 shows that the prediction is borne out at low and high values of $\sigma_{0.2}$, but in the intermediate range the uniform strain was nearly constant. The same ductility results are plotted in Figure 167 to show the effect of oxygen and hydrogen concentrations. It has been demonstrated that a single crystal with 0.63a/oH as a finely dispersed hydride phase did not fail until it had necked to a chisel edge.⁽¹⁶⁶⁾ This indicated that the presence of this second phase had little, if anything, to do with crack initiation. Thus one is led to suspect that the grain boundaries of the polycrystalline samples play an important role in crack initiation, and the dispersed hydrides merely strengthen the matrix, thereby reducing the possibility of glide at the crack tip.

The Effect of Temperature on Ductility

Specimens with compositions similar to those already described were aged at 298°K for three days and then tested at 77°, 178° and 298°K. The ductility was lower at 178° than at 298°K, as would be expected. At 77°K, however, the alloys became much more ductile than they were at room temperature. Metallography showed that slip was the only mode of deformation for tests at room temperature, and in specimens tested at 178°K, twinning played only an extremely minor role. In those samples tested at 77°K, however, twins were found throughout the gage length. Thus, twinning enhances the ductility, by providing a means of deformation for those grains poorly oriented for glide.

Effect of the Disposition of the Hydride

Various heat treatments were used to obtain alloys with different amounts of hydride precipitated in grain boundaries, as platelets within grains, and as finely dispersed needles. The strength and ductility were correlated with the microstructure in the following ways:

- a. Increased numbers of finely dispersed hydride

39311

FIG. 166. Dependence of Ductility on Yield Strength of Quenched, Zr-O-H Alloys.

39315

FIG. 167. Uniform Strain in Various Quenched, Zr-O-H Alloys.

needles produced higher yield stress and lower ductility.

- b. Large hydride particles produced little, if any, strengthening, but they were definitely detrimental to the ductility.
- c. Samples with grain boundary precipitates were least ductile.

2. Dispersion Strengthening of Zirconium by Y_2O_3 , La_2O_3 and ThO_2 (D. G. WESTLAKE)

While the hydride-precipitation strengthening of zirconium is marked, the effect would disappear at elevated temperatures because of dissolution of the hydride phase. Attempts have been made⁽¹⁶⁷⁾ to strengthen

⁽¹⁶⁶⁾ Westlake, D. G., *Strengthening in Crystals of Zirconium-Boron Alloys Containing Oxygen as an Impurity*, Acta Met. 1373-1380 (1964).

⁽¹⁶⁷⁾ Weinstein, D., and Holtz, F. C., *On Dispersion Strengthening of Zirconium*, Trans. A.I.M.E. 227, 1463-1465 (1967).

zirconium by dispersing powdered metal oxides in the matrix using powder metallurgy techniques, but the attempts have not been very successful, primarily because the dispersion is not fine enough. It has been observed by the writer that coarse particles of ThO_2 in a thorium matrix are completely dissolved when the metal is converted to ThH_2 by reaction with hydrogen gas, and that

the ThO_2 was reprecipitated as a very fine dispersion when the hydrogen was removed by vacuum annealing.⁽¹⁶⁸⁾ Attempts were therefore made to apply these techniques to zirconium alloys.

Three zirconium alloys of $7v/o\text{Y}_2\text{O}_3$, $7v/o\text{La}_2\text{O}_3$ and $7v/o\text{ThO}_2$ were hydrided by reaction with hydrogen at 800°C , cooled, encapsulated in quartz under vacuo and annealed at 800°C for 100 hours. After removal of the hydrogen by vacuum annealing at 750°C , the sample was examined metallographically. No change could be detected in the dispersions. Hardness measurements

before and after the treatment were identical with experimental scatter.

The $\text{Zr-}7v/o\text{Y}_2\text{O}_3$ sample was re-hydrided and annealed at 950°C for 336 hours to increase the probability of solution of Y_2O_3 in ZrH_2 . The air-cooled sample was examined metallographically. Coarse particles of the dispersed phase were observed both before and after dehydrogenation, and the hardness of the dehydrogenated samples had not changed. Thus, fine dispersions were not obtained by this technique, presumably, because the dispersoids are not soluble in ZrH_2 .

3. Habit Plane of the Hydride in HCP Metals (D. G. WESTLAKE)

It has been shown that during slow cooling of solid solutions of hydrogen in zirconium, zirconium hydride platelets precipitate parallel to $\{10\bar{1}0\}$ prism planes of the zirconium matrix.^(163,164) Williams⁽¹⁶⁹⁾ also found the $\{10\bar{1}0\}$ planes to be of primary importance as a habit plane for hydride platelets in titanium. Because the prism planes are also the planes of closest packing and the most important glide planes in these metals, an investigation has been initiated to determine whether the relationship is general to all hcp metals. Some relationship between the two might be expected because of the anisotropic stress fields which exist around precipitates, unless there is complete coherency.

The separation between the basal planes is $(\frac{1}{2}c)$ and between the prism planes it is $(a\sqrt{3}/2)$. Therefore,

$$\frac{d_{(0001)}}{d_{(10\bar{1}0)}} = \frac{c}{a\sqrt{3}}.$$

Thus, the prism planes will always be the planes of closest packing, except when $c/a > \sqrt{3}$. At room temperature, many of the hydride-forming hcp metals have c/a ratios considerably less than $\sqrt{3} = 1.73$. A few of these are: Gd, 1.59; Dy, 1.57; Ho, 1.57; Er, 1.57; Y, 1.57; and Hf, 1.58.

A sample of each of the metals named above has been obtained for determination of its glide planes and the habit planes of the respective metal hydrides. To date, the hydride habit planes have been determined for Hf, Gd, Ho, and Er by the pole loci technique. Hafnium-hydride precipitated on prism planes of hafnium, making this system similar to Zr-H and Ti-H. The three rare earth metals, however, have exhibited hydride platelets parallel to the basal plane only. Discussion of the implications of these results must await the determination of the glide planes.

4. Temperature Dependence of the Elastic Moduli in Single Crystals of HCP Metals (E. S. FISHER)

Publication

E. S. Fisher and C. J. Renken, *Single-Crystal Elastic Moduli and the hcp $\rightarrow$ bcc Transformation in Ti, Zr and Hf*, Phys. Rev. **135**, A482-A494 (1964).

The results and conclusions obtained from a study of the temperature dependence of the elastic moduli in single crystals of titanium, zirconium and hafnium in the temperature range between 4° and 1155°K were

⁽¹⁶⁸⁾ Peterson, D. T., Westlake, D. G., and Rexer, J., *The Effect of Thorium Oxide on Thorium-Hydrogen Equilibrium*, J. Am. Chem. Soc. **81**, 4443-4445 (1959).

⁽¹⁶⁹⁾ Williams, D. N., *Hydrogen in Titanium and Titanium Alloys*, TML-100, May 16, 1958 p. 113.

given in ANL-6868 (Annual Report 1963) and have since appeared in the above publication. The elastic moduli, together with similar data that have been reported for other hcp metals, indicated that the occurrence of the thermally induced hcp $\rightarrow$ bcc phase transformation is closely associated with the relative temperature dependence of the two principal shear moduli. In those metals for which such transformations have been reported the c_{66} modulus has a larger negative temperature coefficient at 300°K than does the c_{44} . A tabular listing of the hcp metals revealed that these two factors, the phase transformation and the temperature coefficients of the shear moduli, are related also to the

c/a ratio of the pure metals at 300°K. For metals with $c/a > 1.60$, bcc structures have not been found and, where data existed, the temperature coefficient of c_{66} was either smaller or approximately the same as that for c_{44} . Among the 17 metals with $c/a < 1.60$, hcp $\rightarrow$ bcc transformations had been found in all but four, ruthenium, osmium, erbium and thulium. Evidence that erbium and thulium are likely to have bcc structures at high temperatures has appeared during the past year.⁽¹⁷⁰⁾

Data for the elastic shear moduli were available for 6 of these 17 metals, thallium, zirconium, titanium, hafnium, yttrium and beryllium, and in each case c_{66} had the greater temperature dependence.

A very simplified explanation for the correlation of the temperature dependence of the shear moduli with the c/a ratio was given in terms of the anisotropy of the nearest neighbor distances. For $c/a < 1.60$, these distances are greatest with the basal planes, and thus the modes of thermal vibration with displacements corresponding to the c_{66} shear modulus are the first excited during heating above 0°K. The vibrational frequencies of these thermal waves decrease most rapidly with the increase in volume through thermal expansion, thus accounting for the large decrease with temperature of the c_{66} elastic moduli. Since the bcc structure can be obtained by a simple (10·0)[11·0] shear of the hcp structure, the transformation becomes relatively easy at high temperatures because of the relatively small c_{66} modulus.

It was suggested that the driving force for the transformation is derived from the unique effects of anharmonicity on the vibrational frequencies in the hcp lattices with $c/a < 1.60$. In the cases of titanium and zirconium there are several factors indicating that the vibrational frequencies are increasing with temperatures above 420°K, thus causing an increase in the free energy of the hcp structure, i.e. a decrease in stability relative to that of the bcc structure. It is presumed that these bcc allotropes are favored energetically because they have large-amplitude, or low-frequency, thermal modes, which correspond to low values for the $\frac{1}{2}(c_{11} - c_{12})$ elastic moduli as are found for Li, Na, and other bcc metals.

This simplified model suggests that the larger temperature dependence of c_{66} and the phase transformation are characteristics of the temperature and volume dependence of the phonon frequencies in hcp metals with $c/a < 1.60$ at 300°K. The platinum metals ruthenium and osmium are evidently exceptional, because they do not undergo the hcp $\rightarrow$ bcc transformation and it may be predicted that c_{66} has a smaller temperature de-

TABLE 63. ELASTIC MODULI OF RHENIUM, RUTHENIUM, GADOLINIUM AND DYSPROSIUM AT 298°K

Metal	Density (g/cm ³)	Elastic Moduli (10 ¹² dynes/cm ²)					
		c_{11}	c_{33}	c_{44}	c_{66}	c_{13}	c_{12}
Re	21.024	6.1815	6.8350	1.6062	1.7144	2.041	2.7527
Ru	12.445	5.6640	6.2841	1.8177	1.8887	1.684	1.8866
Gd	7.886	0.6661	0.7189	0.2069	0.2084	0.2130	0.2493
Dy	8.536	0.7591	0.7992	0.2461	0.2498		0.2595

pendence than c_{44} in these two cases. For the remainder of the hcp metals in this c/a group the c_{66} moduli should have the larger temperature dependence.

During the past year a program has been initiated to test the above predictions by determining the temperature dependence of the five fundamental stiffness moduli of those hcp metals for which data are not available. The velocities of ultrasonic waves in single crystals are being measured in the temperature range from 4°K to 923°K.

Results and Discussion

Single crystals of several of the metals are available; rhenium, ruthenium, and beryllium were obtained from outside sources, and dysprosium, gadolinium, and erbium were obtained by heating cast rods at 1450°K for 3 to 4 weeks. Although the grains of the rare earth metals grew to dimensions large enough for preparing three crystals of each metal, with the desired orientations, the dysprosium and erbium crystals contain a considerable amount of second-phase plates that were precipitated preferentially on the basal planes. This phase is apparently due to contamination by tantalum in concentrations of approximately $0.2a/o$. Consequently, the data obtained from these crystals will be subject to question, and therefore, require checking against data from purer specimens.

The measurements of the absolute values of the elastic moduli at 298°K have been completed for rhenium, ruthenium and gadolinium and are given in Table 63. The elastic moduli of rhenium also have been measured by Shepard and Smith⁽¹⁷¹⁾ with the pulse time delay technique. The values in Table 63 disagree with their values by +1% for c_{11} and -0.7% for c_{44} , whereas, c_{33} , c_{66} , and c_{13} are in excellent agreement. The values for dysprosium (Table 63) are subject to some changes, pending the determination of the internal consistency of the data.

The temperature dependence of the elastic moduli in ruthenium has been determined for c_{66} from 4° to 933°K, for c_{44} between 53° and 300°K and for c_{11} between 300°

⁽¹⁷⁰⁾ Miller, A. E. and Daane, A. H., *The High-Temperature Allotropy of Some Heavy Rare Earth Metals*, Trans. A.I.M.E. 230, 568 (1964).

⁽¹⁷¹⁾ Shepard, M. L. and Smith, J. F., private communication.

TABLE 64. CORRELATION OF c/a RATIO IN HCP METALS WITH OCCURRENCE OF HCP $\rightarrow$ BCC PHASE TRANSFORMATION AND WITH TEMPERATURE DEPENDENCE OF ELASTIC MODULI

Metal	c/a at 300°K	$a_0(\text{\AA})$	Sign $\frac{\Delta c/a}{\Delta T}$	Temp. (°K) hcp $\rightarrow$ bcc transformation	$-10^6 \times \left(\frac{1}{M} \frac{\Delta M}{\Delta T} \right)$ at 300°K			
					c_{66}	c_{44}	c_{11}	c_{33}
Cd	1.88	2.973	+	—	867	844	657	409
Zn	1.86	2.660	+	—	538	750	447	278
Co	1.623	2.50	+	—	330	412	178	191
Mg	1.623	3.203	slightly +	—	462	533	300	335
Re	1.615	2.76	—	—	310	203	127†	135†
Tc	1.60	2.735	?	?	—	—	—	—
Tl	1.590	3.50	+	507	887	231	194	530
Sc	1.594	3.308	+	1608	—	—	—	—
Zr	1.593	3.23	+	1135	1000	523	350	200
Gd	1.590	3.63	+	1535	—	—	—	—
Ti	1.587	2.95	+	1155	1000	380	355	203
Lu	1.583	3.505	+	1600	—	—	—	—
Tb	1.583	3.599	+	1583	—	—	—	—
Ru	1.582	2.70	+	—	167	213	111	—
Hf	1.581	3.19	+	~2000	476	325	200	150
Os	1.579	2.73	slightly +	—	—	—	—	—
Dy	1.574	3.592	+	1670	—	344	—	—
Y	1.572	3.645	+	1760	413	333	250	130
Tm	1.572	3.537	+	~1600*	—	—	—	—
Er	1.571	3.559	+	~1600*	—	—	—	—
Ho	1.571	3.576	+	1715	—	—	—	—
Be	1.568	2.281	—	1523	196	184	205	158
Li	1.564	3.086	—	70	—	—	—	—

* Reference 170. References to other data are given in ANL-6868 (Annual Report 1963).

† Reference 171

and 933°K. The temperature dependence of the elastic moduli in rhenium between 4.2° and 300°K has been reported in Reference 2. These data agree reasonably well with our measurements of c_{66} and c_{44} between 50° and 300°K. The temperature coefficients at 300°K computed from the above data are given in Table 64. Although these coefficients at 300°K are relatively small compared to those for titanium or zirconium, c_{44} has a significantly greater temperature dependence than c_{66} for ruthenium, as predicted from the preceding discussion. For rhenium, however, the relative temperature coefficients of the 2 shear moduli are in the reverse order, and thus inconsistent with the preceding discussion.

The measurements of the temperature dependence of the elastic moduli in the rare earth metals are complicated by the various magnetic transitions that occur at temperatures below 300°K. Several attempts have been made to follow the change in velocity of ultrasonic waves for the c_{44} mode of dysprosium on cooling from

300°K or heating from 4°K. Two transitions have been reported for dysprosium, one at 175°K (paramagnetic $\rightarrow$ antiferromagnetic) and a second at 84°K (antiferromagnetic $\rightarrow$ ferromagnetic). Upon cooling from 300°K the velocity increases with almost a perfect linear temperature dependence to 230°K, changes very little between 230° and 220°K, and increases again linearly from 220° to 180°K. Between 180° and 172°K the velocity increases rapidly, but continuously, and a sudden weakening of the pulse pattern occurs at 172°K. Measurements at lower temperatures were somewhat questionable owing to drastic changes in acoustic attenuation. To add to these complications, there appears to be a severe hysteresis, which is associated with the 172°K transition, that causes the measurements obtained during the heating cycle to differ appreciably from those of the cooling cycle. The temperature coefficient for c_{44} given in Table 64 is that obtained from the cooling cycle.

The severe hysteresis and the anomaly in the 220° to 230°K range may well be associated with the large concentration of impurities in the dysprosium crystals. Since the changes in the moduli associated with the magnetic transitions are not of immediate interest, it is intended to restrict the measurements of the elastic moduli in the rare earths to the 300° to 933°K temperature range. Meaningful measurements at low temperatures will apparently require single crystals made from more pure materials.

Conclusions

The results for ruthenium quite clearly indicate that the absence of a hcp to bcc phase transformation implies that c_{44} has a larger temperature dependence than c_{66} for $c/a < 1.60$. The present results for rhenium suggest that the temperature dependence of the frequency spectrum changes systematically as c/a increases above 1.60. Since c/a for rhenium is below the ideal ratio of 1.63, the higher temperature coefficient for c_{66} may be expected. Since no phase transformation occurs, the effects of anharmonicity in the lattice vibrations are, however, evidently quite different from those in the metals with lower c/a . This difference can also be noted in the thermal expansion coefficients along the crystal axes, with c/a decreasing rather than increasing with temperature.⁽¹⁷²⁾ In view of the very small change in the c/a in magnesium with temperature, the anomalous expansion in rhenium may represent an effect associated with the value of the c/a ratio at 0°K, rather than some more unique characteristics.

⁽¹⁷²⁾ Wasilewski, R. J., *Axial Thermal Expansion of Rhen* Trans. A.I.M.E. **221**, 1081 (1961).

C. DIFFUSION STUDIES

1. Diffusion of Palladium in Copper, Silver and Palladium (N. L. PETERSON)

Publication

N. L. Peterson, *Isotope Effect in Self-diffusion in Palladium*, Phys. Rev. **136**, A568-A574 (1964).

Preliminary results for diffusion of Pd¹⁰³ in palladium were given in the Annual Report for 1963 (ANL-6868). The final results are:

$$D = 0.205_{-0.04}^{+0.05} \exp - \left[\frac{63,600 \pm 650}{RT} \right] \text{cm}^2/\text{sec.}$$

The theoretical background for the isotope effect experiment also was given in last year's Annual Report. These measurements are described fully in the above publication. The result is that E , the strength of the isotope effect, which is defined by

$$E = \frac{\frac{D_{103}}{D_{112}} - 1}{\left(\frac{112}{103}\right)^{1/2} - 1},$$

where D_{103} and D_{112} are the self-diffusion coefficients for Pd¹⁰³ and Pd¹¹² respectively, is equal to 0.8134. When this is corrected for the average mass of the palladium atoms in the host lattice, one obtains 0.7929, which is within 1.5 % of the calculated value of the correlation factor for self-diffusion by single vacancies ($f = 0.7815$). This proves that self-diffusion in palladium definitely takes place by the vacancy mechanism, and that the fraction of the translational kinetic energy of the activated state, which is associated with motion in the jump direction, is possessed entirely by the diffusing atom.

Measurements of the isotope effect for the diffusion of palladium in copper and silver, which were proposed in last year's Annual Report, are also under way.

2. Diffusion and Conductivity in the NaCl-ZnCl₂ System* (S. J. ROTHMAN, L. W. BARR,** A. H. ROWE** AND P. G. SELWOOD***)

The association of impurities with vacancies in the alkali halides has long been a subject of theoretical interest. Since both diffusion and ionic conduction in these materials take place via lattice vacancies, studies of diffusion and conductivity can be expected to yield basic information on this subject, and hence the present study.

The theoretical analyses, and the experimental data on the diffusion measurements, were presented in the last Annual Report (ANL-6868). The data on the conductivities have been analyzed since then, and are presented in Figures 168 and 169. The solubility of ZnCl₂ in NaCl was calculated from these data by use of the method of Haven,⁽¹⁷³⁾ and it is shown in Figure 170.

* The experimental work was done in the Solid State Physics Division, AERE, Harwell, Berks., England, during a year's leave by the first author, partially supported by a National Science Foundation Fellowship.

** Solid State Physics Division, AERE, Harwell, Berks., England.

*** Now at Pressed Steel, Ltd., Cowley, Oxford.

(173) Haven, Y., *The Solubility of MgF₂ in Solid LiF*, Rec. Trav. Chim. Pays-Bas **69**, 1505 (1950).

Unfortunately, the solubility at 912°K, the temperature of one of the diffusion isotherms, is uncertain, and it is not known whether the deviation of the experimental points from the calculated diffusion isotherms (Figure 172, ANL-6868) is due to precipitation effects at high ZnCl₂ concentration, C_{Zn} , or not. Further, it appears possible that the curvature in the Arrhenius plot for the diffusion of Zn in heavily doped NaCl (Figure 171, ANL-6868) is also due to precipitation. For this reason, the enthalpy of association can not be calculated from these data, although the values cited for the free energies of association in ANL-6868 still stand. The fact that these are larger than the value expected from theory for the enthalpy of association indicates that the calculations made on the association of divalent cations,^(174,175) which are as large or larger than the Na⁺ ion, cannot be

(174) Bassani, F., and Fumi, F. G., *The Interaction Between Equilibrium Defects in the Alkali Halides: The "Ground State,"* Il Nuovo Cimento **11**, 274 (1954).

(175) Tosi, M. P., and Airoldi, G., *The Interaction Between Equilibrium Defects in the Alkali Halides: The "First Excited State,"* Il Nuovo Cimento **8**, 584 (1958).

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FIG. 168. Conductivity of NaCl Doped with ZnCl_2 ; plots of $\log \sigma T$, where σ is the conductivity in $\text{ohm}^{-1} \text{cm}^{-1}$ and T the absolute temperature in degrees Kelvin, vs $1/T$. The numbers on the curves indicate the Zn concentration in mol. ppm.

applied to divalent cations, such as Zn^{++} , which are much smaller than Na^+ , probably because the relaxation and consequent polarization of the anions is much greater for a small cation than it is for a large one.

The work on this problem has now been finished, and a paper is in preparation.

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FIG. 169. Conductivity Isotherms for NaCl Doped with ZnCl_2 .

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FIG. 170. Plot of Solubility of ZnCl_2 in NaCl in mol. ppm vs. $1/T$. X, *—from breaks in conductivity isotherms; 0 from plots of $\log \sigma T$ vs $1/T$ by Haven's method.⁽¹⁷³⁾

3. The Effect of Magnetic Order on Diffusion (N. L. PETERSON AND S. J. ROTHMAN)

The theoretical basis for these experiments was given in the Annual Report for 1961 (ANL-6516). During the past year, the experimental apparatus, which was described in the Annual Reports for 1961 (ANL-6516) and 1962 (ANL-6677), was further modified. To wit, the motion of the torsion pendulum will be measured by

the change in the capacitance of a variable capacitor, one plate of which is attached to the torsion bar. This is a more accurate, as well as a more convenient measurement than following a light beam by eye, and allows one to work at much higher frequencies.

D. ALLOYING PROPERTIES

1. Magnetization of Iron Alloys (A. T. ALDRED AND M. V. NEVITT)

A system for measuring magnetization by the force method has been put into operation. The experimental procedure is to measure the apparent change of weight of a sample on applying a known magnetic field and field gradient. After correcting for the effect of the specimen holder, the magnetization M is given by

$$M = \frac{\Delta W}{dH/dZ}$$

where ΔW = corrected weight change and dH/dZ = field gradient. In principle this technique is an absolute one if the gradient can be measured separately. This is not true of most other methods where the apparatus is calibrated with a standard of known magnetization, usually iron or nickel.

The equipment is shown schematically in Fig. 171. An Ainsworth automatic vacuum recording balance is mounted on the Arthur D. Little electromagnet. The mounting also supports a stainless steel liquid-helium cryostat. Specimens, in the form of ellipses with major and minor axes approximately 0.2 in. and 0.1 in., are mounted in a gold-plated copper holder, which also contains germanium, carbon, and copper temperature-sensing devices. Temperatures can be measured to within 0.2°K over the range from room temperature to 4.2°K. The specimen holder is suspended from the balance by means of a thin-wall aluminum tube, constrained by copper-beryllium spirals to move only in a vertical direction under the influence of the magnetic field. A special set of tapered magnet pole pieces were obtained to give a constant field gradient in the region of the specimen, and the gradient is measured with a Rawson differential gaussmeter.

The first experiments involved the measurement of the magnetization of iron at room temperature to check the performance of the equipment. Unfortunately the reproducibility was only about $\pm 5\%$ and the mean value was about 5% higher than the accepted value in the literature. After other possible sources of error were ruled out it was concluded that the discrepancy was due to the uncertainty in the gradient at the position of the specimen. This observation led to a very careful study of field-gradient contours in the x , y and z directions in the gap between the pole pieces. It was found that the pole pieces did not provide the uniformity in gradient that was desired and there were no regions of constant gradient ($\pm 0.1\%$) in any direction. The sys-

tematic and random errors encountered in the measurements on iron arose, therefore, from the uncertainty in placing and maintaining the specimen at a fixed position in the gap.

Attempts were made to improve the constancy by shimming the pole pieces with thin strips of steel sheet. In this way a reasonably constant gradient ($\pm 0.3\%$) was obtained in the z direction but it was very difficult to improve, or measure, the constancy in the x and y directions.

Subsequent measurements on iron showed the reproducibility to have been improved to about $\pm 2\%$ but there was still a systematic deviation of about 3% from the literature value for iron.

It was then decided to return for the present time to a relative method and use pure iron to calibrate the gradient. In this manner the absolute error in the gradient is reduced to the error with which the magnetization of iron is known, and the accuracy of the determinations of magnetization, now relative to iron, can be improved effectively, albeit laboriously, by making a large number of repetitive measurements.

Another related problem arose when the measurements were carried to low temperatures. As the alu-

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FIG. 171. Schematic View of Apparatus for Measuring Saturation Magnetization by the Force Method.

TABLE 65. ROOM TEMPERATURE (295°K) SATURATION MAGNETIZATIONS OF SOME IRON ALLOYS

Alloy System	a/o, Solute	$\sigma_{\infty, RT}$ (cgs/g)
Fe-Be	3.7	216.2
	7.6	212.4
	11.0	206.4
	11.5	207.4
	20.6	185.6
Fe-Ga	2.0	213.7
	5.0	207.2
	8.0	201.3
	11.0	193.7
	14.0	186.5
Fe-Mo	2.0	210.9
	5.0	200.1
	10.0	180.2
Fe-Re	2.0	208.0
	5.0	191.6
	8.0	175.1
	15.0	136.6

minum tube contracts on cooling, the specimen moves to a position of different gradient, and a spurious temperature dependence appears in the magnetization. As the variation of gradient with position is linear, this effect has been calibrated through the known temperature dependence of the magnetization of iron.

The experimental procedure has thus become one of making a series of about 20 separate runs on each specimen at room temperature. The specimen is randomly repositioned after each run and so an average value of the magnetization is determined. Then one set of runs at room temperature and low temperatures is made with the specimen in a given position to obtain the ratio of the saturation magnetization at 0°K to the satura-

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FIG. 172. Composition Dependence of the Room Temperature (295°K) Saturation Magnetization of Some Iron Alloys.

tion magnetization at room temperature. The "correct" magnetization at 0°K is then calculated, and from this the atomic moment is obtained.

The results of some preliminary determinations are listed in Table 65. It must be emphasized that these numbers, which are only room temperature values, are provisional and are subject to refinement when more data have been taken. The temperature-dependence results are still being assessed and will not be given. The data are plotted in Fig. 172. It can be seen that the magnetization decreases smoothly with composition. The rate of decrease increases with the atomic weight of the solute. It is not possible to assess the significance of the results until the atomic moments have been determined, and these in turn can only be calculated when the temperature dependences are known.

2. Calibration of Twin Solution Calorimeter (J. B. DARBY, JR.)

Preliminary attempts to calibrate the twin calorimeter at 350°C, by the use of the published values of the heat of solution of Au in liquid Sn, gave results having poor precision. Additional experiments indicated that the scatter was the result of two factors: (a) errors in measuring the temperature of a specimen prior to a solution experiment, (b) perturbations in the thermal balance of the calorimeter resulting from a change in heat leak upon dispersing a specimen. A modification was made so that the specimen-storage and -dispersing mechanism is isolated thermally from the calorimeter and samples are maintained at ambient temperature rather than at the temperature of the tin bath. Subse-

quent tests gave results having a precision better than $\pm 1\%$. The calorimeter was then deemed satisfactory for the resumption of calibration and for exploratory experiments.

An extensive series of specimens of Au at room temperature were dropped into the liquid tin at 425°C to establish a calibration factor for the calorimeter. The heat capacity of Au was determined from the analytical expression given by Kelley⁽¹⁷⁶⁾ and a value of 5200 cal/mole for the heat of solution of Au was selected

(176) Kelley, K. K., U. S. Bureau of Mines Bulletin No. 584, 1960.

from the work of Oriani and Murphy.⁽¹⁷⁷⁾ Subsequent determinations of the heat of solution of Ag in liquid Sn, based on our calibration factor, were found to be substantially higher than the published value.⁽¹⁷⁸⁾ It was realized that as a check of interval consistency this measurement was vulnerable to a large cumulative error resulting from errors in the published values for the heat capacities and heats of solution of both Au and Ag. It appeared that a calibration procedure and consistency check that would be less susceptible to cumulative error would involve the use of the heat capacity of Sn from room temperature to the bath temperature and the determination therefrom of the heats of solution of Ag and Au. This procedure was employed and the latter quantities are in good agreement with the selected values published recently.⁽¹⁷⁸⁾ There is an indication that the value chosen initially for the heat of solution of Au in liquid tin at 425°C was too high by about 150 cal/mole.

While the experimental heat capacities and the heats of solution of Au and Ag appear to be reliable calibration standards for experiments at 425°C, all calibrations of this calorimeter are based on the heat absorbed by Sn when dropped from room temperature into a liquid Sn bath at an elevated temperature. This eliminates any uncertainty concerning the temperature or concentration dependence of the heat of solution of the two noble metals. Also, the possibility of solute-solute interactions occurring between the material used for calibration and the constituents of the alloys under investigation is removed.

The heats of solution of Au, Ag, and Pd in liquid Sn at 425°C have been acquired as the average of at least twelve determinations for each element. They are shown in Table 66 together with the values obtained by other investigators.⁽¹⁷⁸⁾ The data are in good agreement and provide an assurance that our calorimeter is operating satisfactorily. The heats of solution of other transition elements are being explored currently.

⁽¹⁷⁷⁾ Oriani, R. A., and Murphy, W. K., *J. Phys. Chem.* **62**, 327 (1958).

⁽¹⁷⁸⁾ Hultgren, R., Orr, R. L., Anderson, P. D. and Kelley, K. K., *Selected Values of Thermodynamic Properties of Metals and Alloys*, John Wiley and Sons, New York (1963).

TABLE 66. THE HEATS OF SOLUTION OF Au, Ag AND Pd IN LIQUID Sn AT 425°C.

Solute	Present Work		Published Data ⁽¹⁷⁸⁾	
	$\Delta H_{sol'n}$ (cal/g-atom)	Temp°C	$\Delta H_{sol'n}$ (cal/g-atom)	Temp°C
Ag	+3730 $\pm$ 15	425	+3725	450
Au	-5031 $\pm$ 10	425	-5064	425
Pd	-26,169 $\pm$ 194	425	-26,400	423

A determination of the heats of formation of a series of alloys across the Au-Pd system has just been completed. Experiments were carried out at 425°C on alloys spaced at intervals of ten atomic percent across the phase diagram. The data will not be included in this report since the chemical analyses on the alloys have not been completed. The heats of formation are all exothermic and vary with composition in a manner very similar to those for the Ag-Pd and Cu-Pd systems,⁽¹⁷⁸⁾ including a maximum in enthalpy in the vicinity of 40a/oPd. While a complete interpretation of the data remains to be worked out, the maximum in enthalpy at the indicated composition strongly suggests that electronic effects are dominating. Magnetic susceptibility, electrical resistivity, thermoelectric power as well as other property measurements on the Au-Pd system⁽¹⁷⁹⁾ give credence to the interpretation that the *d*-band of Pd is completely filled in the vicinity of 40a/oPd. A paper summarizing the experimental work and interpretation will be submitted for publication in the near future. Also, a description of the calorimeter and its performance will be submitted for publication in due course.

In the immediate future, the experimental effort will be concentrated on the binary systems among the transition elements in the later columns in the three long periods, which form continuous solid solutions. Where possible, the experiments will be coordinated with the investigations deriving free energies from vapor pressures so that a more complete thermodynamic description can be provided.

⁽¹⁷⁹⁾ Mott, N. F. and Jones, H., *The Theory of the Properties of Metals and Alloys*, Dover Publications, Inc., New York (1958).

5. Thermodynamic Properties from Vapor Pressure Studies: Palladium-Silver Alloys (K. M. MYLES)

Publications

1. K. M. Myles and A. T. Aldred, *Thermodynamic Properties of Solid Vanadium-Iron Alloys*, J. Phys. Chem. **68**, 64 (1964).
2. A. T. Aldred and K. M. Myles, *Thermodynamic Properties of Solid Vanadium-Chromium Alloys*, Trans. AIME **230**, 736 (1964).
3. K. M. Myles, *Thermodynamic Properties of Solid Palladium-Silver Alloys*, J. Metals **16**, 767 (1964) Abstract.

The thermodynamics of solid palladium-silver alloys were investigated to study the contributions that are associated with alterations in the electronic structure upon alloying. The thermodynamic properties were calculated from silver vapor pressure data as measured by the torsion-effusion method.

As seen in Figure 173, the activities of silver at 1200°K, with pure silver as the reference state, exhibit fairly large negative deviations from ideality. The activities of palladium, determined with the Gibbs-Duhem relation, are characterized by negative deviations in the silver-rich alloys, and in the palladium-rich alloys by positive deviations. Good qualitative agreement exists between these activities of palladium and those found by Schmahl,⁽¹⁸⁰⁾ who made measurements at 956°K by an oxygen-equilibria method.

The integral free energies, entropies, and enthalpies of formation are shown in Figure 174. Hultgren et al.⁽¹⁸¹⁾

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FIG. 173. Activities of Palladium and Silver at 1200°K. □ experimental; ○ calculated; ▲ Schmahl⁽¹⁸⁰⁾ 956°K.

⁽¹⁸⁰⁾ Schmahl, N. G., Z. Znorg. Allgem. Chem., **266**, 1 (1951).

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FIG. 174. Integral Free Energies, ○, Entropies, Δ, and Enthalpies, □, of Formation of Palladium-Silver Alloys at 1200°K. ▲ ΔH, Hultgren, et al.,⁽¹⁸¹⁾ 1000°K; ▼ TΔS from ΔH, Hultgren, et al.,⁽¹⁸¹⁾ 1000°K; and ΔF, present work, 1200°K.

and Oriani and Murphy⁽¹⁸²⁾ have measured enthalpies of formation of several palladium-silver alloys near 1000°K by means of liquid-tin solution calorimetry. The present results agree quite favorably with these data. When the enthalpies reported by Hultgren at 1000°K are combined in the Gibbs-Helmholtz relationship with the free energies determined here at 1200°, the resulting entropies are in accord with those of the present study.

As there is no evidence that any deviations from random mixing occur at 1200°K,⁽¹⁸³⁾ the configurational entropy and enthalpy, which are associated with non-

⁽¹⁸¹⁾ Chan, J. P., Anderson, P. D., Orr, R. L. and Hultgren, R., 4th Technical Report, Minerals Research Laboratory, Berkeley, Calif., October 1, 1959.

⁽¹⁸²⁾ Oriani, R. and Murphy, W. K., Acta Met., **10**, 879 (1962).

⁽¹⁸³⁾ Rao, C. N., Rao, K. K., Can. J. Phys. **42**, 1336 (1964).

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FIG. 175. Estimated Nonconfigurational Contributions to the Excess Entropy of Palladium-Silver Alloys at 298°K and Values Derived from Experimental Data of Present Work at 1200°K. I vibrational (electronic + lattice), II magnetic (a, paramagnetic palladium with randomly oriented moments; b, diamagnetic silver; c, hypothetical paramagnetic palladium with no moments).

randomness, are considered to be negligible. The estimated nonconfigurational contributions to the excess entropy at 298°K are plotted in Figure 175. The electronic and lattice vibrational contributions were estimated from low temperature specific heat data of Hoare and Yates.⁽¹⁸⁴⁾ The magnetic entropy is dependent upon the change that occurs upon alloying in the degree of randomness in the orientation of the atomic magnetic moments associated with the palladium atoms. By applying classical Boltzmann statistics, Weiss and Tauer⁽¹⁸⁵⁾ have derived an expression that describes the limiting value of the magnetic entropy for metals that obey a localized electron model. Unfortunately, palladium at ambient temperatures is best described in terms of a collective electron model governed by the statistics of Fermi-Dirac. Although the classical limit to the Fermi-Dirac statistics is effectively reached at sufficiently elevated temperatures, it is unlikely that either electron model accurately describes the behavior of palladium at 1200°K. In view of this dilemma, the magnetic entropy for the palladium-silver alloys has

⁽¹⁸⁴⁾ Hoare, F. E., Yates, B., Proc. Roy. Soc., **A240**, 42 (1957).

⁽¹⁸⁵⁾ Weiss, R. J., Tauer, K. J., Phys. Rev., **102**, 1490 (1956).

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FIG. 176. Estimated Vibrational Contribution to the Enthalpy of Palladium-Silver Alloys at 298°K and Values Derived from Experimental Data of Present Work at 1200°K.

been estimated by means of a simple expansion of the relationship of Weiss and Tauer. The calculated values are thought to be larger in magnitude than the true magnetic contribution to the entropy.

The electronic and lattice vibrational contributions to the enthalpy, computed at 298°K from the electronic specific heat coefficients and Debye temperatures, are quite small and negative as seen in Figure 176. The enthalpy term associated with the transfer of electrons upon alloying from the 5s-band of silver to the 4d-band of palladium is negative. The minimum in the enthalpies at approximately 60 a/o silver is indicative, if the band structure is rigid, of the completion of the filling of the 0.6 hole in the 4d-band of palladium.

The good agreement between the enthalpies measured by calorimetric methods and those computed from the vapor pressure data suggests that the entropies of the present work are also fairly reliable. However, as noted in Figure 175, the estimated contributions to the entropy are several times larger numerically than the experimental values. This discrepancy may be rationalized in part by assuming that the vibrational contributions to the entropy and the enthalpy, which often cannot be accurately approximated at elevated temperatures from low temperature specific heat data, are considerably too large numerically. If this assumption is correct, then, as may be seen in Figure 176, the bulk of the enthalpy must be attributed to contributions arising from alterations in the electron distribution upon alloying.

Intermediate Phases in Binary Systems Containing Technetium (J. B. DARBY, JR.)

Publications

1. J. B. Darby, Jr., L. J. Norton and J. W. Downey, *Technetium Compounds with the MgZn₂ Structure*, J. Less-Common Metals, **6**, 165 (1964).

A survey of the intermediate phases in the systems Tc-Si and Tc-Al has been completed. Table 67 summarizes the findings by listing the composition at which intermediate phases were found and the crystal structures and lattice constants of the phases that were identified.

The occurrence of Laves phases in the systems Th-Tc₂ and U-Tc₂ has been investigated. X-ray metallography on representative samples from the Th-Tc alloys annealed at 900°C for four weeks and quenched in water revealed the existence of a Laves phase of the C-14-type. A Laves phase has not been found in the U-Tc system; the diffraction patterns suggest that a complex and, as yet, an unidentified structure exists at the U-Tc₂ composition. The crystal structure of the compound U₂Tc, stable at 900°C, has also been investigated and tentatively identified as being isostructural with U₂Ru.⁽¹⁸⁶⁾ The high impurity content of the Tc metal used as a starting material in preparing the al-

TABLE 67. STRUCTURES OF THE PHASES IDENTIFIED IN THE Tc-Al AND Tc-Si SYSTEMS

Alloy Composition (at. %)	Structure Type	Lattice Parameters (Å)
33.3 Al	MoSi ₂ (C11b)	$a_0 = 2.977 \pm 0.001$ $c_0 = 9.476 \pm 0.002$ $c/a = 3.183$
66.7 Al	Unknown	—
75.0 Al	Unknown	—
92.3 Al	WAl ₁₂	$a_0 = 7.528 \pm 0.001$
20.0 Si	W (A2)	$a_0 = 3.009 \pm 0.001$
25.0 Si	Fe ₃ Zn ₁₀ or Cu ₃ Zn ₈ (D8 ₁ or D8 ₂)	$a_0 = 9.014 \pm 0.001$
37.5 Si	W ₅ Si ₃ (D8m)	$a_0 = 9.403 \pm 0.001$ $c_0 = 4.849 \pm 0.001$ $c/a = 0.516$
50.0 Si	FeSi (B20)	$a_0 = 4.755 \pm 0.001$
66.7 Si	Possibly isostructural with MnSi ₂	—

loys limits the reliability of these preliminary findings, so the work will be repeated on alloys prepared with Tc of greater purity. When satisfactory lattice parameters have been obtained the survey of intermediate phases containing technetium will be terminated.

5. A Scheme for Correlating the Occurrence of Intermediate Phases (A. E. DWIGHT)

In the 1963 Annual Report, ANL-6868, a plot showing the area of stability, in terms of composition, was given for compounds of AB₂ composition in which A and B were elements of the third transition series. As a continuation of this work, other composition-stability plots have been drawn for AB, AB₂ and AB₃ compounds. The type of plot that was used in Figure 175 of ANL-6868 and is used in Figure 177 of the present report, has the A elements from a selected transition series of the periodic table plotted as the abscissa against the B elements from a selected transition series as ordinate. A total of nine plots are required to accommodate all possible combinations. In this arrangement a composite partner (A or B comprised of two elements) is restricted to elements of the same long period. To circumvent this restriction a second type of area-of-stability plot has evolved, in which the stoichiometry and the A element are fixed on any one plot, and the B element may be from any part of the periodic table. Figures 178, and 180 are of this type. The data that are in-

cluded in Figures 177 through 180 will be presented first, followed by a discussion of the implications and uses of the plots.

The A elements in Figure 177 are Hf, the lanthanides (except Pm and the divalent Eu and Yb) and Ba. The B elements include Fe through As. Since other investigators have established the presence or absence of AB compounds in many of the binary systems, our experimental work was intended to fill in gaps, resolve conflicting data, and search for compounds in a few ternary systems.

It is fairly certain that no AB compounds exist in the Hf-Fe⁽¹⁸⁷⁾, La-Fe⁽¹⁸⁸⁾, Ce-Fe⁽¹⁸⁸⁾ or Gd-Fe⁽¹⁸⁸⁾ systems. When the B element is Co, Hf forms the CsCl-type structure⁽¹⁸⁹⁾ and our recent work shows that Ni can be

⁽¹⁸⁷⁾ Svecnikov, V. N. and Shurin, A. K., *The Equilibrium Diagram of Fe-Hf*, Doklady Akademii Nauk USSR **139**, 895 (1961).

⁽¹⁸⁸⁾ Gschneidner, K. A., *Rare Earth Alloys*, Van Nostrand (1961).

⁽¹⁸⁹⁾ Dwight, A. E., *CsCl-type Equiatomic Phases in Binary Alloys of Transition Elements*, Trans. of the Met. Soc., A.I.M.E. **215**, 283 (1959).

⁽¹⁸⁶⁾ Berndt, A. F., *The Unit Cell of U₂Ru*, Acta Cryst. **14**, 1301 (1961).

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FIG. 177. Areas of Stability of AB Compounds between Hf, the Lanthanides and Ba as A Elements; B Elements of the First Long Period.

substituted for at least 20 at. % Co without destabilizing the CsCl-type structure. This is shown in Figure 177 by including two ternary Hf-Co-Ni alloys in the CsCl-type area of stability. Novy *et al.*⁽¹⁹⁰⁾ and Savitskii *et al.*⁽¹⁹¹⁾ agree that a GdCo compound exists although other investigators⁽¹⁸⁸⁾ have not found it. It is probable that an area of stability exists for some of the lanthanide-Co equiatomic compounds, but the structure type and extent of the area of stability are still unknown.

When the B element is Ni, binary equiatomic compounds are numerous and their crystal structures are well established. HfNi was reported⁽¹⁹²⁾ to have a CrBor-type structure. A ternary CsCl-type Hf₂Lu₃Ni₅ was reported in ANL-6868, and its significance is discussed later. The crystal structures of eleven lanthanide-Ni compounds were also reported in ANL-6868 (Eu and Yb, being divalent, are not expected to conform with the other lanthanides and were not investigated. Pm is not available in large enough quantities for alloy studies. TbNi was investigated but its structure was not solved.)

Chao, Luo and Duwez⁽¹⁹³⁾ have reported that alloys of Cu with Sm through Tm (again excluding Eu) form

⁽¹⁹⁰⁾ Novy, V. F., Vickery, R. C. and Kleber, E. V., *The Gd-Co System*, Trans. of the Met. Soc. A.I.M.E. **221**, 588 (1961).

⁽¹⁹¹⁾ Savitskii, E. M., Terekhova, V. F., and Burov, I. V., *Equilibrium Diagram of the Co-Gd System*, Russian J. Inorg. Chem. **7**: 1335 (1962).

⁽¹⁹²⁾ Kirkpatrick, M. E., Bailey, D. M., and Smith, J. F., *The Structures of Zr₂Ni, ZrNi and the Hf Analogs*, Acta Cryst. **15**, 252 (1962).

⁽¹⁹³⁾ Chao, C. C., Luo, H. L., and Duwez, P., *CsCl-type Com-*

the CsCl-type structure in their equiatomic compounds. CeCu was reported by Larson and Cromer⁽¹⁹⁴⁾ to have the FeBor-type structure. We have made equiatomic alloys of all lanthanides (except Pm, Eu and Yb) with Cu and concur with the findings mentioned above. Our data for SmCu, TbCu, HoCu, and TmCu are given in Table 68. Data were published⁽¹⁹⁵⁾ earlier for GdCu, DyCu, ErCu and LuCu, all of which have the CsCl-type structure. LaCu, CeCu, PrCu and NdCu were found to have the FeBor-type structure, but the lattice parameters and atomic positional parameters need further refinement.

Most of the lanthanide-Zn equiatomic compounds have been reported⁽¹⁹⁶⁾ to have the CsCl-type structure. Our data (Table 68) confirm the existence of a CsCl-type structure in PrZn. BaZn was reported⁽¹⁹⁶⁾ to have the CsCl-type structure.

Our results on ErGa, SmGa and PrGa (Table 68) indicate that these compounds have the CrBor-type structure. Since the work of Iandelli,⁽¹⁹⁷⁾ Baenziger and

pounds in Binary Alloys of Rare Earth Metals with Zn and Cu, J. Appl. Phys. **35**, 257 (1964).

⁽¹⁹⁴⁾ Larson, A. C. and Cromer, D. T., *The Crystal Structure of CeCu*, Acta Cryst. **14**, 545 (1961).

⁽¹⁹⁵⁾ Nevitt, M. V., "Alloy Chemistry of Transition-Elements" in book *Electronic Structure and Alloy Chemistry of the Transition Elements*, P. A. Beck, Editor, Interscience (1963).

⁽¹⁹⁶⁾ Pearson, W. B., *A Handbook of Lattice Spacings and Structures of Metals and Alloys*, Pergamon (1958).

⁽¹⁹⁷⁾ Iandelli, A., "Intermetallic Compounds of the R Earth Metals" in *The Physical Chemistry of Metallic Solutions and Intermetallic Compounds*, **1**, Chemical Publishing Co. (1960).

ioriarty,⁽¹⁹⁸⁾ and Cable⁽¹⁹⁹⁾ for other lanthanide-Ga compounds also indicated a CrBor-type structure, it is probable that the entire series of trivalent lanthanides forms the CrBor-type structure with Ga.

Little is known of lanthanide-Ge compounds except that PrGe,⁽¹⁹⁷⁾ DyGe and GdGe⁽¹⁹⁸⁾ were reported to be of the CrBor-type. Arsenic was reported by Schob and Parthé⁽²⁰⁰⁾ to form NaCl-type equiatomic compounds with 12 of the lanthanides.

When *A* elements from the third long period are plotted against *B* elements from the first long period, as in Figure 177, a construction results that is useful, as will be discussed later. However, to study ternary compounds whose components may originate in all three long periods, a plot of the type shown in Figures 178, 179 and 180 is preferable. Figure 178 includes equiatomic uranium compounds. The plot is labelled UX rather than UB to avoid confusion with boron. There are relatively few binary UX compounds. Those which are known are UCo⁽¹⁹⁶⁾ which is a distorted CsCl of a unique type, USi (FeBor type⁽¹⁹⁶⁾) and UGa⁽²⁰¹⁾ which is a unique orthorhombic structure. URu, URh, UPd, UPt are known to exist but their crystal structures have not been determined. Our work indicates UIr has the CrBor-type structure, but lattice parameters and atomic positional parameters need further refinement. A solid solution exists, at least at some temperature, between UHf, UZr, UTi and UNb equiatomic alloys. In all other UX alloys the structure is either two phase or unknown.

Ternary $U_{50}(X'X'')_{50}$ compounds were previously unknown, but we have found a family of such compounds. Seven of these are listed in Table 68. A typical example is $U_{50}Rh_xNi_{50-x}$ where *x* may vary from 15 to 40. Our experimental alloy compositions are shown as small circles in Figure 178, with the open circles denoting a single phase alloy, and half-closed circles denoting alloys containing two-or-more phases. The area within which the new ternary phase is stable is enclosed with a heavy line. The crystal structure of the new phase is face-centered cubic, with certain reflections missing; the requirement for a reflection to occur is that $h + k + l$ must either equal $2n + 1$ or $4n$. The B32 (NaTl-type) is the most probable choice for the structure type. An intensity calculation was made for U_2RhNi assuming that U occupied the Na sites and that Rh and Ni occupied the Tl sites. Agreement with the observed in-

⁽¹⁹⁸⁾ Baenziger, N. C., and Moriarty, J. L. Jr., *Gd and Dy Intermediate Phases I*, Acta Cryst. **14**, 946 (1961).

⁽¹⁹⁹⁾ Cable, J. W., Koehler, W. C., and Wollan, E. O., *Magnetic Order in Rare Earth Intermetallic Compounds*, Phys. Rev. **131**, A240 (1964).

⁽²⁰⁰⁾ Schob, O. and Parthé, E., *AB Compounds with Sc, Y and Rare-Earth Metals*, in press.

⁽²⁰¹⁾ Makarov, E. S., *Crystal Chemistry of Simple Compounds*, Consultants Bureau, 1959.

FIG. 178. Areas of Stability for UX Compounds.

FIG. 179. Areas of Stability for UX_2 Compounds.

tensities was considered good enough to support the choice of the NaTl-type structure.

Figure 179 shows an area of stability plot for UX_2 compounds. From the literature⁽¹⁹⁶⁾ it is noted that USi_2 , UGe_2 , and UHg_2 have the $AlBor_2$ type. No ternary data are known for the $AlBor_2$ -type compounds, therefore a dashed line is used to enclose assumed areas of stability. UPt_2 has an orthorhombic structure,⁽²⁰²⁾ and there is an area of solid solutions enclosing UTi_2 , UZr_2 , UHf_2 and UNb_2 (at least at high temperatures). Except for the UX_2 compounds noted above, either there are Laves phases or no UX_2 compounds exist.

The crystal structures of binary UX_2 Laves phases

⁽²⁰²⁾ Hatt, B. A. and Williams, G. I., Acta Cryst. **12**, 655 (1959).

have been reported by various investigators.^(196,203) Ternary MgZn_2 -type Laves phases in the U-Mo-Si system⁽²⁰⁴⁾ and in the U-Mn-Al, U-Fe-Al, U-Co-Al systems⁽²⁰⁵⁻²⁰⁷⁾ are included in Figure 179. Unpublished ANL data⁽²⁰⁸⁾ support the identification of these ternary compounds, and indicate the presence of a ternary MgZn_2 -type UIrAl compound. Our experimental work is shown by small circles on light lines connecting the elements of a composite *B*-partner.

The area-of-stability plot in Figure 179 must be used with discretion, as it contains data on ternary systems some of which involve *B* elements from adjacent periods (e.g. U-Ru-Ir) and some of which involve *B* elements from widely separated periods (e.g. U-Ir-Al). As a result of this combination of ternary data, the MgZn_2 field overlays the composition UCu_2 . It must not be inferred that UCu_2 is an MgZn_2 -type compound (there actually is no UCu_2) but rather that if UCu_2 existed it probably would have the MgZn_2 -type structure. The area-of-stability plot is in no sense an equilibrium diagram. The principal point that Figure 179 is intended to demonstrate is that the MgZn_2 -type structure, which exists in the binary UNi_2 compound, can be synthesized in the U-Mn-Al, U-Fe-Al, U-Co-Al, U-Ir-Al and U-Os-Al ternary systems. Ternary MgZn_2 -type compounds in the five systems just mentioned lie in the same area of stability as does the binary UNi_2 .

Figure 180 is a similar area-of-stability plot for UX_3 compounds. It has been reported⁽¹⁹⁶⁾ that UPd_3 has a TiNi_3 -type structure, and UPt_3 an Mg_3Cd type.⁽¹⁹⁶⁾ It was also reported that URu_3 ,⁽¹⁹⁶⁾ URh_3 and UIr_3 (ANL-6099) have the Cu_3Au -type structure. The structure of UCo_3 is unknown, and according to Reference 196 UAl_3 , UGa_3 , UGe_3 , USi_3 , UIn_3 , UTl_3 all have the Cu_3Au -type. UHg_3 has a hexagonal structure.⁽¹⁹⁵⁾ UAu_3 exists but its crystal structure is unknown. Our experimental findings, when placed on Figure 180, show that the Cu_3Au area, which is centered on URh_3 , is quite extensive.

When compounds having the same crystal structure type are grouped together to form, in terms of composition, an area of stability, plots such as Figures 177 through 180 are the result, and ternary compounds may

FIG. 180. Areas of Stability for UX_3 Compounds.

be rationalized thereby. For example, we find (ANL-6677) that Hf_2NiFe is a ternary CsCl-type compound, while Co, lying between Ni and Fe in the periodic table, forms a binary HfCo compound with the CsCl-type structure. Apparently the CsCl-type structure is stabilized by a certain electron concentration, and it is immaterial whether the *B* element is Co or a mixture of Fe and Ni. Referring to Figure 177, HfCo lies within the area of CsCl stability while HfNi and the non-existent $[\text{HfFe}]$ lie above and below HfCo . It is observed that the composite *B* partner ($\text{Fe} + \text{Ni}$) straddles the area of stability. Selecting *B* partners which straddle the area of stability has proven to be a reliable method of predicting ternary compounds, subject to some limitations to be mentioned later. A more extreme example of ternary compound stabilization was found in the Lu-Ni-Ga system (Table 68). A ternary CsCl-type compound was found. The mixture of Ni and Ga apparently synthesizes the electron contribution made by Zn (although LuZn has not yet been made, it will almost certainly have the CsCl-type structure, as do the eleven other lanthanide-Zn compounds. The Ti_2RhCu compound listed in Table 68 is analogous to Lu_2NiGa , in that Rh and Cu together appear to approximate the electron contribution made by Ni (TiNi is a binary CsCl-type compound). Two more examples, which were reported in ANL-6868, are Er_2PdRu and Y_2PdRu , in which $\text{Pd} + \text{Ru}$ synthesize Rh.

The synthesis of an electron contribution by a mixture of two *B* elements is the probable explanation for the occurrence of two ternary Laves phases. UNiRu and $\text{U}_2\text{Ni}_3\text{Rh}$, reported in ANL-6868 as MgCu_2 -type can be rationalized by considering that the mixture of Ni a Rh, and of Ni and Ru, approximates the electron contribution made by Co, since UCo_2 is a binary MgCu_2 -type and Co lies between Ni and Ru (and possibly

⁽²⁰³⁾ Sikirica, M. and Ban, Z., "New Phase in the System U-Mo-Si" in *New Nuclear Materials Including Nonmetallic Fuels*, II, I.A.E.C. (1963).

⁽²⁰⁴⁾ Rough, F. A. and Bauer, A. A., *Constitution of Uranium and Thorium Alloys*, BMI-1300 (1958).

⁽²⁰⁵⁾ Petzow, G. and Steeb, S., *The Pseudobinary System UMn_2UAl_2* , *Zeit. fur Met.* **55**, 456 (1964).

⁽²⁰⁶⁾ Petzow, G., Steeb, S. and Rank, R., *The Pseudobinary System $\text{UF}_2\text{-UAl}_2$* , *Zeit. fur Met.* **53**, 526 (1962).

⁽²⁰⁷⁾ Steeb, S. and Petzow, G., *Structure of the $\text{U}_2\text{Co}_3\text{Al}$, U_2OsAl_3 and UAlMn* , *Zeit. fur Met.* **55**, 453 (1964).

⁽²⁰⁸⁾ Darby, J. B. Jr., private communication.

TABLE 68. INTERMETALLIC COMPOUNDS STUDIED IN 1964

A Elements*	B Elements*	$a_0(\text{\AA})$	$b_0(\text{\AA})$	$c_0(\text{\AA})$	c/a	Type
Sm	Cu	3.535				CsCl
Tb	Cu	3.478				CsCl
Ho	Cu	3.445				CsCl
Tm	Cu	3.413				CsCl
Pr	Zn	3.683				CsCl
Tb	Ag	3.626				CsCl
Tm	Ag	3.563				CsCl
Lu ₂	Ni Ga	3.368				CsCl
Ti ₂	Rh Cu	3.086				CsCl
Y ₂	Ir Pt	3.440				CsCl
Er Hf	Pd ₂	3.386				CsCl
Zr	Ag	3.474		6.601	1.90	TiCu
Hf Ta	Os ₂	3.174		6.558	2.06	TiCu
Cr	Pt	3.822			1.00	CuAu
Nd	Ga	4.44	11.24	4.17	0.94	CrBor
Sm	Ga	4.39	11.11	4.15	0.94	CrBor
Er	Ga	4.26	10.73	4.04	0.95	CrBor
U ₅	Ni ₂ Rh ₃	6.438				NaTi
U ₅	Ni ₄ Ir	6.316				NaTi
U ₅	Ni ₄ Pd	6.316				NaTi
U ₅	Ni ₄ Pt	6.361				NaTi
U ₅	Pd ₃ Rh ₂	6.585				NaTi
U ₂	Pd Pt	6.648				NaTi
U ₅	Rh ₄ Co	6.45				NaTi
La	Cu	7.532	4.625	5.711		FeBor
Ce	Cu	7.370	4.623	5.648		FeBor
Pr	Cu	7.343	4.584	5.604		FeBor
Nd	Cu	Not yet determined				FeBor
Er	Pt ₃	4.054				Cu ₃ Au
Tm	Pd ₃	4.054				Cu ₃ Au
Nb	Ru ₂ Ni	3.816				Cu ₃ Au
Ta ₅	Ir ₄ Ni ₁₁	Not yet determined				MgCd ₃
Sc	Ag ₂	3.519		8.992	2.535	MoSi ₂
Y	Ag ₂	3.701		9.201	2.486	MoSi ₂
Gd	Ag ₂	3.729		9.287	2.490	MoSi ₂
Tb	Ag ₂	3.710		9.247	2.492	MoSi ₂
Dy	Ag ₂	3.695		9.210	2.493	MoSi ₂
Ho	Ag ₂	3.681		9.181	2.494	MoSi ₂
Er	Ag ₂	3.668		9.159	2.497	MoSi ₂
Tm	Ag ₂	3.642		9.140	2.503	MoSi ₂
Lu	Ag ₂	3.628		9.113	2.512	MoSi ₂
Sc	Au ₂	3.508		8.725	2.487	MoSi ₂
Y	Au ₂	3.691		8.959	2.427	MoSi ₂
Gd	Au ₂	3.728		9.020	2.420	MoSi ₂
Tb	Au ₂	3.707		8.987	2.424	MoSi ₂
Dy	Au ₂	3.691		8.961	2.428	MoSi ₂
Ho	Au ₂	3.677		8.940	2.431	MoSi ₂
U ₂	Os **	13.366	3.335	5.167		U ₂ Ru
U ₂	Rh **	13.122	3.421	5.159		U ₂ Ru
U ₂	Ir **	13.210	3.457	5.095		U ₂ Ru

* The use of a stoichiometric ratio for a ternary alloy does not mean the composition range is restricted to that ratio, but that the indicated structure and lattice parameters were found at that ratio.

** Lattice parameters by A. F. Berndt.

between Ni and Rh in electron concentration). The MgZn₂-type compound U₄Mo₃Si₃⁽²⁰³⁾ is an example of stabilization of a ternary compound in which the B

partners Mo and Si not only straddle an MgZn₂ area of stability but lie an appreciable distance away from the area of stability.

A limitation to the electron concentration "synthesis effect" is that the location of the synthesized B partners in the periodic table is important. It is quite possible to synthesize the effect of Co, Rh, Ru, Os and Ni but not of Pd or Pt insofar as is known at present.

Not all ternary compounds can be explained by the electron concentration "synthesis effect", as it might be called. An example of a different stabilization effect was mentioned earlier in the Hf₂Lu₃Ni₅ (ANL-6868) compound. The limiting binary compounds are HfNi (CrBor) and LuNi (FeBor). Both are orthorhombic. The ternary Hf₂Lu₃Ni₅ has a CsCl-type structure. It has been noted in ANL-6868 that only limited solubility of a third element in a CrBor-type or FeBor-type compound is found. The explanation that seems most probable for the existence of the ternary Hf₂Lu₃Ni₅ is that neither the CrBor nor FeBor structures can tolerate the lattice strain that would exist due to the difference in size of the Hf and Lu atoms. Hence both structures are destroyed and a new, simpler structure emerges. The CsCl-type can obviously withstand considerable lattice strain as shown by its existence over a wide range of radius ratios and in a large number of ternary systems. ErHfPd₂ (Table 68) is a homolog of Lu₃Hf₂Ni₅.

The explanation of a simple ternary structure displacing two complex binary structures is advanced to explain the occurrence of the ternary U₂NiRh (NaTi-type) and its homologs. As noted above, all binary UX compounds are complex, yet the ternary compounds are face-centered cubic. Here again it appears that the binary compounds will not tolerate ternary substitutions, hence are destabilized in favor of a simpler crystal structure.

The Ta₂₅Ir₂₀Ni₅₅ compound (Table 68) is a ternary MgCd₃-type lying between TaIr₃ (Cu₃Au-type) and TaNi₃ (TiCu₃-type). The two limiting binaries are formed by stacking ordered layers in *abc* or *abcdef* sequences, respectively. The ternary is formed by stacking ordered layers in an *ab* sequence. The occurrence of this ternary compound may also be a manifestation of the "structure simplification" effect.

Table 68 lists a number of miscellaneous compounds not discussed above. These do not contribute to the four figures in this report but are significant when placed on other area of stability plots. The most numerous group of compounds in Table 68 are the MoSi₂-type. ScAu₂ was selected as the subject of X-ray intensity calculations. A paper incorporating our data on ScAu₂ and the other MoSi₂-type examples has been submitted to Acta Crystallographica.

6. A Study of Atomic Size in XFe_2 Laves Phases by Means of the Mössbauer Effect (M. V. NEVITT)*

In a study of the crystal chemistry of alloy phases, atomic size is usually assessed in terms of an "atomic radius" parameter derived from interatomic distances. While this approach has validity and usefulness, it has some limitations. One of these is the fact that unless there are nearest neighbors of the same kind in the structure the radii cannot be uniquely determined from the measured distances and the single assumption of touching spherical atoms. Another limitation lies inherently in treating the atom as a rigid sphere. It has become clear that the volume defining the field of influence of an atom in a metallic crystalline lattice may vary with its surroundings and may not be spherical.

In the search for an independent experimental parameter that reflects atomic size we have been attracted to the Mössbauer effect. Several investigations^(209,210,211)

have shown that the excitation energy of the Mössbauer level in Fe^{57} decreases with increasing hydrostatic pressure, and the conclusion has been drawn that this effect is due almost entirely to the increase in electronic charge density at the nucleus resulting from the decrease in the size of the iron atom. Our aim has been to test the plausible hypothesis that the pressure effect has an analog in XFe_2 Laves phases (structure types C14, C15 and C36) in which the volume of the Fe atom, as calculated from interatomic distances, varies both positively and negatively by more than 10% from its volume in α iron, while the X atoms change their identity but maintain the same configuration. Using the Mössbauer effect, we have measured the isomer shift, the magnetic hyperfine field and the quadrupole hyperfine field for Fe^{57} in a series of these lattices at 4, 78, 300 and 800°K.

39654

FIG. 181. Shift of the Centroid Plotted against Fractional Change in Volume for XFe_2 Compounds. Shift and volume change are relative to α -Fe. The line passing through the origin is a fit to the pressure results on α -Fe.

* This work was done collaboratively with C. W. Kimball, Northern Illinois University, a consultant to the Metallurgy Division, and R. S. Preston, Physics Division, Argonne National Laboratory.

⁽²⁰⁹⁾ Pound, R. B., Benedek, G. B., and Drever, R., Phys. Rev. Letters 7, 405 (1961).

⁽²¹⁰⁾ Nicol, M., and Jura, G., Science 141, 1035 (1963).

⁽²¹¹⁾ Pipkorn, D. N., Edge, C. K., Debrunner, P., DePasquali, G., Drickamer, H. G., and Frauenfelder, H., Phys. Rev. 135, A1604 (1964). * This work was done collaboratively with C. W. Kimball, Northern Illinois University, a consultant to the Metallurgy Division, and R. S. Preston, Physics Division, Argonne National Laboratory.

The isomer shift changes with the volume of the iron atom in a manner similar to that observed for metallic iron under pressure, the rate of change lying between the values for bcc and hcp iron. The 300°K and 800°K shifts are plotted against the fractional volume change in Figure 181. On the same graph the linear fit to the pressure results on α iron is shown as a solid line passing through the origin with dashed-line extrapolations. In assessing the volume dependence of the room-temperature shifts, smaller weight is given to SmFe_2 , GdFe_2 and ErFe_2 because they have larger probable errors.

While the results generally confirm the hypothesis, there are two other striking features. First, the slope is small, which shows that the configuration of s and d electrons, as reflected in the isomer shift, is less dependent upon the volume of iron in Laves phases than in α -iron under pressure, and/or our calculation of the atomic volumes from a spherical model of the atom has over-

estimated the range of volumes that iron has in the Laves phases. Second, the fluctuations of the experimental points about the straight-line fits are also small. From this we infer that the other component of the compound, irrespective of its own electron configuration, exerts no first-order effect except through its constraint on the volume available to the iron atom.

This work was described in a paper given at the International Conference on Magnetism at Nottingham, England, in September, 1964. A more complete description including the results on magnetic and quadrupole hyperfine fields, may be found in the published version, which will appear in a proceedings volume early in 1965.

It is not clear how generally applicable, in intermediate phases containing iron, is the relationship between the atomic volume and the charge density at the Fe^{57} nucleus. Work in this area is continuing.

7. Magnetic Susceptibility Measurements of Actinide Carbides (D. J. LAM AND M. V. NEVITT)

The methods of preparation and properties of U and Pu monocarbides and their solid solutions have been reported in ANL-6677 and the 1963 Annual Report. The alloys used in this investigation were prepared by arc melting, and the alloys were subsequently homogenized at 1410°C. An additional heat treatment at 570°C was performed for the $\overline{\text{PuC}}^*$ alloys. Table 69 lists the intended compositions, crystal structure and lattice parameters of the alloys studied so far.

The susceptibility apparatus used for this investigation has been described in ANL-6677. The specimens were sealed in 99.9999 % Al capsules with partial pressure of helium to facilitate heat transfer at low temper-

ature. Corrections for the susceptibility of the aluminum capsule were made by using an average value of the measured susceptibilities, from 4.2 to 300°K, of ten identical empty capsules. No temperature dependent susceptibility was found in any of the capsules. For the final check, a specimen of Th metal was encapsulated in an aluminum capsule and susceptibility measurements were made at 4.2° and 300°K. The susceptibilities of Th were 0.39×10^{-6} emu/gm at 4.2°K and 0.42×10^{-6} emu/gm at 298°K. The room-temperature value and the absence of a temperature dependence is in agreement with information in the literature.⁽²¹²⁾ A calibrated copper-constant thermocouple was used for temperature measurements and control. Since the control thermocouple was not attached to the specimen, a temperature difference between the two existed. This difference has been evaluated by attaching another thermocouple to the specimen and measuring the temperature difference between the specimen and the control thermocouple. The temperatures reported are those of the specimen, corrected for the difference. The susceptibility was measured as a function of field ($H_{\text{max}} = 11,000$ Oe), and ferromagnetic corrections were made after it had been shown that they were not a function of temperature. Results are given in Table 70.

Temperature variations of the magnetic suscepti-

TABLE 69. CRYSTALLOGRAPHIC DATA FOR MONOCARBIDES OF URANIUM AND PLUTONIUM

Alloy.	Crystal Structures	Lattice Parameters
$\text{U}_{50}\text{C}_{50}$	NaCl type	4.960 ± 0.001
$\text{U}_{40}\text{Pu}_{10}\text{C}_{50}$	NaCl type	4.965 ± 0.001
$\text{U}_{25}\text{Pu}_{25}\text{C}_{50}$	NaCl type	4.969 ± 0.001
$\text{U}_{20}\text{Pu}_{30}\text{C}_{50}$	NaCl type	4.972 ± 0.001
$\text{U}_{10}\text{Pu}_{40}\text{C}_{50}$	NaCl type	4.974 ± 0.001
$\text{Pu}_{54}\text{C}_{46}$	NaCl type	4.967 ± 0.001
$\text{Pu}_{56}\text{C}_{44}$	NaCl type	4.962 ± 0.001

* The symbol $\overline{\text{PuC}}$ is used to denote the phase without implying stoichiometry.

⁽²¹²⁾ Smith, J. F. and Greiner, J. D., Phys. Rev. **115**, 884 (1959).

TABLE 70. THE SUSCEPTIBILITY AT 25°C OF THE MONOCARBIDES OF URANIUM AND PLUTONIUM

Specimen	$\chi(10^{-6} \text{ emu/gm})$
$\text{U}_{50}\text{C}_{50}$	3.10 ± 0.08
$\text{U}_{40}\text{Pu}_{10}\text{C}_{50}$	3.69 ± 0.08
$\text{U}_{25}\text{Pu}_{25}\text{C}_{50}$	3.58 ± 0.08
$\text{U}_{20}\text{Pu}_{30}\text{C}_{50}$	3.78 ± 0.08
$\text{U}_{10}\text{Pu}_{42}\text{C}_{48}$	4.51 ± 0.08
$\text{Pu}_{34}\text{C}_{46}$	5.57 ± 0.08
$\text{Pu}_{56}\text{C}_{44}$	4.30 ± 0.08

40504

FIG. 182. Plot of χ^{-1} vs. Temperature for $\text{Pu}_{56}\text{C}_{44}$.

bility of the binary carbides of uranium and plutonium have been measured from 4.2 to 370°K. The paramagnetic susceptibility of $\overline{\text{UC}}$ is relatively independent of temperature from the preliminary measurements at 298°, 77° and 4.2°K. The susceptibility of $\overline{\text{PuC}}$ depends on the carbon concentration increasing with C/Pu ratio, and strongly depends on temperature. Figures 182 and 183 show the reciprocal of the gram susceptibility, χ_g , as a function of temperature for $\text{Pu}_{56}\text{C}_{44}$ and $\text{Pu}_{54}\text{C}_{46}$. From the linear portion of the plot an effective moment of 1.65 Bohr magneton was obtained for both compounds.

The values of χ_g below 55°K are complicated by the fact that the magnetizations $M = \chi:H$, are a function of time t , as shown in Figure 184. This time-dependent magnetization can be expressed in the form of

$$M(T) = M(0) + C[1 - \exp - t/\tau]$$

The present results indicate that the parameters $M(0)$, C and τ are functions of the C/Pu ratio, the temperature and the magnetic field strength.

This effect was shown to be related to the applied magnetic field and not the length of time at temperature in zero field in the following experiment. The $\text{Pu}_{56}\text{C}_{44}$ alloy was cooled from 77°K to 4.2°K and held at that temperature in zero field for 30 minutes. During that time, the balance recorded a constant weight. A

40503

FIG. 183. Plot of χ^{-1} vs. Temperature for $\text{Pu}_{54}\text{C}_{46}$.

40502

FIG. 184. Time Dependence of the Magnetization at 4.2°K of PuC Alloys in Various Magnetic Fields.

magnetic field of 2533 Oe was then applied and the magnetization was recorded for 70 minutes. The sample was then warmed up to 77°K, held overnight, cooled down to 4.2°K the next day, and held at that temperature for 100 minutes in zero field before a magnetic field of 2533 Oe was applied. The magnetization was

40501

FIG. 185. Time Dependence of the Magnetization at 4.2°K of $\text{Pu}_{56}\text{C}_{44}$. (After test [a], specimen was warmed to liquid nitrogen temperature, then given test [b]. See text for details).

again recorded for 70 minutes. The results are shown in Figure 185. It can be seen that the two magnetization curves are essentially identical except the difference of 70 minutes in the time scale. Similar results were obtained for the $\text{Pu}_{54}\text{C}_{46}$ alloy. The mechanism responsible

for this effect, which appears to anneal out near liquid nitrogen temperature, is not understood at the moment. Detailed investigations of the dependences of temperature, C/Pu ratio, and time of the magnetization of the binary and ternary carbides are in progress.

8. Superconductivity in Alloys of Transition Metals (S. T. ZEGLER)

During 1964, calibration of the experimental apparatus for measuring T_c , the superconducting transition temperature, was completed, permitting determinations of T_c in the temperature range 1.7 to 14°K.

The work described in preliminary form in the last Annual Report, ANL-6868, concerned with the effect of the substitutions of Co, Ru, Pd, Os, Ir, Pt or Au for Rh in the compound Nb_3Rh , was completed. All substitutions were found to increase the cell volume of Nb_3Rh and, except for Pt and Au, to decrease the superconducting transition temperature. In suitable amounts, Pt and Au were found to increase T_c but not above those of the binary compounds Nb_3Pt and Nb_3Au . The data indicate that T_c increases as the ratio of valence electrons to atoms increases from 6 to 6.5 but decreases with increasing cell volume.

Zr-Nb, Zr-Rh and Zr-Nb-Rh Alloys

Measurements of the superconducting transition temperature have been made on a number of solid-solution alloys and intermediate phases in which zirconium is the major component. T_c is plotted against e compositions of the alloys in Figures 186 and 187.

At 1000°C β -Zr and Nb are mutually soluble in all proportions⁽²¹³⁾ and in alloys containing 20a/oNb or

greater, the body-centered cubic structure is retained upon water quenching. Consistent with the findings of Hulm and Blaughner⁽²¹⁴⁾, the T_c of the metastable solid solutions was found to have a maximum at approximately 70a/oNb (Figure 186a). The influence upon T_c of Rh additions to Zr-Nb alloys is shown in Figure 186b. At a fixed atomic ratio, Zr/Nb, additions of Rh up to the solubility limit are seen either to have no effect or to decrease T_c only slightly.

The solubility of Rh in β -Zr was determined to be slightly in excess of 7a/o at 1000°C and slightly less than 7a/o at 780°C. In α -Zr the solubility of Rh was determined to be less than 0.5a/o at 600 and 780°C. At 0.5 and 1.0a/oRh the beta phase upon quenching from 1000°C transformed to martensitic alpha, designated α' , while in alloys containing from 2 to 4a/oRh, beta transformed to a metastable phase, whose crystal structure is tentatively considered to be isostructural with the ω phases commonly observed in Ti and Zr alloys. Retention of the beta phase was observed in the

⁽²¹³⁾ Rodgers, B. A. and Atkins, D. F., Trans. A.I.M.E. **203**, 1034 (1955).

⁽²¹⁴⁾ Hulm, J. K. and Blaughner, R. D., Phys. Rev. **123**, 1569 (1961).

40656

FIG. 186. T_c versus Composition for Zr-Nb and Zr-Nb-Rh Solid Solutions.

40655

FIG. 187. T_c versus Composition for Zr-Rh Alloys.

quenched Zr-7a/oRh alloy. In Figure 187 the transition temperatures for the alloys are plotted versus their nominal compositions. The three metastable structures have higher transition temperatures than pure α -Zr, $T_c = 0.546^\circ\text{K}$,⁽²¹⁵⁾ and, consistent with Raub and Andersen's⁽²¹⁶⁾ observations for cast alloys, there is a general increase in T_c with Rh concentration. In alloys quenched from 600°C , which contained the equilibrium phases, α -Zr plus the compound Zr_2Rh , transitions from the

⁽²¹⁵⁾ Eisenstein, J., *Revs. Modern Phys.* **26**, 277 (1954).

⁽²¹⁶⁾ Raub, Ch. J. and Andersen, C. A., *Zeit. Phys.* **175**, 105 (1963).

TABLE 71. SUPERCONDUCTING TRANSITION TEMPERATURES OF V-Tc ALLOYS

Alloy	$T_c(^{\circ}\text{K})$	$T_f(^{\circ}\text{K})$	$T_c - T_f(^{\circ}\text{K})$
V-10Tc	<1.7		
V-40Tc	<1.7		
V-50Tc	<1.7		
V-60Tc	7.80	7.52	0.28
	6.16	5.83	0.33
V-75Tc	8.82	8.40	0.42
	7.68	7.65	0.03
V-95Tc	10.3	9.04	1.26
	7.88	7.60	0.28
Tc	8.38	7.78	0.60

normal to the superconducting state occurred over broad temperature intervals, as wide as 4.4°K , indicating chemical inhomogeneity. Similar behavior has been observed for Zr-Rh alloys annealed at alpha phase temperatures by Buckel *et al.*⁽²¹⁷⁾ In Figure 187 the indicated T_c values for the two-phase alloys are the temperatures at which the onset of superconductivity was observed to occur. The fact that the T_c values are much higher than those of the metastable phases is associated with the presence in the alloys of the compound Zr_2Rh , which was determined to have a T_c of 10.8°K .

Compounds of Zirconium

Several intermediate phases containing zirconium were tested for superconductivity. Zr_2Ir , which is isostructural with Zr_2Rh (Strukturbericht type C16), was found to have a transition to superconductivity at 7.9°K . Lattice parameters determined for Zr_2Rh are $a_0 = 6.4937 \pm 0.0005\text{\AA}$, $c_0 = 5.6058 \pm 0.0006\text{\AA}$, $c/a = 0.8633$; for Zr_2Ir , $a_0 = 6.5115 \pm 0.0008\text{\AA}$, $c_0 = 5.6734 \pm 0.0011\text{\AA}$, $c/a = 0.8713$. Other compounds found to have normal conductivity down to 1.7°K are: Zr_2Pd (C11b), Zr_2Ag (C11b), ZrRu (B2), ZrRh , ZrPd and ZrAg .

V-Tc Alloys

Transition temperatures were determined for V-Tc alloys on which Van Ostenburg *et al* had earlier measured Knight shifts and magnetic susceptibilities.⁽²¹⁸⁾ The data are given in Table 71. T_c is the temperature at the onset of superconductivity and T_f the temperature at which the transition was complete. All the alloys containing up to 50a/oTc were bcc solid solutions and all were normally conducting down to 1.7°K . At 60, 75 and 95a/oTc, two transitions were observed, indicating the presence of more than one superconducting phase

⁽²¹⁷⁾ Buckel, W., Dummer, G., and Gey, W., *Phys. revue Materie*, **1**, 67 (1963).

⁽²¹⁸⁾ Van Ostenburg, D. O., Lam, D. J., Trapp, H. D. and MacLeod, D. E., *Phys. Rev.*, **123**, 1550-1554 (1962).

E. NUCLEAR MAGNETIC RESONANCE STUDIES

1. Vanadium-Aluminum Alloys (D. O. VAN OSTENBURG AND D. J. LAM)

Publication

D. O. Van Ostenburg, D. J. Lam, H. D. Trapp, D. W. Pracht and T. J. Rowland, *Nuclear Magnetic Resonance and Magnetic Susceptibilities of Alloys of V with Al*, Phys. Rev. **135**, A455 (1964).

The alloys investigated are the body-centered cubic substitutional solid solutions extending from pure V to V containing 40a/oAl. The Knight shifts of both V^{51} and Al^{27} were measured over a range of external magnetic fields and at various temperatures from -150 to 100°C . The V^{51} absorption line width was also measured as a function of composition, external magnetic field and temperature.

The Knight shift K is considered to derive from three distinct mechanisms: (1) The contribution K_s from the contact hyperfine interaction between the nuclear magnetic moment and the field caused by the spin magnetization of the s conduction electrons. (2) The contribution K_d due to exchange polarization of inner s electrons by the polarized electrons in the conduction bands and unfilled d shells. (3) The contribution K_{orb} due to the field induced at the nucleus coming from the orbital motion of electrons in partially filled degenerate bands. The susceptibility χ includes diamagnetic contributions from the ion cores χ_i and from the conduction electrons χ_L , and paramagnetic contributions from the electron spins and their orbital motion.

In the bcc solid solution region the V^{51} Knight shift increases slightly from 0.567% in pure V to 0.586% in the 40a/o alloy. The Al^{27} shift is negative, increasing from -0.038% at 5a/oAl to -0.031% at 40a/oAl. The magnetic susceptibility decreases monotonically from 287×10^{-6} emu/mole for pure V to 160×10^{-6} emu/mole for 35a/oAl in V. Through the use of low-temperature specific-heat data on this system it is concluded that essentially all of the V^{51} Knight shift is the result

of orbital paramagnetism and that this also accounts for most of the measured susceptibility in these alloys.

The rigid-band model, which appears to have some validity in the case of the body-centered cubic transition-element alloys is not directly applicable here if, as would be supposed, Al additions to V decrease the electron/atom ratio (e/a) in V-Al alloys. If one counted those electrons outside of closed shells as contributing to the band, V would have $e/a = 5$ and Al 3. A decrease in e/a would indicate a decrease in the Knight shift, and an increase in the electronic specific heat as for Ti-V alloys.⁽²¹⁹⁻²²⁰⁾ Such behavior is contrary to the experimental data for V-Al alloys. The proposed interpretation is consistent with recent specific-heat results on ternary Ti-V-Al and V-Cr-Al alloys⁽²²¹⁾ in which it is found that the electronic specific-heat coefficient γ is decreased by adding Al to Ti-V and V-Cr binary alloys. The decrease in γ appears to result from a decrease of density of states, which, in the simplest view, is unaccompanied by any change in E_F . That is, the density-of-states curve shrinks to smaller values while E_F remains fixed at a value determined by the transition-metal composition only. Since the s level in Al would correspond to an energy deep in the s - p band, the states at the Fermi surface are primarily p -like and thus make little or no positive contribution to K_{Al} , the Knight shift of the Al, via the contact interaction. The negative shift of the Al is probably caused by polarization of the core s electrons by the $3p$ electrons. For a more detailed description the reader is referred to the publication.

⁽²¹⁹⁾ Van Ostenburg, D. O., Lam, D. J., Trapp, H. D., and MacLeod, D. E., Phys. Rev. **128**, 1550 (1962).

⁽²²⁰⁾ Cheng, C. H., Gupta, K. P., Van Reuth, E. C., and Beck, P. A., Phys. Rev. **126**, 2030 (1962).

⁽²²¹⁾ Pessall, N., Gupta, K. P., Cheng, C. H., and Beck, P. A., J. Phys. Chem. Solids **25**, 993 (1964).

2. Vanadium-Hydrogen Alloys (D. O. VAN OSTENBURG AND D. WESTLAKE)

A study of the vanadium-hydrogen system was recently initiated in order to study the relationships between the solid solution and hydride phases. The composition range of interest is from pure vanadium up to about 17a/oH in V. A preliminary investigation of V⁵¹ in the V-17a/oH and V-9a/oH systems shows that when both phases are present two nmr absorption lines are present. These arise from the fact that the electronic structure about vanadium is different in the solid solution and hydride phase. As the temperature is raised

e.g. so that only the single solid-solution phase is present, a single absorption line remains. In the 17 and 9a/o samples the phase boundary was determined to be at $96 \pm 2^\circ\text{C}$ and $52 \pm 2^\circ\text{C}$ respectively. This differs from that quoted in the literature⁽²²²⁾ by several degrees. This work is still in its early stages.

⁽²²²⁾ *The Thermodynamic Properties of the Systems Nb-H, V-H and Ta-H*, E. Veleckis Thesis, Illinois Institute of Technology, January 1960.

3. Vanadium-Techetium Alloys (D. O. VAN OSTENBURG, D. J. LAM AND J. J. SPOKAS*)

Publication

J. J. Spokas, D. J. Lam and D. O. Van Ostenburg, *Nuclear Spin-Lattice Relaxation of V⁵¹ and Tc⁹⁹ in V-Tc Alloys*, Bull. Am. Phys. Soc. **9**, 621 (1964) B5.

To illuminate further the electronic properties of transition metals and their alloys, the pulsed nmr spectrometer described below has been used to study nuclear-spin-lattice relaxation times, T_1 , in these alloy systems. This section reports the T_1 measurements of V⁵¹ and Tc⁹⁹ in the V-Tc alloys.

The V-Tc system forms a stable bcc solid solution from pure V to 60a/oTc in V. Approximately 10a/oV can be dissolved in hcp Tc and the two solid solutions exist in a two-phase field between 60 and 90a/oTc. There is a CsCl ordered bcc structure at the equiatomic composition. Knight shift and magnetic susceptibility measurements previously have been made in these same alloys.⁽²¹⁹⁾

In metals and alloys the most important relaxation path for nuclear spins is via the conduction electrons. This relaxation mechanism is manifested by means of its, $T_1T = \text{const.}$, temperature dependence. For transition metals with unfilled d shells the relaxation rate can be partitioned in much the same manner as the magnetic susceptibility and Knight shift. Thus, the measured relaxation rate is the sum of the following contributions:

$$(T_1T)_{\text{meas.}}^{-1} = (T_1T_s^{-1} + (T_1T)_{\text{orb.}}^{-1} + (T_1T)_{\text{dip.}}^{-1} + (T_1T)_{\text{c.p.}}^{-1} + (T_1T)_q^{-1}.$$

$(T_1T)_s^{-1}$ is the contact term. This arises through the interaction of the s electrons with the nucleus and is

40330

FIG. 188. NMR Relaxation Times in V-Tc, V-Cr and V-Fe Alloys and the Density of States Curve for the V-Cr system.

directly related to the square of the s density of electron states at the Fermi surface. $(T_1T)_{\text{orb.}}^{-1}$ is the relaxation via the orbital motion of the electrons and is directly related to the square of the d density of state at the Fermi surface. $(T_1T)_{\text{dip.}}^{-1}$ represents the relaxation due to dipolar interaction of the nuclei with the conduction electrons. Obata⁽²²³⁾ has shown that this rate is much smaller than that from the orbital effects except for rather special cases. It shall thus be neglected here. $(T_1T)_q^{-1}$ depicts the relaxation rate due to electric quadrupole interactions between the nuclei and the non- s electrons. This also can be shown to be negligible compared to the other terms. Finally, $(T_1T)_{\text{c.p.}}^{-1}$ comes from relaxation induced by core polarization. Yafet and Jaccarino⁽²²⁴⁾ discuss this term and state that in van

⁽²²³⁾ Obata, Y., J. Phys. Soc. Japan **18**, 1020 (1963).

⁽²²⁴⁾ Yafet, Y., and Jaccarino, V., Phys. Rev. **133**, A1630 (1964).

* Consultant to the Metallurgy Division, St. Procopius College.

nam this term should be small compared with the orbital one.

For a discussion of the bcc region of the V-Tc alloys it is assumed that the contact and orbital terms are predominant. Since in transition metals the d density of states is larger than that of the s electrons, it is expected that of the two the orbital term will be predominant. A plot of $(T_1T)^{-1/2}$ vs. e/a should then follow the d density of state curve vs. e/a . Figure 188 is a plot of $(T_1T)^{-1/2}$ for three transition metal alloy systems.⁽²²⁵⁻²²⁶⁾ It is at once evident that such is the case. The density

⁽²²⁵⁾ Butterworth, J., Proc. Phys. Soc. (London) **83**, 71 (1964).

⁽²²⁶⁾ Masuda, Y., and Okamura, K., J. Phys. Soc. Japan **19**, 1249 (1964).

of states for V-Cr is shown but this is similar for V-Fe⁽²²⁷⁾ in the non-ferromagnetic bcc region, and allegedly for V-Tc in the bcc region. If the density of states were accurately known for the V-Tc alloys, a more detailed analysis could be made. Thus far, the experimental results show that the controlling influence determining the composition dependence is the composition dependence of the density of states in the d band. The rigid band approximation seems valid as an aid in the determination of the composition dependence of spin-lattice-relaxation times in transition-transition metal alloys.

⁽²²⁷⁾ Cheng, C. H., Wei, C. T., and Beck, P. A., Phys. Rev. **120**, 426 (1960).

4. Actinide Metals and Compounds (D. O. VAN OSTENBURG, D. J. LAM AND M. BRODSKY)

Publication

D. O. Van Ostenburg, D. J. Lam, M. B. Brodsky and H. D. Trapp, *NMR in PuAl₂*, Bull. Am. Phys. Soc. **9**, 261 (1964) GE11.

PuAl₂

Work on this system has continued since the 1963 Annual Summary. As stated in that report the Al²⁷ resonance line consists of a central line and four satellites. The satellite spacings are such as to yield a quadrupole coupling constant in the vicinity of 3.8 Mc/sec. The width of the central line is composed of contributions from the second order quadrupole interaction, the anisotropic Knight shift, the dipolar interaction, etc. Studies of the central line versus field at room temperature yield an isotropic Knight shift of 0.2% and an anisotropic Knight shift of -0.02%. The second order

quadrupole effects on the central line yield a coupling constant in agreement with that determined from the satellite spacing. This work will be continued on ternary systems in which U replaces the Pu up to the compound UAl₂.

Neptunium Metal

A search for the Np²³⁷ nuclear resonance signal in metallic Np was initiated. This nucleus is believed to have a nuclear spin of 5/2 and a magnetic moment of 6 ± 2.5 mm. Thus an absorption signal should occur at about 20 Mc/sec in a field of 10,000 Oe. Measurements were made over a range of field strengths and frequencies covering possible nuclear moments ranging from 3.39 to 8.8 mm. No signal was detected. Later it was learned that the samples contained magnetic impurities. Consequently, pure metallic specimens are in preparation as well as several compounds.

5. Titanium Metal (D. O. VAN OSTENBURG)

Titanium contains two isotopes Ti⁴⁷ and Ti⁴⁹ of natural abundance 7.75% and 5.51% respectively which are suitable for nmr research. Both species are easily detectable in liquid TiCl₄. A search was made in natural titanium metal for these isotopes with no signal detected. Consequently, a sample enriched with Ti⁴⁹ was obtained from Oak Ridge in the form of thin foils. A sample was prepared by stacking the foils upon one another insulated with Saran wrap. A search was made

by fixing the frequency at ~2.4 Mc/sec and varying the field from about zero to 15 kOe. Again no signal detected. The failure to observe a signal implies that there are strong quadrupolar interactions associated with the Ti nuclei and the hexagonal lattice producing a resonance line too broad to be detected. The search will be continued in both the enriched pure hexagonal Ti and in cubic alloys containing the enriched Ti.

6. Pulsed NMR Apparatus (J. J. SPOKAS,* D. J. LAM AND D. O. VAN OSTENBURG)

A coherent pulsed nuclear resonance apparatus has been designed and constructed. Although this apparatus has been in use in measuring nuclear spin lattice relaxation times for essentially the entire year, a number of significant additions and improvements have been made to it during the past year. Notable among these are a digital pulse timer, a high-power, broad-band, radio frequency bridge, a low temperature probe, and three broad band-pass rapid recovery radio-frequency receivers operating at the frequencies of 4, 12, and 18 Mc/sec respectively.

The pulse timer can provide all the special timing sequences that are needed in pulsed-type nuclear magnetic resonance experiments. These include two- and three-pulse sequences for thermal and transverse relaxation measurements via Bloch decays, spin echoes, and stimulated echoes. There also is a provision for a train of pulses like that needed to observe transverse relaxation by means of the Carr-Purcell technique. The timer uses the same crystal controlled oscillator as that from which the intense RF pulses used to excite the sample are derived. Consequently, the timing pulses are phase

locked to the RF reference; but more than that, the countdown circuits have been designed to maintain a fixed phase relationship between the timing pulses and the RF reference even as the pulse spacings are varied. This feature is particularly important when intense short RF exciting pulses, which consist of little more than a build-up and decay transient, are used. The great accuracy achieved in our time measurements with this unit essentially removes measurement of time from consideration in the accuracy of relaxation experiments.

A low-temperature probe designed to allow samples to be inserted through a pair of insulated concentric metal tubes has been built and used in measurements carried out at 77°K and 4.2°K. The concentric tubes also serve as a co-axial transmission line through which the intense RF exciting pulses reach the sample. Attempts to insert a new sample while the temperature of the probe is kept low have been frustrated by the samples freezing fast to the insertion tube. A modified probe wherein a sample can be vacuum outgassed before lowering to the cold end of the probe is being built. This should circumvent the freezing problem. With the recent completion of three RF receivers, the system allows a choice of four operating frequencies.

* Consultant to the Metallurgy Division. St. Procopius College.

F. X-RAY AND NEUTRON DIFFRACTION STUDIES

1. Neutron Diffraction Instrumentation (M. H. MUELLER, L. HEATON, R. L. HITTERMAN, AND S. S. SIDHU)

Neutron Spectrometer I

During the past year the electronic equipment for Neutron Spectrometer I has been completely replaced. The original electronic equipment had been in use on Spectrometer I since the initial installation of the instrument in 1954 at the CP-5 Reactor. This spectrometer is operating as a basic powder unit with the provision of typewrite print-out of both angle and intensity together with the option of strip chart and/or x - y recorder plotting of the data. The electronic circuitry on this new unit is almost entirely solid stated.

Neutron Spectrometer II

Several auxiliary instruments are in various stages of development for use on this instrument. A cryostat has been designed and constructed to accommodate various types of samples; such as, powder, single crystal or solidified gas, and to hold these samples at controlled temperatures between helium temperature and room temperature. This is being carried out with helium-exchange gas and an electronic servo-controlled heater. This control has been built and is currently being tested by an outside vendor. Provision is made for removing and inserting samples without breaking the jacketed vacuum. An elevating mechanism and goniometer, MY-2690 and MY-2672 respectively, have been constructed for mounting and aligning the cryostat on Spectrometer II. The goniometer has been constructed with sufficiently large arcs, 11.4 cm from top of goniometer to center of radius, so that it should be possible to accurately align a single crystal. This cryostat arrangement allows the collection of zero-level intensities only, however. In order to obtain upper levels without tilting the cryostat, provision has been made to rotate the counter detector in a vertical plane about the center of the instrument. This then permits normal beam operation but requires the calculation of appropriate angles for setting of the detector with respect to the sample. Drawings for this normal beam technique are shown in shop drawings CS-2397-21.

This technique has the disadvantage of limiting the reciprocal lattice points available without remounting

the crystal. Initial trials have also indicated that a θ - 2θ scan does not always give correct integrated intensities. The errors appear to be greater the higher the azimuthal angle (upper levels) and the higher the counter arm angle. To date the maximum error has been approximately 7%—that is, the integrated intensity from the normal beam technique is this much lower than that obtained from the orienter technique. In spite of these difficulties it should be possible to obtain intensity data, which may require an instrumental correction, by using the cryostat with the normal beam technique.

Since the above technique has inherent instrumental correction, we have been concerned for some time with the design of a cryostat in which we could orient a crystal with ± 0.01 precision about two axes—the φ and χ axes of the orienter technique. This would make it possible to collect all of the data with the detector at the zero level and would thus simplify corrections and make much more of the reciprocal lattice available. The design of the Cryo-orienter is now in the final stage. We have chosen to move the entire cryostat, which is mounted on a circle, to accomplish the two-angle motion. This eliminates small mechanical motions at low temperatures with attendant lubrication problems. As a bonus in this design we have found that we can add a fourth circle motion to the crystal and thus rotate about a perpendicular to the diffraction plane. This is indeed very useful in analyzing for the double Bragg scatter of neutrons in single crystals. All of the motions on the instrument are basic one degree per revolution of the drive shaft; hence, it will be easy to use automatic program equipment.

Neutron Diffractometer I

The automatic programing equipment with card input and output has been installed on Diffractometer I. Since this unit is basically for the collection of three-dimensional intensity data the four angles, φ , χ , 2θ and ω are set up automatically before scanning over the peak. Although the equipment has been working, there are some debugging problems.

2. Crystallographic Computer Programs (L. HEATON AND M. H. MUELLER)

Since the CDC-3600 is now the main production computer at the Laboratory, we have converted all of the crystallographic programs over to its use. In some cases this has been easy where they were written in Fortran; for example the Busing, Martin, Levy least-squares and error-function programs⁽²²⁸⁾ have been adapted to the 3600. In other cases the programs have been re-written. The actual programing has been carried out by J. Gvildys of the Applied Math Division.

Lattice Constant Least Squares Program, B-106

Several years ago a computer program (MET-124) was written to carry out a least-squares method of obtaining the lattice constants (unit cell edges) of crystal systems with orthorhombic or higher symmetry. The program provided for using as many as three separate correction terms for eccentricity, absorption, divergence, etc.; however, one, two, three, or none at all, could be used. The exact trigonometric function or functions used in these correction terms could be selected from several existing in the program; however, the *particular type* correction term or its physical significance (eccentricity, absorption, etc.) is less important than whether the chosen term or terms satisfactorily remove the systematic errors. The degree of the removal of these errors could be judged by a plot of 2θ versus the V 's (difference between observed and calculated $\sin^2 \theta$) after the solution had been carried out. If the systematic errors were satisfactorily compensated, the plot of V 's would have random deviation from a horizontal straight line. If desired, a weighting factor could also be used for each reflection which could include an observation weight or trigonometric function or both. In order to carry out the approach designated above it is necessary to calculate a number of least-squares solutions with a given set of data and a variety of combinations of correction terms and weights in order to find the best solution. B-106 is a current revision of the above described program (MET-124). This revision, which is based on the same approach, also includes the triclinic and monoclinic systems (cell edges and angles). The program has been written in

Fortran, does not require input starting parameters, and refines in a single cycle without reiteration. We intend to write a full ANL report to replace the description of the former program (MET-124), which appeared as ANL-6176 (now depleted).

The program has been tried out on all crystal systems including monoclinic and triclinic. The results obtained on a triclinic test are compared with National Bureau of Standards data on sodium tetrametaphosphate tetrahydrate⁽²²⁹⁾ as shown below.

	N.B.S.	B-106
a	6.653 Å	6.654 Å $\pm$ 0.002
b	9.577 Å	9.578 Å $\pm$ 0.003
c	6.321 Å	6.319 Å $\pm$ 0.002
α	103.40°	103.38° $\pm$ 0.02
β	106.98°	107.00° $\pm$ 0.02
γ	93.29°	93.28° $\pm$ 0.01

The above result, from the B-106 program, was obtained by least squaring only without the application of a systematic term or weighting.

Fourier Program, B-114

This program performs two and three-dimensional Fourier summations for crystallographic purposes to produce Patterson, electron-density, and neutron-scattering-density patterns, when Fourier coefficients are derived from X-ray and neutron diffraction data. B-114 is a re-edited and modified version of the Sly-Shoemaker program⁽²³⁰⁾ and is written in Fortran 63. The program input is simplified by removing all modification and patching cards and all sense switch requirements. Many of the above input instructions are performed automatically when the user supplies the space group number as listed in the International Tables.⁽²³¹⁾ Thus far, input is based on space groups 1-74 with the intention of adding the others. In this program the user is dealing with the actual diffraction coordinates and not with the machine coordinates.

⁽²²⁹⁾ Swanson, H. E., Morris, M. C., Stinchfield, R. P., and Evans, E. H., *Standard X-ray Diffraction Powder Patterns*, U.S. Dept. of Commerce, National Bureau of Standards, Monograph 25, 1963.

⁽²³⁰⁾ Sly, W. G., and Shoemaker, D. P., *MIFRI, Two- and Three-Dimensional Crystallographic Fourier Summation Program for the IBM-704 Computer*, MIT 6-1-1960.

⁽²³¹⁾ *International Tables for X-ray Crystallography*, Vol. I, The Kynoch Press, Birmingham, England, 1952.

⁽²²⁸⁾ Busing, W. R., Martin, K. O., and Levy, H. A., *A Fortran Crystallographic Least-Squares Program*, ORNL-305, 1964 and *A Fortran Crystallographic Function and Error Program*, ORNL-306, 1964.

3. Neutron Diffraction Structure Determination of Uranyl Nitrate Hexahydrate (J. C. TAYLOR* AND M. H. MUELLER)

39358

FIG. 189. Configuration about Uranium Atom.

In the last Annual Report⁽²³²⁾ we pointed out that earlier infra-red and X-ray investigations carried out on this compound had left doubts as to the basic structure and naturally had given no indication of hydrogen positions. Therefore, we undertook a neutron study to resolve the basic structure and also felt it would present a challenge to determine this structure by single crystal means since more than 40% of the atoms were hydrogens. We felt this could pose a problem due to the large spin scatter due to hydrogen and might require the substitution of deuterium. This was found unnecessary, however, and the determination has been completed.

The structure is orthorhombic with $a = 13.197 \pm 0.003 \text{ \AA}$, $b = 8.035 \pm 0.002 \text{ \AA}$, $c = 11.467 \pm 0.003 \text{ \AA}$ and space group $\text{Cmc}2_1$. Intensities of 1136 independent reflections with 2θ less than 105° were obtained with $\lambda = 1.065 \text{ \AA}$. The structure was solved from the three-dimensional neutron Patterson and Fourier syntheses and refined by full-matrix least squares to an R factor of 4.0% with statistical weighting of the data.

A near-planar hexagon of coordinated oxygens surrounds the uranyl group equatorially, as shown in Fig. 189. The uranyl grouping is nearly linear but unsymmetrical with regard to the $\text{U}-\text{O}$ bond lengths. Four of the coordinated oxygens come from two non-equivalent bidentate nitrate groups and the other two are equivalent water oxygens. In the two nitrate groups,

39361

FIG. 190. Hydrogen Bonding.

39357

FIG. 191. Water Molecule Sheets.

the $\text{N}-\text{O}$ bonds involving coordinated oxygens are 0.06 and 0.03 Å longer than the respective $\text{N}-\text{O}$ bonds involving the non-coordinated oxygens. Also, asymmetry is found in the $\text{O}-\text{N}-\text{O}$ bond angles of the

* Resident Research Associate from University of New South Wales, Australia.

⁽²³²⁾ Annual Report for 1963, Metallurgy Division, ANL-6868, p. 334.

nitrate groups. The hydrogen bonds are relatively weak; the O (water)—O (water) bonds lie in the range 2.68–2.75 Å while the O (water)—O (nitrate) hydrogen bonds are of length 2.93 and 2.99 Å (Fig. 190). The water molecules associate into sheets perpendicular to the *a*-axis (Fig. 191).

A report of a two-dimensional neutron study of this compound by Makarov and Melik'yan⁽²³³⁾ recently appeared in Chemical Abstracts (September 14, 1964). These authors gave a near-complete set of hydrogen coordinates which, however, showed complete disagree-

ment with our results. Makarov and Melik'yan base their analysis on the coordinates proposed by Fleming and Lynton⁽²³⁴⁾ in an X-ray study, using one of the two possibilities for the water oxygens suggested by Fleming and Lynton. These water sites were shown by our refinement to be incorrect and thus the disagreement between the hydrogen coordinates of Makarov and Melik'yan and those of the present investigation is not surprising.

It is our present plan to continue the study of uranyl hydrates by investigating $\text{UO}_2(\text{NO}_3) \cdot 3\text{H}_2\text{O}$ and $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$. Crystals of both compounds have been prepared.

⁽²³³⁾ Makarov, E. S., and Melik'yan, A. A., *Proceedings of the Working Conference on Slow Neutron Physics*, held December 7–12, 1961. AEC-tr-5734 issued May, 1963.

⁽²³⁴⁾ Fleming, J. E., and Lynton, H., *Chem. and Ind.*, **79**, 1416 (1960).

4. Structure Determination of Manganese Silicide (M. H. MUELLER AND H. W. KNOTT)

Very small single crystals of a manganese-silicon phase have been obtained from an arc-melted button of nominal composition MnSi_2 . Since some free silicon is always present as a second phase, it would seem as if the manganese-silicon phase has a composition somewhere between $\text{MnSi}_{1.5}$ and MnSi_2 . X-ray diffraction powder patterns indicate a tetragonal cell with $a_0 = 5.506$ Å and $c_0 = 17.522$ Å. Boren⁽²³⁵⁾ in 1933 found a tetragonal MnSi_2 phase with $a_0 = 5.524$ Å and $c_0 = 17.46$ Å and 48 atoms per unit cell. In a current investigation, Schwomma⁽²³⁶⁾ indicates that the composition of this phase is approximately $\text{MnSi}_{1.7}$ and that the

cell is tetragonal with a_0 about 5.51 Å but c_0 about 48.13 Å.

Approximately 1700 reflections have been examined by X-ray diffraction by using a single crystal orienter on an X-ray diffractometer. Density determinations indicate 40 to 48 atoms per unit cell. Crystallographic computer programs involving Patterson, Fourier and least-squares techniques are now being used to attempt to determine the exact composition, space group, and atomic positions in the unit cell.

This structure seems to belong to the same family as several other bi-metallic compounds whose structures are as yet also not completely solved, one such compound is TeSi_2 as reported by J. Darby and J. W. Downey.⁽²³⁷⁾

⁽²³⁷⁾ Private Communication.

⁽²³⁵⁾ Boren, B., Kemi, Arkio, *Mineral Geol.*, **11A**, 1933, p. 10.

⁽²³⁶⁾ Schwomma, O., Nowotny, H., and Wittman, A., *Monatshfte Fur Chemie*, **94**, 1963, p. 681.

5. Atomic Distributions in Liquid Binary Alloys (L. HEATON AND R. BUSCHERT*)

An attempt is being made to determine the distributions of like atoms about themselves and about unlike atoms in a liquid binary alloy by using the method suggested by Keating.⁽²³⁸⁾ This approach requires that the scattering curves of both neutrons and

X-rays by the liquid alloy be observed. Since the relative scattering amplitudes of the component atoms are different for X-rays and neutrons, one can in principle derive the component distributions from the two scattering curves.

The binary alloy chosen for this investigation is $50a/o\text{NaK}$ because it offers the advantages of a melt-

* Purdue University, West Lafayette, Indiana.

⁽²³⁸⁾ Keating, D. T., *J. Appl. Phys.*, **33**, 923 (1963).

...g point slightly below room temperature, good transmission for both X-rays and neutrons, and the neutron scattering amplitudes for both components, Na and K, are essentially the same. Scattering curves for both neutrons and X-rays by NaK have been collected, corrected and Fourier inverted to obtain radial pair

distributions. These radial distributions indicated that the scattering data were of sufficient quality to proceed. At the present, various means of normalizing the two independent (neutron and X-ray) sets of data to compatible units are being investigated.

6. Crystal Structure of YD_3 (M. H. MUELLER, L. HEATON AND S. S. SIDHU)

X-ray diffraction powder patterns have indicated that YD_3 is hexagonal with an $a_0 = 3.659\text{\AA}$ and $c_0 = 6.586\text{\AA}$. A neutron powder pattern of this compound shows at least two extra reflections between the (003) and (110) indicating that the unit cell described above is not correct. Spacing calculations have indicated that

the correct unit cell may involve a doubling of the a_0 or c_0 with the better agreement shown by the former. Intensity calculations for the neutron pattern based on the small cell have also shown considerable discrepancy. Further work is in progress on this structure.

7. Neutron and X-ray Diffraction Study of LiRh (S. S. SIDHU, K. D. ANDERSON AND D. D. ZAUBERIS)

Lithium and rhodium form a Li-Rh binary alloy at approximately 1 to 1 molar ratio. The X-ray scattering by lithium is small as compared with that of rhodium, but the coherent nuclear scattering amplitudes of the two nuclei are comparable. Therefore, an investigation of the alloy was made by the combined neutron and X-ray diffraction techniques to determine unambiguously the positions of lithium atoms in the structure. It was found that the unit cell is hexagonal. Space group $P\bar{6}$; $a_0 = 2.649 \pm 0.003\text{\AA}$, $c_0 = 4.357 \pm 0.002\text{\AA}$, $c = 1.645$, with one Rh at (0,0,0) and one Li at $(\frac{1}{3}, \frac{2}{3}, \frac{1}{2})$ and calculated density $\rho = 6.88\text{ g.cm}^{-3}$. The interatomic distances are: Rh-Rh = $2.649\text{\AA}$, Li-Li = $2.649\text{\AA}$ and

Rh-Li = $2.663\text{\AA}$. A redetermination of the coherent nuclear scattering amplitude of rhodium was made in connection with this investigation and was found to be, $b_{\text{Rh}} = 0.591 \times 10^{-12} \pm 0.004\text{ cm}$.

The most interesting feature of the structure was the presence of (001), (003), (111), (113) and (005) reflections in both the neutron and the X-ray diffraction patterns. These reflections resulted only from the occupation of preferred positions by each type of atom in the unit cell, such as Rh atoms in one layer and Li in the other, the layers alternating along c -axis at $c_0/2$ distance apart.

8. Neutron Diffraction Study of Chemical Order-Disorder in $PtMn_3$ (S. S. SIDHU, K. D. ANDERSON AND D. D. ZAUBERIS)

The crystal structure of $PtMn_3$ is cubic and similar to that of $AuCu_3$, which has been extensively used to study order-disorder phenomena for this type of structure. A neutron diffraction study of the chemical order-disorder in $PtMn_3$ was made by utilizing the nuclear properties of Mn and Pt nuclei. The coherent nuclear scattering amplitude of manganese is, $b_{\text{Mn}} = -0.36 \times 10^{-12}\text{ cm}$ and of platinum, $b'' = 0.95 \times 10^{-12}\text{ cm}$. In a disordered crystal structure of the stoichiometric $PtMn_3$ alloy, the manganese atoms scatter thermal

neutrons 180° out of phase with those of platinum. As a result the structure becomes a nuclear null-matrix and no diffraction peaks appear in its neutron pattern. However, when even a partial ordering takes place in the structure, diffraction peaks appear. Since these reflections result only when ordering takes place and their intensities depend upon the degree of ordering, they permit a precise determination of the disorder parameter.

For example, if the lattice sites in the unit cell of

TABLE 72. OCCUPANCY OF LATTICE SITES IN UNIT CELL

	0,0,0	$\frac{1}{2}, \frac{1}{2}, 0; \frac{1}{2}, 0, \frac{1}{2}; 0, \frac{1}{2}, \frac{1}{2}$	Total
Pt	$1-\gamma$	γ	1
Mn	γ	$3-\gamma$	3

Note: where γ = fraction of Pt atoms that change sites.

106-8117

FIG. 192. Structure Factor $|F|$ as a Function of Disorder Parameter (γ).

PtMn₃ were occupied as given in Table 72, then structure factor for the partly ordered alloy is:

$$F_{hkl} = \{(1 - \gamma)b_{\text{Pt}} + \gamma b_{\text{Mn}}\} + \frac{1}{3}\{\gamma b_{\text{Pt}} + (3 - \gamma)b_{\text{Mn}}\} \{e^{\pi i(h+k)} + e^{\pi i(h+l)} + e^{\pi i(k+l)}\} \quad (1)$$

For mixed Miller indices planes the above expression becomes:

$$F_{hkl} = \left(1 - \frac{4}{3}\gamma\right)(b_{\text{Pt}} - b_{\text{Mn}}) \quad (2)$$

For a completely ordered sample, $\gamma = 0$, and

$$F_{hkl} = b_{\text{Pt}} - b_{\text{Mn}} \quad (3)$$

and for a completely disordered sample, $\gamma = 0$, and

$$F_{hkl} = 0 \quad (4)$$

The F_{hkl} values as a function of γ are given in Fig. 192.

The experimental values of F_{hkl} factors for the disordered and the ordered samples of PtMn₃ were obtained from measured integrated intensities of a number of diffraction peaks in the neutron pattern of each sample and by calculating $F_{hkl}(0)$ for $\sin \theta/\lambda = 0$. Numerical value of the disorder parameter, γ , for a sample that appeared to be disordered when examined with X-rays, but partly ordered when examined with neutrons, was 0.667. This means that the sample was 11 percent ordered. For an ordered sample the value for γ was zero. These values are indicated in Fig. 192.

9. Magnetic Structure in PtMn₃ (S. S. SIDHU, K. D. ANDERSON AND D. D. ZAUBERIS)

The crystal structure of PtMn₃ is cubic with 4 atoms per chemical unit cell. It orders with the platinum atom at the corner position and the manganese atoms at the face-centered positions. Neutron diffraction patterns made of a fully ordered sample showed that PtMn₃ exhibits two types of spin arrangements. The unit cell of one is the same as the chemical cell and has the magnetic moments aligned oppositely in alternating layers perpendicular to (001) direction. The Néel temperature of this form is 115°C. The second spin arrangement is associated with a tetragonal cell, which is related to the chemical cell by:

$$A_0 = \sqrt{2} a_0; \quad C_0 = 2 a_0; \quad c = \sqrt{2} a_0$$

and

$$H = h + k; \quad K = h - k; \quad L = 2l$$

where the lattice parameters and the Miller indices in capital letters are those of the tetragonal cell. The magnetic moment alignment in the tetragonal cell is also antiferromagnetic. The spin transformation from one arrangement to the other is such that the degree of alignment in the tetragonal cell is proportional to that of disalignment in the chemical cell. The Néel temperature of the second form of arrangement is approximately 250°C.

Neutron diffraction measurements made of an approximately eleven percent ordered sample of PtMn₃ showed that it also exhibits both types of spin arrangements. The intensities of magnetic peaks, however, are proportional to the degree of chemical ordering, indicating definitely the dependence of magnetic ordering on the chemical ordering in the sample.

10. Chemical Order in $\text{Mn}_{1.75}\text{Co}_{2.25}\text{C}_{0.93}$ Carbide (S. S. SIDHU, K. D. ANDERSON, D. D. ZAUBERIS, AND F. P. CAMPOS)

06-7793

FIG. 193. Diffraction Patterns of $(\text{MnCo})_4\text{C}$. (a) Filtered Fe Radiation, (b) Neutron $\lambda = 1.08\text{\AA}$.TABLE 73. STRUCTURE FACTORS FOR ORDERED $\text{Mn}_{1.75}\text{Co}_{2.25}\text{C}_{0.93}$

Miller indices	X-rays*	Neutrons*
	F_{hkl}	$F_{hkl} \times 10^{12} \text{ cm}$
hkl all odd	$1.75f_{\text{Mn}} + 2.25f_{\text{Co}} - 0.93f_{\text{C}}$	$-b_{\text{C}}$
hkl all even	$1.75f_{\text{Mn}} + 2.25f_{\text{Co}} + 0.93f_{\text{C}}$	$+b_{\text{C}}$
Mixed indices		
$h + k + l$ odd	$\chi(f_{\text{Mn}} - f_{\text{Co}}) - 0.93f_{\text{C}}$	$\chi(b_{\text{Mn}} - b_{\text{Co}}) - 0.93b_{\text{C}}$
$h + k + l$ even	$\chi(f_{\text{Mn}} - f_{\text{Co}}) + 0.93f_{\text{C}}$	$\chi(b_{\text{Mn}} - b_{\text{Co}}) + 0.93b_{\text{C}}$

Note*: f is the X-ray scattering factor, b is the nuclear scattering amplitude and χ is a constant of the ordering of the metal atoms.

A carbide of composition $\text{Mn}_{1.75}\text{Co}_{2.25}\text{C}_{0.93}$ was prepared from a manganese-cobalt alloy that was practically a nuclear null-matrix. Its crystal structure is of Mn_4N -type⁽²³⁹⁾ (C2) with the metal atoms at: $0\ 0\ 0$; $\frac{1}{2}\ \frac{1}{2}\ 0$; $\frac{1}{2}\ 0\ \frac{1}{2}$; $0\ \frac{1}{2}\ \frac{1}{2}$, and the carbon atom at: $\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$ position. The lattice parameter is $3.786\text{\AA}$ and the nearest

distance of approach of metal atoms is $2.675\text{\AA}$. This structure has certain unique properties. While the metal atoms occupy random positions in the lattice of the alloy, they are ordered in the structure of the carbide. As seen in Fig. 193 the X-ray diffraction lines from mixed Miller indices planes for which $h + k + l$ is even, that is, (110) , (211) , (310) , (321) , etc., are either absent or very weak as compared with the lines for which $h + k + l$ is odd. This would mean the $\chi(f_{\text{Mn}} - f_{\text{Co}})$ for these reflections, as given in Table 73 is of the order of $0.93f_{\text{C}}$, such that the structure factor, $F_{hkl} = \chi(f_{\text{Mn}} - f_{\text{Co}}) + 0.93f_{\text{C}} \approx 0$. The absence of $h + k + l = \text{even}$ lines and the relative intensities of $h + k + l = \text{odd}$ lines lend to determinations of (1) the type of order the metal atoms take and (2) the valency of the carbon atom.

In the neutron pattern the diffraction peaks for both the $h + k + l = \text{odd}$ and the $h + k + l = \text{even}$ planes appear. The relative intensities of the former are markedly greater than those of the latter. This again indicates that the metal atoms in the carbide are ordered. The tentative results are as follows:

	$(0\ 0\ 0)$	$(\frac{1}{2}\ \frac{1}{2}\ 0)$; $(\frac{1}{2}\ 0\ \frac{1}{2})$; $(0\ \frac{1}{2}\ \frac{1}{2})$	$(\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2})$	Total
Mn	0.81	0.94		1.75
Co	0.19	2.06		2.25
C			0.93	0.93

⁽²³⁹⁾ Taki, W. J., Heikes, R. R., and Shirane, G., Phys. Rev. 5, 1893-1897 (1962).

11. Ordering in FeV (M. H. MUELLER AND L. HEATON)

A neutron diffraction pattern of 36 % Fe-V alloy has been made. It can be indexed on the basis of a cubic unit cell with an approximate $a_0 = 2.95\text{\AA}$ which is in agreement with the value reported by X-ray measurements. In the neutron pattern, however, all primitive reflections appear with considerable strength indicating

that a CsCl-type ordering of the Fe and V is indeed present. Work is in progress in obtaining patterns of 25 and 15a/o Fe. Intensities will be analyzed for evidence of degree of order; however, the cast ingots now being used as samples may give some orientation problems.

G. CORROSION RESEARCH

1. Mechanism of Aqueous Corrosion of 1100 Aluminum (S. MORI AND R. E. LOESS)

Kinetics

Experiments have been performed to determine and compare the logarithmic corrosion of 1100 aluminum in distilled water for the exposure interval 4–45 days. Method and materials were chosen to be as nearly identical as possible. At 50 and 70°C, with and without oxygen (helium-saturated), the logarithmic rate constants and "intercepts" (extrapolated amounts of corrosion at one day) are given in Table 74, as averages of four specimens.

Increasing temperature and oxygen content of the water are seen consistently to increase the rate constant. The intercept has been increased by an increase in temperature, but decreased by an increase in oxygen content.

According to the rate expression previously derived,⁽²⁴⁰⁾ there are three basic constants combined in the logarithmic rate constant, as follows:

$$\frac{s}{c(e^{s/b} - 1)}$$

where s is the thickness at which locally growing oxide cracks, b is the rate constant for the growth of uncracked film, and c is related to the permeability of cracked oxide. Using some assumptions concerning the variation in the basic constants with temperature and oxygen content, we had hoped that results of the four tests in Table 74 would make possible the determination of s , b and c . Unfortunately, simultaneous solution of the expressions resulted in loss of significance in differences between nearly equal experimental constants. It is possible only to say that b is less than the corrosion rate constant, but not less than one-tenth of it. There are corresponding limitations to the values of the other constants. Apparently it will be necessary to find another method of evaluating the constants that seem basic to the mechanism.

Corrosion Product Lost

The amount of aluminum lost to the solution from two separate specimens corroding in 70°C oxygenated water was determined at various times over a 99 day $\pm$ period. Reproducibility was reasonably good.

Results approximated two straight lines when plotted against the logarithm of time (Figure 194). For the specimen plotted, the slope was 0.20 mg/dm²-cycle for the first six days and 0.48 mg/dm²-cycle after this time, while the metal corrosion rate constant was 3.43 mg/dm²-cycle. The ratio of corrosion rate to dissolution rate was about seven after the six-day period, and at no time was the dissolution nearly as rapid as was corrosion. The significance of the relationship observed is not apparent, but it does seem to be true that the rate of corrosion is not determined by the rate of dissolution.

On the assumption (in accord with X-ray diffraction data) that the adherent corrosion product consists only of boehmite (AlOOH) and bayerite Al(OH)₃, the product composition can be calculated from knowledge of specimen weight gain, amount of metal corroded, and amount of product dissolved. On the assumption of such compositions, the total amounts of bayerite and boehmite produced during corrosion were calculated on two bases: (a) only bayerite dissolves, (b) only boehmite dissolves.

The results are somewhat inaccurate, perhaps because of water adsorbed on the nominally dry corrosion product at the times of weighing. In Figure 195 is shown the total amount of bayerite that had been produced, calculated in terms of the aluminum content. Slopes of the two lines are approximately the least-squares values. Subsequent to the time of the first point at three days, no more bayerite was produced. If only bayerite dissolved, there was apparently no change in total bayerite. If boehmite dissolved, some of the bayerite in the adherent product must have transformed to boehmite. This is unlikely, since previous results indicate that bayerite is the stable oxide in equilibrium with water at this temperature.

The calculations indicate that only boehmite was produced subsequent to three days' exposure. The change in the aluminum content of the boehmite with time should thus be the same as the change in the amount of corrosion with time. In Table 75 the logarithmic rate constants (least squares values) are compared. Errors are estimated, and are approximate. It is evident that the comparison favors the choice that only bayerite dissolves during long-term corrosion. This seems reasonable on the basis that the bayerite is in immediate contact with the water, and is believed to

⁽²⁴⁰⁾ Draley, J. E., Mori, S. and Loess, R. E., J. Electrochem. Soc., **110**, 622–627 (1963).

TABLE 74. EFFECTS OF TEMPERATURE AND OXYGEN CONTENT ON AQUEOUS CORROSION OF 1100 ALUMINUM

Temperature	Saturating Gas	Log. Rate Const., $\text{mg} \cdot \text{dm}^{-2} \cdot \text{cycle}^{-1}$	Log. Intercept, $\text{mg} \cdot \text{dm}^{-2}$
50°C	Oxygen	3.14	36.59
	Helium	2.62	37.43
70	Oxygen	3.60	37.55
	Helium	3.50	38.42

106-8322

FIG. 194. Loss of Corrosion Product during Corrosion of 1100 Aluminum in Oxygen-Saturated Water at 70°C.

106-8344

FIG. 195. Calculated Aluminum Content of Bayerite Formed during Corrosion of 1100 Aluminum in Oxygen-Saturated Water at 70°C.

TABLE 75. LOGARITHMIC RATE CONSTANTS FOR BOEHMITE PRODUCTION AND FOR CORROSION—1100 Al, $\text{H}_2\text{O}(\text{O}_2)$, 70°C

	Rate Constant, $\text{mg} \cdot \text{dm}^{-2} \cdot \text{cycle}$
Metal corroded	3.43 ± 0.02
Boehmite produced, assuming only bayerite dissolved	3.49 ± 0.1
Boehmite produced, assuming only boehmite dissolved	3.88 ± 0.1

have a substantially greater contact area than does the boehmite.

Under these circumstances, it appears that the dis-

solution of boehmite is negligible and that this process does not have a regulatory role during corrosion under the conditions of these tests.

Effects of Polarizing Current on Corrosion Rate

We have believed that the principal cause of oxide film cracking is the formation of some of the corrosion product hydrogen beneath it. Under these circumstances the liberation of hydrogen should have a direct influence on the corrosion rate: reduction in the rate of hydrogen evolution should reduce the corrosion rate, and the converse (directly opposite to the effects predicted by the simple electrochemical theory). Furthermore, it should be possible to estimate the fraction of the hydrogen that causes film damage by determining

106-7822

FIG. 196. 1100 Aluminum Polarized Cathodically in 70°C Oxygen-Saturated Water.

106-7821

FIG. 197. 1100 Aluminum Polarized Anodically in 70°C Oxygen-Saturated Water.

the change in the corrosion rate constant as a function of applied current.

Accordingly, corrosion tests were run in which constant currents were maintained (1, 10 and 100 μ a per 28 cm²) between platinum auxiliary electrodes and 1100 aluminum specimens. The results are presented in Figures 196 and 197. The predicted effects were at least approximately realized: increasing cathodic current (Figure 196) caused increasing amounts of corrosion (although the zero-current test result was somewhat out of line), and increasing anodic current decreased the amount of corrosion for at least the first few days.

The effects of the highest polarizing currents could

easily have been due to the production of excess alkalinity (cathodic) or acidity (anodic). In the latter case this is supported by sample appearance. It is known that the high anodic polarizing current did not simply force aluminum oxidation, since the corrosion rate was considerably less than would correspond to the anodic current.

The experiments did not give data in the form of logarithmic rate constants that could be analyzed in terms of the model outlined. It is hoped that suitable data can be obtained by determining corrosion behavior while specimens are polarized to several constant potentials.

2. Electron Optical Studies of Corrosion Films (R. K. HART, J. K. MAURIN AND D. G. PILNEY)

Film Growth on Pure Aluminum in High-Temperature and High-Pressure Steam

It was reported in the last Annual Report (ANL-6868) that some specimens corroded at 540°C and 70.3 kg/cm² (gauge) were partially disintegrated into white powder product. Additional experiments have shown that between approximately 375°C and 450°C and at pressures of 42.2 to 70.3 kg/cm² reaction products are mixtures of α - and γ -alumina. Early film growth does not prevent disintegration from grain-boundary attack and in most cases the metal is converted to corrosion product in a short time.

X-ray analysis of this corrosion product has shown that the relative amounts of α - and γ -Al₂O₃ present in this material varied appreciably from sample to sample, as judged from relative intensity differences in the diffraction patterns. Proportions ranged from nearly all α -Al₂O₃ to nearly all γ -Al₂O₃.

On specimens that were corroded under conditions to produce thin protective films of γ -Al₂O₃ many small pits were observed. These pits measured less than 2 microns across and were either square or triangular in shape. They were located within crystal grains as well as at grain boundaries. The pits appeared to be mainly associated with aluminum grains having 100 and 111 planes in the surface.

As these pits were not found present on electropolished surfaces, the possibility of thermal etching was considered. Experiments in which the thermal conditions of the steam exposure were duplicated in vacuum showed some grain boundary enhancement but no etch pits.

Both stripped films and surface replicas from corroded specimens showed that these pits were open at the surface level and not bridged with oxide. If such pits are formed through attack of the metal by steam it is surprising that no accumulation of corrosion product has been observed in them.

The Growth of Oxide Nuclei on Thin Metal Foils in the Electron Microscope

A research program has been started to investigate the texture and growth of crystalline oxide nuclei on a variety of metals in the electron microscope. The metals selected for investigation to date are aluminum, iron, zirconium and beryllium.

Before this work could commence the existing vacuum conditions in the Siemens Electron Microscope had to be improved. This was accomplished in a temporary way by using a redesigned specimen chamber and an auxiliary pumping system. This system has a liquid-nitrogen trap and is capable of maintaining the space surrounding the specimen at approximately 10⁻⁶ torr. The remainder of the microscope column operates at about 10⁻⁵ torr, which is achieved by the regular microscope pumping system. Specimens are heated on a hot stage capable of temperatures in excess of 1000°C.

Preliminary experiments have been carried out on aluminum and iron foils. The starting material in each case has been the purest obtainable. These metals were rolled into 0.13 mm foil and then thoroughly vacuum annealed. From this stock, specimens suitable for transmission electron microscopy, were obtained by electro-thinning. A number of polishing baths have

106039

160,000×

FIG. 198. Aluminum Foil Electrothinned in 1:4 Perchloric Acid/Ethyl Alcohol and Heated at 540°C for 45 Minutes in Oxygen at 1.0×10^{-5} Torr. Fringe spacings on nuclei vary from 50Å to 57Å.

been investigated and the most suitable for thinning each metal was selected.

For this type of investigation it is imperative that the oxide film left on the specimen after thinning be as thin as possible; ideally one would like to start with no film at all.

After initial viewing in the microscope suitable specimens were heated and allowed to remain at temperature for one hour or more. The pressure in the region surrounding the specimen was adjusted from 10^{-4} torr to 10^{-6} torr by the introduction of pure oxygen. At regular intervals during heating the specimen was observed and electron micrographs taken. At the end of each run the specimen was cooled to room temperature under the best vacuum conditions obtainable. It was then transferred to a regular specimen holder for high-resolution electron microscopy and diffraction.

Electron micrographs of oxide nuclei on aluminum and iron foils are shown in Figures 198 and 199. It has been found that within the boundary of an individual

grain the nuclei are parallel aligned, suggesting that an epitaxial relationship exists with the underlying metal. Also the number of nuclei increase with time and the number/time relationship is being determined.

A prominent feature observed in many nuclei is the occurrence of moiré fringes. Fringes shown in Figure 198 have a separation from 50Å to 57Å whereas those in Figure 199 have a separation from 40Å to 43Å. These distances are no doubt related to lattice distances in the oxide and metal and are being investigated more thoroughly. This type of interference phenomenon should also shed light on defect relationships between specific oxide nuclei and the underlying metal.

Corrosion Films Produced in Aqueous Media

A considerable amount of research has been done over the past few years on the aqueous corrosion of nickel and iron-bearing aluminum alloys in the temperature range 260°–350°C. The corrosion rate at any given temperature depends to a large degree on the conditions under which the tests are run. In particular,

106558

120,000×

FIG. 199. Iron Foil Electrothinned in 1:4 Perchloric Acid/Ethyl Alcohol and Heated at 540°C for 1 Hour in Vacuum of 1.9×10^{-5} Torr. Fringe spacings on nuclei vary from 40 Å to 43 Å.

large variations in corrosion behavior have been reported when high flow rates have been used.

According to one interpretation, pH changes within cracks in the oxide film lead to precipitation of new oxide and a resulting increase in protectiveness. Removal of the fresh colloid precipitate by high velocity water prevents such plugging. In the latter case, plugging could be accomplished only by the random settling out of agglomerated colloidal particles.

Electron microprobe analyses were carried out on two corrosion-resistant Al-Ni-Fe alloys (X8001 and A288), which varied only slightly as to their composition. They were corroded in both static and flowing water at 260°C, at which temperature their corrosion characteristics have appeared identical. In the flowing system either small amounts of iron oxide colloid or graphite colloid were added in an effort to determine what effect they had on the growing oxide.

Figure 200 is a transverse section through the corrosion film on X8001 after corrosion in a flowing system

containing 8 ppm iron oxide colloid. Microprobe traces for aluminum, iron and nickel across this oxide are shown in Figure 201. It will be noted that there is an increase in the iron concentration in the outer layer and a decrease in the nickel content. The nickel in fact reaches a maximum concentration about midway through the oxide and then decreases again to the oxide/metal interface.

The corrosion product film built up on alloy A288 in flowing water containing 8 ppm colloidal graphite is shown in Figure 202. It appears that no buildup of graphite had occurred on the surface. We were unable to analyze for carbon in the microprobe. Microprobe traces were made for aluminum, iron and nickel and the results shown in Figure 203. From these results there does not appear to be any significant reduction of iron or nickel near the surface although the aluminum content of the oxide was a little lower in that region.

In summary, iron oxide colloid when added to the

110791

800X

FIG. 200. Transverse Section of Film on Alloy X8001 after Corrosion in Flowing Water Containing 8 ppm Iron Oxide Colloid at 260°C for 28 Days.

39410

FIG. 201. Electron Microprobe Traces for Aluminum, Iron and Nickel across Film on alloy X8001. Specimen corroded in flowing water containing 8 ppm iron oxide colloid at 260°C for 28 days.

110773

750X

FIG. 202. Transverse Section of Film on A31 Alloy A288 after Corrosion in Flowing Water Containing 8 ppm Colloidal Graphite at 260°C for 28 Days.

39409

FIG. 203. Electron Microprobe Traces for Aluminum, Iron and Nickel across Film on Alloy A288. Specimen corroded in flowing water containing 8 ppm colloidal graphite at 260°C for 28 days.

water of a flowing system, appeared to be fairly readily absorbed to form an outer layer rich in iron. This layer did not reduce the corrosion rate; in fact kinetic data showed the reverse held true. This was probably a result of higher pH of the iron colloid solution rather than

an absorption effect. In the case of colloidal graphite there was no indication that it was absorbed into the oxide surface. Correlation of probe analysis of oxide films with corrosion behavior can be attempted only after more results are available.

3. Mechanism of High-Temperature Corrosion of Aluminum Alloys

(W. E. RUTHER AND D. DORMAN)

Static Conditions

The kinetics of the reaction between high-temperature water and a corrosion-resistant aluminum alloy are being studied. With suitably precise data, it should be possible to test equations derived from theoretical considerations of the corrosion processes involved and thus provide insight into the actual corrosion mechanism.

The first experiment in the current series was performed at a temperature of 260°C in a refreshed autoclave system with samples of aluminum alloy A288 (1w/oNi 0.5w/oFe 0.1w/oTi 0.03w/oSi). Data for four individual samples were obtained with an eddy-current thickness gauge; the experiment was terminated after 143 days exposure.

The corrosion curves of the four individual samples diverged early in the test as illustrated in Figure 204. The values for a single sample are shown with lines indicating the extent of the spread in data. It is believed that the individual determinations are sufficiently precise to require interpretation of the rather obvious changes in corrosion rate along the curve for the individual sample. Transitions in corrosion rate, such as observed in this experiment are believed to be associated with the partial rupture of relatively large areas of the protective portion of the corrosion coating. A period of relatively rapid corrosion occurs during the repair of the ruptured areas by the formation of a fresh protective layer. In any case, rate transitions complicate the interpretation of corrosion mechanism through the use of kinetics data and initial testing of analytical models will probably have to be confined to the period prior to the first transition.

Some clues as to what must be considered in the analytical model can be obtained by comparing this recent experiment with previous tests as shown in Figure 204. The experiment with X8001 (1958) was quite similar to the recent one with A288 aluminum.

The differences were in method of starting the tests, the suspension of the samples, and (after 20 days) in the number of samples in the test. The average metal

106-8323

FIG. 204. Corrosion at 260°C.

losses (Figure 204) for these two experiments are shown with the values of corrosion obtained from static nonrefreshed (except monthly) autoclave tests. The results are consistent with the hypothesis that corrosion increases with refreshment (measured per unit of corroding Al surface). Other tests⁽²⁴¹⁾ have indicated identical corrosion behavior for X8001 and A288 up to 70 days at 260°C in a single refreshed autoclave. The rather large increase in corrosion rate of the A288 (refreshed) compared with the X8001 is attributed to the slightly higher refreshment flow and particularly to the addition of fresh additional samples to the X8001 test after the 24 day exposure period.

In the nonrefreshed test, the amount of corrosion was closely proportional to the square root of time. It is suggested that the first model to be analytically tested should involve a parabolic film-formation process coupled with some film-degenerating process associated with the refreshment of the test. The parabolic film-growth concept is basic to many corrosion processes and results most simply from the case in which the corrosion rate is inversely proportional to the thickness of

⁽²⁴¹⁾ Jour. Nuc. Mat. 6, 157-171 (1962).

TABLE 76. COMPARISON OF ACTUAL AND CALCULATED CORROSION PRODUCT AT 143 DAYS

Sample	Actual* (CH ₃ OH-I ₂)	Calculated from Metal Loss	Difference
1	211 mg	318 mg	107 mg
2	225	323	98
3	205	289	84
4	199	285	86
			375

* These figures may be $\approx 1\%$ low due to loss in preparing for dissolution.

106-8306

FIG. 205. Corrosion of 8001 Aluminum in Solutions (100 ppm) Flowing at 8 meters/sec.

the film, suggesting a film of uniform protective quality.

The simplest model would involve direct dissolution of the protective oxide owing to its (limited) solubility in the 260°C water. The corrosion product left on the samples at the end of the experiment (Table 76) can be used to test this model.

If one assumes a refreshment flow of 9 cc/min (≈ 13 liters/day) and a solubility of 0.25 mg Al_2O_3 /liter for X8001⁽²⁴²⁾ a total loss of 460 mg of Al_2O_3 might be expected if the effluent were saturated, or 540 mg $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$. This compares with 375 mg measured loss in this test. Thus the solubility is adequate to account for the measured losses. However, it is also obvious (Table 76) that simple dissolution of the outer coating is not the whole process involved since that would imply equal losses from each sample (areas are equal) whereas in fact the loss of each sample apparently was dependent on the total corrosion of that specimen. Expressions derived on the basis of parabolic film growth and of loss either at a constant rate or proportional to the amount of film failed to fit the data.

Experimental observation of the multitudes of tiny etch pits left in the defilmed corroded metal also

should be explainable by the model chosen. More sophisticated models are being examined at this time.

Attempts are being made to reduce the divergence in behavior of individual specimens through different surface preparations. The differences are perhaps due to clustering of the second phase in the alloy, leading to a "herringbone" corrosion pattern in the rolling direction and may require the selection of another alloy or the remelting and chill casting of this one to minimize this difficulty.

Dynamic Conditions

This phase of the program has been largely directed towards attempting to verify (or disprove) a colloidal corrosion product hypothesis advanced about two years ago.⁽²⁴³⁾ In tests this year we have tried to influence the dynamic corrosion rate of X8001 aluminum by deliberately adding chemicals with a known complexing ability for aluminum such as ammonium citrate, tartrate or acetate to the test environment. As shown in Figure 205, the effect at the 100 ppm level was very slight. The only significant change in slope for the curves was noted with dibasic ammonium citrate and this could be attributed to the lower pH of this solution. In any event the high corrosion rates predicted by the hypothesis were not obtained.

Refreshed static corrosion tests were also performed with each of these solutions. The corrosion rates were quite similar to that obtained for distilled water. In the case of the tartrate and, to a much less extent the citrate, the intercept on the weight-loss axis was reduced to nearly zero, a striking difference from water and the other solutions. Examination of these specimens showed the outer surface had thousands of tiny crystalline mounds attached to the surface. This suggests that in static solution the outpouring from the defected protective oxide during the early stages of the corrosion reaction was precipitated more completely and more rapidly than usual in water, slowing the reaction in the defect and reducing the intercept of the weight loss curve. It seems unusual that a complexing ion at room temperature for aluminum (tartrate) should cause a more rapid precipitation at 260°C.

Although 100 ppm is a concentrated solution compared with the total solid level previously measured for the dynamic system (< 1 ppm), it is a very dilute solution when considered in the usual terms of complexing aluminum ions. Therefore two tests were run in more concentrated solutions, with the results shown in Figure 206. In this case the expected higher corrosion rate was obtained. Ammonium acetate was chosen only for convenience in operating the experi-

(242) Report HW 61089.

(243) Corrosion of Reactor Materials, pp. 477-498, IAEA, Vienna, 1962.

106-8305

FIG. 206. Corrosion of 8001 Aluminum in Flowing (8 meter/sec) Solutions.

ment. The effect of pH was quite small in the 5.4-7 range with the concentrated solutions. Curves for distilled water and the dilute solution are included for comparison.

Refreshed static corrosion tests in the concentrated solutions did not show any significant changes in corrosion rate as compared with distilled water but the intercept was reduced as described previously for the dilute tartrate solution.

Dynamic Corrosion with Applied Currents

One of the dynamic test loops was modified to permit electrical connections to small cylindrical samples. External electric currents were passed during the corrosion exposure. For each test a control specimen without current was included to check on the experimental reproducibility. Because of the requirements for electrical connections it was not possible to use the usual thickness gauge samples, so defilmed metal losses after seven days exposure have been plotted in Figure 207 to show the effect of polarizing currents. The dependence of total corrosion on applied current was in the same direction as that determined for

106-8318

FIG. 207. Corrosion of 8001 Aluminum in Flowing Water (5.6 meter/sec) with Electrical Currents Applied.

samples in a static system several years ago. The explanation offered at that time was that less hydrogen damage occurred to the aluminum oxide when the sample was connected as an anode.

The experiment had been undertaken to see if the precipitation characteristics of the colloidal corrosion products circulating through the system could be altered by the electric field. The nature of the deposited film on the stainless steel counter electrode was distinctly different as the electrode was made positive or negative. When made negative by an external battery (or by directly coupling it to corroding aluminum), the stainless acquired a velvet black deposit. When made positive, a very limited amount of a light grey deposit was noted. Attempts to identify these deposits are continuing but are hampered by the smallness of the quantity present.

4. Oxidation of Zirconium (J. E. DRALEY, D. H. BRADHURST, AND C. J. VAN DRUNEN)

Kinetics

Careful examination of recorded weight gains of polycrystalline zirconium in 400 and 10 mm oxygen 700°C indicates that oxidation does not proceed in accordance with the parabolic or cubic rate law, as has variously been reported. A straight line is apparently not formed between the log of weight gain and

the log of time, although the deviation from a straight line with a slope of one-third is small.

Consideration of irregularities in the curves suggests a breakdown or cracking of the film. Accordingly, a rate expression has been derived on the assumptions that local film growth is parabolic, and that local cracking occurs whenever a constant thickness of such

106-8342

FIG. 208. Oxidation of Zirconium in Oxygen 700°C, 400 mm pressure.

106-8309

FIG. 209. Variation in Oxidation Rate with Applied Voltage, for Zirconium at 700°C.

protective film occurs. The expression provides an excellent fit to the data for at least a few hours. The behavior is illustrated in Figure 208.

Since oxygen diffuses into the metal at a significant rate at this temperature, it will be necessary to take this into account in the derivation of a final rate expression.

Electrical Measurements

The relationships between the free-energy changes during oxidation, oxidation rate, and the potential developed across the growing oxide film can be expressed as follows:

$$E_a + E = iR_i \quad [1]$$

$$E_c - E = iR_e \quad [2]$$

$$E_0 = E_a + E_c = i(R_i + R_e) \quad [3]$$

where E_0 is the potential corresponding to the free

energy of formation of zirconium oxide, E_a is the half-cell potential for the oxidation of zirconium into ions in (defect-structure) ZrO_2 , E_c is the half-cell potential for the reduction of oxygen into ions in ZrO_2 , E is the potential of the metal with respect to the exterior oxide surface, i is the oxidation current, R_i is the overall retardance for the anodic process (including ionic migration), and R_e is the overall retardance for the cathodic process (including electron transport).

In accord with the first equation, it should be possible to alter the oxidation rate by the application of a potential. With conducting oxide powder used for surface contact, the overall oxidation rate was indeed reduced when the metal was made more negative. (See Figure 209). The effect is apparently limited by the ability to maintain a uniform potential on the surface of the oxide film. At points of contact of the contacting powder the amount of oxidation was quite small, but the film grew up around the particles, so that a considerable fraction of the surface oxidized relatively rapidly. The application of anodic potentials increased the growth rate only at the tiny points of contact, so that the bulk of the area oxidized at or near the unpolarized rate.

The resistance of the film to the passage of a small external current should be equivalent to that of a parallel circuit of R_i and R_e :

$$R_{ext} = \frac{R_i R_e}{R_i + R_e} \quad [4]$$

The four equations can be solved simultaneously for R_i , R_e , E_a and E_c . With E , E_0 , R_{ext} and i (from weight gain rate) known, the expression for E_c is:

$$E_c = E + \frac{E_0}{2} \left(1 + \sqrt{1 - \frac{4iR_{ext}}{E_0}} \right)$$

It has proved difficult to measure reliable values of R_{ext} because of the requirement to compensate for the contact resistance and the area effective in conducting current through the oxide film. These problems have now been overcome and it is possible on a routine basis to measure the required quantities.

For a characteristic run, E_a , E_c , R_i and R_e are plotted in Figure 210. With the assumption that E_0 is constant, E_c is observed to increase with time while E_a decreases. Since the assumption is unverified, it must be considered that E_a and E_c are roughly of the same magnitude but their variation with time is unknown. These potentials can be expected to reflect the defect structure of the oxide.

The ratio of R_e to R_i varies from about 16 to 23 for the period of measured increase in their values. From equation [3] it can be seen that R_e is essentially proportional to the oxidation current. Kinetic analysis of

n_e is thus equivalent to kinetic analysis of the direct oxidation rate: the rate varies approximately with $t^{-2/3}$ as the amount of reaction varies with $t^{1/3}$. However, R_i apparently varies with $t^{1/2}$ for the first 200 minutes, and then becomes erratic. This parabolic behavior suggests some relatively uncomplicated diffusion process. One such process is the diffusion of oxygen into the metal; there is not sufficient evidence to allow deduction that this is limiting for ionic diffusion through the oxide.

106-8340

FIG. 210. Calculated Constants for One Specimen.

..6-8310

FIG. 211. Stress in Zirconium Oxide Films as a Function of Film Thickness.

It is evident that the electrical measurements provide a powerful tool in the study of oxidation processes. As in most profitable research the results pose some intriguing questions.

Stress in Growing Oxide Films

Presumably the cause of oxide cracking is stress produced in the thickening oxide. Reaction mechanisms could be more thoroughly described if such stresses were known and correlated with mechanical properties of the oxide film.

Estimates of the stress in growing oxide films have been made from measurements of the curvature of thin zirconium bars oxidized predominantly on one side. The stress in the film is given by the expression

$$S = \frac{Et^2}{6rd}$$

where E is Young's modulus for the basis metal and t its thickness, r is the radius of curvature of the bar, and d the thickness of the oxide film. Young's modulus for zirconium at 700°C was measured with the use of a four-point bending jig and an Instron Tensometer.

The results are summarized in Figure 211 in which the magnitude of the compressive stress in the film is plotted as a function of oxide thickness. The calculated stresses are high and compressive, which is to be expected if the film forms by the inward diffusion of oxygen. Values of stress were calculated on the assumption that all the bending observed was due to the stress in the oxide film of known thickness. The extent to which this assumption is valid is not known: an appreciable amount of oxygen diffuses into the metal during the oxidation of zirconium at 700°C, and it is possible that some contribution to the bending could be due to the resulting expansion of the zirconium lattice. This would have the effect of reducing the calculated values of stress.

The presence of a maximum in the curves in Figure 211 suggests that some mechanism of stress relief is operating during film growth. The thickness at which the maximum occurs might be termed critical if this stress relief is due to cracking of the film.

It may be seen that the position of the maximum is at about 1.5 μ at 500°, but in the range 5–7 μ at 700°C. The level of stress is also higher for the lower temperature. Both of these observations are consistent with the idea that some stress relief is occurring by plastic deformation of the film at the higher temperature. This relief could be due either to simple annealing of the film, or deformation by creep mechanism due to the combined action of the compressive stress in the film and the relatively large flux of ions through the film as growth proceeds.

5. Polarization Studies (R. A. LEGAULT AND W. J. BETTIN)

Corrosion Measurements

Since the difficulties encountered in making polarization measurements increase markedly with the purity of the water used, an attempt was made to ascertain whether the small amounts of impurities present in our normal demineralized-plus-distilled water have a sufficiently large effect on the corrosion process to warrant coping with the additional difficulties. To this end, both weight-gain and weight-loss measurements were made on 1100 aluminum immersed in boiling distilled water and in boiling high-purity water for periods of up to one month. Resistivities for the two are about 7 and 15 megohm-cm at 25°C, compared with 18.6 for "theoretically pure" water.

Figure 212 shows that the cumulative weight-loss data obtained on 1100 aluminum in boiling distilled water go through a maximum during this exposure time. The test samples were electrochemically stripped to constant weight in a chromic acid-phosphoric acid bath. The inflection point noted in the curve after 14 days exposure indicates: 1) that a second oxide (one that is not strippable under these conditions) is formed, 2) that the second oxide forms as the result of a transformation in the original oxide, and 3) that the transformation apparently takes place in that portion of the oxide adjacent to the metal surface.

Figure 213 shows that the cumulative weight-gain obtained on 1100 aluminum in boiling distilled water also goes through a maximum. This inflection point in the curve could be explained as follows: 1) the original oxide is transformed into another that is less hydrated, and 2) beyond the inflection point, the oxide formed experiences a rate of loss to the solution that is higher than its rate of formation. It is possible that both processes contribute to this decrease in weight gain since the weight-loss data described above do show that a transformation occurs, but the size of the weight-gain decrease is too large to be accounted for by an oxide transformation alone.

Data similar to those reported above were obtained in comparable experiments performed in ultrahigh-purity water. Both the cumulative weight-loss data and the cumulative weight-gain data are shown in Figure 214. These data differ from those obtained in distilled water in that there are two inflection points shown during this immersion period, with the second one occurring at a higher level of corrosion than the first. This is taken to indicate that the oxide transformation takes place sooner and more readily in ultrapure water than it does in distilled water. It also indicates that the corrosion process involves the successive breakdown and repair of a protective film.

This breakdown-repair sequence probably also takes place in distilled water over longer immersion periods.

It was concluded from the differences in behavior observed in these two test media that the greater difficulties encountered in making polarization measurements in high-purity water could not justifiably be avoided.

Electrochemical Measurements

The extremely high resistivity of pure water ultimately led to current-interruption techniques for measuring polarization. A desire to minimize the disturbance suffered by the test system as a result of making the polarization measurements required the use of the smallest practicable polarizing currents. The necessity for minimizing AC contributions to the measurements prompted a striving for the simplest measuring system possible. The difficulty of achieving reversibility in a reference electrode, even in the very low range of polarizing currents employed, necessitated attaining an extremely high impedance in the reference leg of the measuring circuit. These considerations resulted in the apparatus shown schematically in Figure 215.

The measurements involve photographing the polarization potential decay curves that result when the polarizing current is turned off. The ohmic over-potential contribution to the polarized potential decays

106-8336

FIG. 212. Corrosion of 1100 Aluminum in Boiling Distilled Water.

early instantaneously whereas the contribution of interest decays in times of the order of one second. By using an appropriate oscilloscope scan rate one is able to block out the ohmic over-potential portion of the decay curve and to measure the remainder quite accurately. The high impedance necessary in the reference leg of the measuring circuit is attained with a pair of balanced cathode followers.

The polarizing currents used are of the order of 10^{-7} amperes and in this range we find a linear relationship between polarizing current and activation over-potential. The slope of the current-potential line obtained in such measurements has units of resistance and is identical to what has been called "retardance." This quantity has been found to be inversely proportional to the metal dissolution rate in many systems. Corrosion-rate values obtained electrochemically in this manner on 1100 aluminum in high-purity water are in reasonable agreement with values calculated from weight-change measurements obtained under similar conditions.

These measurements can be made in a matter of seconds, hence represent an approximation to an instantaneous rate determination as opposed to the cumulative determinations obtained in weight-change

106-8325

FIG. 213. Corrosion of 1100 Aluminum in Boiling Distilled Water.

106-8334

FIG. 214. Corrosion of 1100 Aluminum in Boiling Ultrahigh-Purity Water.

106-8333

FIG. 215. Block Diagram of Polarization Apparatus.

measurements. Detailed variations in rate as a function of time, especially when used in conjunction with potential-time variations, should be interpretable in terms of reaction mechanism. In addition, a detailed

106-8314

FIG. 216. Corrosion Rates for Aluminum in High-Purity Water at 95°C. From Cathode Polarization Measurements.

106-8308

FIG. 217. Open Circuit Potentials of Aluminum in High-Purity Water at 95°C.

study of individual decay curves holds the possibility of differentiating between the individual contributions to the activation portion of the polarization.

Rate-time and potential-time data have been obtained on both 1100 aluminum and high-purity aluminum in high-purity water at 95°C. Typical measurements are shown in Figures 216 and 217. On 1100 aluminum the potentials were considerably less negative and the rates were significantly lower. One can thus conclude that the alloying constituents present in 1100 aluminum provide a net retardance to the anodic or metal dissolution half-reaction. Immediately after

immersion, however, the corrosion rate on 1100 aluminum is approximately the same as that on high-purity aluminum, whereas the potential on 1100 aluminum is considerably less negative than that on high-purity aluminum. It is indicated that initially the alloying constituents in 1100 aluminum serve to retard the anodic process and to assist the cathodic process. This suggests that the function of these alloying constituents is to provide a random distribution of preferential sites for the reduction reaction, and thereby to promote the formation of a uniform film of corrosion product.

The corroded samples differ considerably in appearance. The corrosion product on 1100 aluminum is an adherent, uniform, grey film; that on high-purity aluminum is a very much thicker, translucent, crystalline material, which can easily be removed. The film on 1100 aluminum is too thin and adherent to allow the convenient removal of a sufficient quantity from

which to get an X-ray diffraction pattern. Such a pattern was obtained, however, from the oxide formed on the high-purity aluminum, and it indicated the presence of both boehmite and bayerite in the corrosion-product film.

The study of the corrosion behavior of pure aluminum in high-purity water is being extended to include the effect of small additions of iron, and possibly the other alloying constituents in 1100 aluminum. The examination of other pure materials in both single-crystal and polycrystalline forms is planned.

H. CERAMIC MATERIALS RESEARCH

1. Defect Equilibria of Plutonium Dioxide (L. M. ATLAS AND G. J. SCHLEHMAN)

An apparatus for equilibrating metal oxides at high temperatures with gases having known oxygen pressures was completed early in the year and checked with TiO_{2-x} . Experiments then progressed to a study of PuO_{2-x} at 100°C intervals from 1100°C to 1600°C. The experimental techniques used were as follows: PuO_{2-x} samples in the form of porous ceramics are heated in a once-through stream of $\text{He-H}_2\text{-H}_2\text{O}$ mixture until equilibrium is reached. The DC electrical resistance of the equilibrated specimen is then measured by using its four supporting wires as probes. Next, the solid is rapidly cooled to a low enough temperature to prevent any appreciable reaction between it and the atmosphere. This permits the reducing gas to be replaced by an He-4v/oO_2 mixture without the PuO_{2-x} undergoing a significant change of composition. The solid is now reheated to 800°C in a fixed volume of the oxidizing gas, which converts PuO_{2-x} to $\text{PuO}_{2.00}$. The corresponding change of gas composition is monitored with a thermal-conductivity gas-analyzer.

A limited number of experiments were carried out at 1200 and 1300°C with oxygen-deficient rutile to check the gas-analysis system against the thermogravimetric data of Moser, Blumenthal and Whitmore.⁽²⁴⁴⁾ A comparison of the relative partial molar free energies of oxygen in TiO_{2-x} , (F_o^M), given by the two different methods is presented in Table 77. Considering that the Argonne values of F_o^M at $x = 0.0025, 0.005$, and 0.0075 were interpolated from only three or four points at each temperature, the agreement between the two sets of data is quite good.

The variation with oxygen pressure of the composition and electrical resistivity of PuO_{2-x} is presented in Figs. 218 and 219 as plots of $\log x$ vs $\log p(\text{O}_2)$ and $\log \rho$ vs $\log p(\text{O}_2)$. Solid lines in these figures were calculated from least-squares analyses; dashed lines have been drawn in only approximately. The plotted resistivities are normalized values for a hypothetical ceramic having zero v/o porosity; they have been calculated by applying Belle and Lustman's⁽²⁴⁵⁾ relation to data obtained from porous specimens.

⁽²⁴⁴⁾ Moser, J. B., Blumenthal, R. N., and Whitmore, D. H., *Further Studies of Nonstoichiometric Rutile (TiO_{2-x})*, presented 36th Annual Meeting, American Ceram. Soc. Paper No. 50-B-64 (April 22, 1964).

⁽²⁴⁵⁾ Belle, J., and Lustman, B., *Properties of UO_2* , WAPD-184 (1957) or TID-7546, pp. 432-441 (1957).

TABLE 77. PARTIAL MOLAR FREE ENERGIES OF OXYGEN IN TiO_{2-x}

T (°C)	(x) in TiO_{2-x}	Measured Oxygen Pressure (atm.)	F_o^M (kcal/mole)	F_o^M (Moser et al.) (kcal/mole)
1200	0.0023	1.9×10^{-11}	-73	
	0.0025	—	-74*	-73
	0.0042	1.4×10^{-12}	-80	
	0.0050	—	-82*	-83
	0.0072	1.5×10^{-13}	-87	
	0.0075	—	-87*	-88
1300	0.0025	—	-62*	-63
	0.0038	5.2×10^{-10}	-67	
	0.0050	—	-72*	-71
	0.0051	6.7×10^{-11}	-74	
	0.0075	—	-78*	-76
	0.0080	6.6×10^{-12}	-81	
	0.0090	7.6×10^{-12}	-81	

* Interpolated values.

In Fig. 220, oxygen pressures have been converted to partial molar free energies of oxygen in PuO_{2-x} , which are then plotted against $\log x$. For comparison purposes, some of the 1100°C data of Markin, Bones, and Gardner⁽²⁴⁶⁾ are also included in Fig. 220. Unfortunately, the close agreement found for the TiO_2 results is not repeated here. No explanation for the discrepancy can be offered at this time other than the suggestion that it might be connected with differences of oxide purity. It should be noted, however, that results of the Argonne gas-analysis technique have been corroborated at 1400 and 1600°C by weight change measurements (cf. the points marked by crosses in Fig. 218).

Discussion

The conventional mass-action analysis of nonstoichiometric PuO_2 has been described in a previous ANL report.⁽²⁴⁷⁾ This type of analysis assumes that: (a) all of the defects are formed by a change in the oxygen content of the solid; (b) these defects lose electrons that go into a conduction band; (c) the electrons

⁽²⁴⁶⁾ Markin, T. L., Bones, R. J., and Gardner, E. R., *Thermodynamic Data for Plutonium Oxides*, U.K.A.E.A. Report AERE-R4724 (1964).

⁽²⁴⁷⁾ Atlas, L. M., *Defect Equilibria of Plutonium Oxides*, in Annual Report for 1963, Metallurgy Division, ANL-6868, 355-362 (1963).

FIG. 218. Variation of x in PuO_{2-x} with Oxygen Pressure. FIG. 219. Variation of Electrical Resistivity of PuO_{2-x} with Oxygen Pressure.

and the defects have activity coefficients of one; (d) the concentrations of O^{2-} and Pu^{+4} ions at regular lattice sites are essentially constant. These assumptions lead to a linear log-log relation between x and $p(\text{O}_2)$ whose slope should be the same as the slope for $\log 1/\rho$ vs $\log p(\text{O}_2)$. Moreover, this slope should tend to decrease as the temperature rises (because of increased thermal dissociation of the defects). Figures 218 and 219 show that neither of these predictions are correct for PuO_{2-x} . The slope anomalies might be explained

by assuming that an appreciable concentration of electrons are derived from sources other than the dominant defect, i.e. from impurity ions, surface states, or even intrinsic dissociation. The concentration of these electrons might not be dependent on $p(\text{O}_2)$; nevertheless they would add to the electrical conductivity and would also tend to drive the defects into less dissociated states. The net effect could be to make $\log 1/\rho$ vs $\log p(\text{O}_2)$ shallower than $\log x$ vs $\log p(\text{O}_2)$. Moreover, if the electron concentration from the addi-

tional source increases rapidly with a rise of temperature, the resulting suppression of defect dissociation could cause the slopes to become *steeper* rather than shallower. One weakness of this argument is that a combination of oxygen-dependent and oxygen-independent electron sources should make the two log-log plots nonlinear; one might expect a change of slope to occur at values of $p(\text{O}_2)$ where dominance shifts from one electron source to the other. No such curvature is evident in either the 1100°C or 1400°C lines of Figs. 218 and 219.

The observed slopes might also be explained by revising the simple mass-action treatment to include the following considerations:

a. Electrons dissociated from defects are mostly retrapped at regular cation sites; i.e., the equilibrium constant for the reaction $\text{Pu}_i^{+3} + e \rightarrow \text{Pu}_i^{+4}$ is much greater than one.

b. The activity coefficient for free electrons (γ_e) varies according to the expression $[e]^y$, where y is a function of $[e]$ (Rosenberg⁽²⁴⁸⁾), and brackets $[]$ denote concentration. However, if $[\text{Pu}_i^{+3}] \gg [e]$, γ_e is likely to be nearly equal to one except for very high defect concentrations ($x > 0.1$).

c. The activity coefficients for Pu_i^{+3} (γ_P) and for the defects (γ_i) vary with their concentration, and in the experimental region follow the simple function $(kp(\text{O}_2))^m$, where k and m are nearly constant at constant temperature (m being < 1).

Under these conditions, and assuming that quadruply charged plutonium interstitials (Pu_i^{+4}) predominate, the defect concentration x varies with $p(\text{O}_2)$ as follows:

$$\log x \approx -(1/5 + 4m_1/5 + m_2/5)$$

$$\log p(\text{O}_2) + A_1, \quad (2)$$

where m_1 and m_2 are the exponents for γ_P and γ_i in the function $[kp(\text{O}_2)]^m$, and A_1 is a constant that incorporates the various equilibrium constants. The resistivity (ρ) then varies with $p(\text{O}_2)$ as follows:

$$\log(\mu\rho) \approx (1/5 - m_1/5 + m_2/5)$$

$$\log p(\text{O}_2) + A_2, \quad (3)$$

where μ is the Hall mobility of the electrons.

Note that if $m_1 \neq 0$, the slope of a plot of $\log x$ vs $\log p(\text{O}_2)$ should be somewhat steeper than the slope of $\log(1/\rho)$ vs $\log p(\text{O}_2)$. The exponent m_1 may be evaluated by subtracting equation (2) from equation (3), giving the following expression:

$$\log(\rho x) \approx m_1 \log p(\text{O}_2) + \log \mu + A_3. \quad (4)$$

⁽²⁴⁸⁾ Rosenberg, A. J., *Activity Coefficients of Electrons and Holes at High Concentrations*, J. Chem. Phys. **33**, No. 3, 665-667 (1960).

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FIG. 220. Relative Partial Molar Free Energy of Oxygen in PuO_{2-x} .

Therefore, a log-log plot of ρx vs $p(\text{O}_2)$ at constant temperature should have a slope $= m_1$. Except for a change in the constant A_3 , equation (4) is valid regardless of the type of defect that is assumed to be dominant. Applying equation (4) to the PuO_{2-x} data, $m_1 \approx 0.04$ at 1100°C and 0.09 at 1400°C. Now, if m_2 for γ_P is not very different from m_2 for γ_i , the two constants tend to cancel in equation (3) and the slope approaches $1/5$. This agrees very well with the value $1/4.9$ derived from the resistivity data at 1100°C (Fig. 219), and suggests that Pu_i^{+4} is the predominant defect at that temperature. In equation (2), m_1 and m_2 are additive, and if they are similar in value the slope approaches $-(1/5 + m_1)$. Since $m_1 \approx 0.04$, the predicted slope at 1100°C is $-1/4.2$, as is actually observed (Fig. 218).

At 1400°C the resistivity line has a slope of $1/4.2$, which is consistent with the defects being either triply charged plutonium interstitials or singly charged oxygen vacancies. However, if interstitials predominate at 1100°C, the same is likely to be true at 1400°C (the regular spacing between the resistivity lines in the range 1100°C to 1400°C suggests that a change of defect type does not take place in this interval). The effective charge of the interstitials appears to decrease from $+4$ at 1100°C to $+3$ at 1400°C. The fact that a temperature rise tends to suppress rather than enhance dissociation of the interstitials suggests that the enthalpy of the reaction $\text{Pu}_i^{+3} \rightarrow \text{Pu}_i^{+4} + e$ is greater than that for the reaction $\text{Pu}_i^{+3} \rightarrow \text{Pu}_i^{+2} + e$.

Future Plans

Plans for the coming year include extending the range of measurements of x and ρ as functions of $p(\text{O}_2)$

at 1200°, 1300°, 1500°, and 1600°C. If the results appear to show abrupt changes of entropy with temperature, additional experiments will be carried out at 50° or even closer intervals in the critical region.

The program will then proceed to a study of the effect of impurities on the oxygen dissociation pressure of PuO_{2-x} .

2. Effect of Surface Structure on Catalytic Activities of Oxides (M. L. VOLPE)

In the last Annual Report (ANL-6868) the apparatus used for this research was described and some preliminary results on the catalytic decomposition of N_2O were given. During the past year, this investigation of the various structural factors influencing catalytic activity for the N_2O decomposition has continued. Attempts have been made to determine the effect of dislocation density and neutron irradiation on the activity of MgO single crystals; the effect of crystallographic orientation has been investigated with cobalt oxide single crystals. Finally, a comparison has been made of the activity of pure cobalt oxide vs that of a cobalt oxide-magnesium oxide single crystal.

Apparatus and Method

The apparatus and method used were essentially that which was described in ANL-6868. Slight changes in the equipment were made in order to insure constancy of temperature within the reaction zone. The temperature now varies by less than one percent from point-to-point, and the average temperature is measured with an accuracy of less than one-half percent.

Crystal Preparation

The MgO single crystal catalysts were prepared by cleaving Norton crystals (99.9% MgO) into thin wafers ($\{100\}$ orientation) of dimensions approximating $1\frac{1}{2} \times 1\frac{1}{2} \times 0.05$ cm, then polishing by dipping for a few seconds in hot conc. H_3PO_4 , and rinsing in distilled water, acetone, and methanol. The cleaving was done on a machine, which could reproducibly cleave the crystals to form sheets as thin as 0.025 cm.

For radiation studies, a 6.3 mm thick crystal was exposed to an integrated dose of 2×10^{19} nvt in CP-5. The original faces were then cleaved off, and the crystal cleaned by dipping in a solution of 5 parts saturated NH_4Cl , one part water, one part H_2SO_4 ; and then washing in water, acetone and methanol.

The CoO-MgO was prepared by diffusing Co^{++} into an MgO single crystal as described in ANL-6868. The faces were mechanically polished parallel to the $\{100\}$ planes with silicon carbide and diamond powder, chemically polished in hot H_3PO_4 , and washed as above. It was subsequently repolished with diamond

paste for a series of experiments in which mechanically polished, rather than chemically polished surfaces were desired.

Cobalt oxide single-crystal wafers (about 1 mm thick) were cut from a large crystal parallel to the $\{110\}$, $\{111\}$, and cleaved parallel to $\{100\}$. All wafers were subjected to mechanical polishing followed by a few seconds' dip in hot H_3PO_4 (electron diffraction patterns confirmed the absence of a disturbed layer). This treatment was followed by a few minutes in cold H_3PO_4 and the usual washing.

X-ray Laue patterns and diffractometer tracings and electron diffraction patterns (100 Kv electrons) showed that in each case, the actual orientation was within a degree or two of the nominal. However, the interplanar spacings were more appropriate to Co_3O_4 than to CoO . Nevertheless, it was found, through chemical analysis, that the over-all O/Co ratio for the crystal was 1.03. Apparently, then, the catalyst surface composition is Co_3O_4 , to a depth of a few microns.

In spite of considerable effort spent on polishing techniques, chemical polishing of the cobalt oxide revealed certain "inclusions", which appeared as "plateaus" as large as 10μ across and 1μ high. They were almost absent in $\{100\}$ crystals, present to an extent of perhaps 5% on $\{110\}$ crystals, and to about 20–30% on $\{111\}$ crystals. From the experimentally measured O/Co ratio, and from the information given by light and electron microscopy and X-ray and electron diffraction, we conclude that the cobalt oxide catalysts consist of CoO with a surface layer of oriented Co_3O_4 , containing variable amounts of randomly oriented Co_3O_4 projections.

Results

Table 78 lists the data obtained. Each one of the net rates at 442°C and each corresponding activation energy (E_a) was found from an Arrhenius plot of rates that were measured at a number of temperatures. The pre-exponential factors were calculated in the usual way from the rates at 442°C and the E_a 's. For $\{110\}$ cobalt oxide catalyst, each listed "series" refers to runs made at successively decreasing temperatures. With this catalyst, linear Arrhenius plots were ob-

TABLE 78. DECOMPOSITION RATE DATA OF N₂O

Catalyst	Series No.	Area (cm ²)	P _{N₂O} (torr)	Net Rate at 442°C (mole cm ⁻² hr ⁻¹ torr ⁻¹)	E _a (kcal. mole ⁻¹)	Pre-Exp (mole cm ⁻² hr ⁻¹ torr ⁻¹)
Co ₃ O ₄ {100}		3.79	90.3	1.1 × 10 ⁻⁸	21	0.03
Co ₃ O ₄ {110}	1	1.73	89.0	1.0 × 10 ⁻⁸	24.5	0.33
	2	1.73	89.0	1.6 × 10 ⁻⁸	24.5	0.52
	3	1.73	89.0	2.2 × 10 ⁻⁸	24.5	0.72
	4	1.73	89.0	2.6 × 10 ⁻⁸	24.5	0.86
Co ₃ O ₄ {111}	1	2.60	90.3	4.3 × 10 ⁻⁹	23	0.052
	2	2.60	89.0	4.0 × 10 ⁻⁸	20	0.053
CoO-MgO {100}*	1	3.15	88.5	6.6 × 10 ⁻¹⁰	26	0.065
	2	3.15	45.5	3.4 × 10 ⁻¹⁰	26	0.033
CoO-MgO {100}†		4.8	89.6	4.0 × 10 ⁻¹¹	36	5.7
MgO-Irr. {100}		6.65	45.5	3.8 × 10 ⁻¹⁰	33	5.0
Blank						
(Silica Walls of Reaction Tube)	1	46	89.6	1.2 × 10 ⁻¹¹	35	0.64
(Silica Walls of Reaction Tube)	2	46	45.5	7.6 × 10 ⁻¹¹	29	0.05
(Silica Walls of Reaction Tube)	3	46	45.5	12 × 10 ⁻¹¹	35	0.64

* Mechanically polished only.

† Mechanical polish followed by chemical polish.

tained only for decreasing temperatures. It was found that after such a series, increasing the temperature activated the sample so that on subsequently decreasing the temperature, plots were obtained that had the same slope but a higher intercept than the original. This "hysteresis" was not observed with catalysts having {100} or {111} orientation; the data listed for them in Table 78 resulted from randomly varying the temperature. "Net rates" were calculated by subtracting from the observed rates in the presence of catalyst, appropriate "blanks" obtained when no catalyst was in the reaction zone (N₂O decomposition due solely to silica walls of the reaction zone). In the case of pure cobalt oxide, these blanks were one per cent or less of the total rate; for MgO-CoO the blank rate amounted to ~20% of the total rate.

It was impossible to measure the catalytic activity of pure single crystals of MgO (with or without the addition of fresh dislocations) not only because of the relatively high "blank" (catalysis by the silica walls above), but also because of an apparent interference of the MgO with the wall reaction. Thus, when MgO was in the reaction zone, not only was there observed no increase in rate over the blank rate, but in many cases the rate with MgO present was less than the blank (effective surface area of silica walls: 46 cm²; area of MgO: 17.6 cm²). This behavior is shown in Table 79, which gives the results of experiments in which runs with MgO present were "sandwiched" between runs made in the absence of MgO. The reproducibility of the blank runs as well as the significant decrease in rate in the presence of MgO are clearly illustrated.

While unirradiated MgO inhibits catalysis by the

TABLE 79. EFFECT OF MgO ON "BLANK" RATE

Catalyst	Run No.	P _{N₂O} (torr)	Temp. (°C)	Total Rate (microns/hr)
Blank (Reaction Tube Only)	1	45.5	426	128
Blank (Reaction Tube Only)	2	45.5	426	127
Blank and MgO	3	45.5	425	97
Blank and MgO	4	45.5	336	7.1
Blank and MgO	5	45.5	426	85
Blank and MgO	6	45.5	381	23
Blank	7	45.5	380	33
Blank	8	45.5	426	113

TABLE 80. EFFECT OF IRRADIATED MgO ON BLANK RATE

Catalyst	Run No.	P _{N₂O} (torr)	Temp. (°C)	Total Rate (microns/hr)
Blank + MgO (Irr.)	1	45.5	422	57
Blank	2	45.5	426	70
Blank + MgO (Irr.)	3	45.5	427	120
Blank	4	45.5	426	128

walls, neutron-irradiated MgO seems to enhance it. This effect is demonstrated in Table 80 (compare runs 1 and 2; 2 and 4). Again the data refer to an alternation of runs made in the presence of MgO catalyst with those made in its absence. While in the case of unirradiated MgO the decrease in rate is at least partially restored when the MgO is removed from the reaction zone, for the irradiated MgO, the increased rate observed in the presence of catalyst remains when the

catalyst is removed. Irradiated MgO increases the blank rate permanently. The data given in Table 78 for irradiated MgO were obtained by subtracting from the observed rates in the presence of catalyst, blank rates that were measured in a series of runs that immediately preceded them. This arbitrary procedure is of questionable validity in view of the above considerations.

Discussion

Because of the mutual interference between N_2O decomposition on the silica wall and decomposition on MgO, no quantitative data on the catalytic activity of MgO can be deduced. Such data may result from future high-surface-area experiments involving packing of the reaction zone with many thin MgO wafers in order to minimize the importance of the wall reaction. The rates for irradiated MgO, presented in Table 78, are about 25 times greater than the reported rate for nonirradiated MgO powders.⁽²⁴⁹⁾ It would appear from this that irradiation enhances catalysis by the walls or by MgO, but the data do not permit us to assign this increase to one or the other. Whatever the interrelationship between the wall reaction and the MgO crystals is, it does not seem to be the result of instrumental errors. [We have recalibrated thermocouples and pressure gauges, carefully examined and measured the reaction-zone temperature gradient and have run experiments at room temperature with N_2O and at high temperatures in the absence of N_2O (both of these last gave apparent rates that were negligible compared to the blanks). Also we have found that the cradle used to move the crystals into and out of the reaction zone does not affect the rate.] Nor does it seem likely that preferential adsorption of oxygen is the cause. The adsorption capacity of even irradiated MgO for oxygen is just too low.^(250, 251, 252) (We calculate that the change in pressure in our apparatus due to oxygen adsorption on our MgO crystals would be less than one micron.) We feel that the most likely interpretation involves the production or removal by the MgO of some impurity in the N_2O that acts as inhibitor or catalyst. Experiments are in progress to test this hypothesis.

⁽²⁴⁹⁾ Dell, R. M., Hess, R. A., and Weller, S. W., *Catalytic Decomposition of Nitrous Oxide over Magnesium Oxide*, Second Int. Cat. Cong., 1967 (1961).

⁽²⁵⁰⁾ Matsuma, I., Kubokawa, Y., and Toyama, O., *Decomposition of N_2O on MgO and CoO*, Nippon Kogaku Zasshi **81**, 1205 (1960).

⁽²⁵¹⁾ Winter, E. R. S., *The Reactivity of Oxide Surfaces* in ADVANCES IN CATALYSIS, Vol. X, W. G. Frankenberg, Ed., Academic Press, New York (1958).

⁽²⁵²⁾ Charman, H. B., and Dell, R. M., *Fast Neutron Damage at the Surface of Metal Oxides*, J. Phys. Chem. Solids, **23**, 1567 (1962).

For MgO-CoO and pure Co_3O_4 , catalysis by the walls was only a minor factor. The data of Table 78 show that pure Co_3O_4 is a more active catalyst than MgO-CoO by a ratio of 250 to 17. The higher activity of the mechanically polished MgO-CoO in comparison with the chemically polished sample can be attributed to either surface roughness or to a preferential solution of cobalt by the H_3PO_4 . Experiments with cleaved MgO-CoO crystals could distinguish between these alternatives. We feel that the effect cannot be due to a larger surface area in the mechanically polished crystal because the observed activation energies are so different.

Electron-probe analysis showed the surface concentration of cobalt in these mixed crystals to be between 50 and 100a/o. Thus from the standpoint of simple dilution of cobalt ions by magnesium ions, the large difference in rate between the pure Co_3O_4 and the MgO-CoO is unexpected. It cannot be due to CoO being less active than Co_3O_4 , because Matsuma, *et al.*⁽²⁵⁰⁾ report that CoO is the more active oxide, having an activation energy for this reaction of about 7 kcal/mole. A key to understanding this difference in activity may be found in the results of some measurements made on the electrical conductance of both the mechanically polished and the mechanically-plus-chemically polished crystals. The conductance was found to be orders of magnitude less than the pure cobalt oxide crystals. (For this reason we found it impossible to make electron diffraction studies on the mixed crystal.) This might be considered further evidence for the correspondence between semiconductivity and catalytic activity.⁽²⁵³⁾

The data of Table 78 show a somewhat higher activation energy and pre-exponential term for the {110} orientation than for the {100} and {111}, indicating that there are more reaction sites having lower activity on {110} and fewer sites having high activity on the other faces. An interpretation of this in terms of crystal structure has not yet been made. The {100} and {111} sites could be lattice positions, containing relatively exposed ions, which are approximately equal in number on both {100} and {111} faces. The {110} sites could be positions, containing relatively unexposed ions, which are more prevalent on the {110} face and about twenty times as numerous as the more active sites. These less active sites could possibly be created by high temperature reaction with N_2O .⁽²⁵⁴⁾

⁽²⁵³⁾ Schwab, G. M., "Experiments Connecting Semiconductor Properties and Catalysis" in *Semi-Conductor Surface Physics* [QC611C748].

⁽²⁵⁴⁾ The creation of active sites in catalysis by metals has been reported by Gwathmey [Cunningham and Gwathmey, *Advances in Catalysis*, Vol. IX (1957)], while Parravano has demonstrated this effect in oxides [G. Parravano, *Gass. Chimica Ital.* **91**, 467 (1961)].

I. IRRADIATION EFFECTS

1. Swelling and Growth in Uranium (B. A. LOOMIS)

Publications

1. B. A. Loomis, T. H. Blewitt, A. C. Klank and S. B. Gerber, *Elongation of Uranium Single Crystals During Neutron Irradiation*, Appl. Phys. Letters, **5**, No. 7, 135-137 (1964).
2. B. A. Loomis, *Swelling of Irradiated Uranium-Zirconium Alloys on Annealing*, Nuclear Science and Engineering, **20**, No. 1, 112 (1964) Letter to the Editor.

Swelling of Uranium on Postirradiation Annealing

The effect of preirradiation heat treatment and of a brief postirradiation anneal at a temperature in the beta range on the swelling of irradiated uranium during annealing at 620°C has been studied. The irradiated specimens—sealed in evacuated quartz capsules—were heated rapidly by insertion in a preheated furnace to minimize the effect of lower temperatures on heating to 620°C. This procedure provided a heating rate for the specimens of about 125°C per minute. The short anneal of the uranium in the beta phase before the anneal at 620°C consisted of heating the specimen to 720°C in about six minutes, holding at 720°C for three minutes, and cooling in air to 20°C. The procedures for determining the changes in density and for observing the microstructures of the annealed specimens in the electron microscope have been described previously.⁽²⁵⁵⁾

The data obtained from annealing specimens with different burnups at 620°C for 75 hr are shown in Figure 221 where each datum point represents a different specimen, and the swelling is expressed as the ratio of the change in density on annealing to the density of the specimen after irradiation. These results show that irradiated specimens, recrystallized in the alpha phase before irradiation, decrease in density on annealing substantially more than irradiated specimens quenched from the beta range before irradiation for burnups greater than 0.04 %. Also, it is clearly shown in Figure 221 that a brief anneal in the beta phase before annealing at 620°C greatly reduces the swelling.

Bubbles with diameters generally larger than one micron are visible on grain boundaries of recrystallized material in specimens of each preirradiation heat treatment (Figures 222, 223, 224). However, the specimens

deformed and recrystallized before irradiation are about 85 percent recrystallized after irradiation and annealing whereas the beta-quenched specimens are about 65 percent recrystallized. Small bubbles with diameters generally less than 0.5 micron are fairly uniformly distributed in the unrecrystallized material of specimens of each heat treatment.

The effect of a postirradiation beta anneal, before the high-alpha anneal, on the diameter and distribution of bubbles in specimens annealed at 620°C is apparent on comparison of the photomicrographs in Figures 224 and 225 (data points A and B, respectively, in Figure 221), together with the ranges of bubble diameters in these specimens presented in Table 81. The bubbles in the irradiated specimen that received a brief anneal in the beta range before the annealing at 620°C are more uniformly distributed and generally smaller in diameter (Figure 225) than the bubbles in the specimen that, after irradiation, only received an

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FIG. 221. Effect of Preirradiation Heat Treatment and of a Postirradiation Pulse Anneal at 720°C in the Beta Region on Swelling of Irradiated Uranium at 620°C.

⁽²⁵⁵⁾ Loomis, B. A., and Pracht, D. W., J. Nucl. Mat., **10**, 346 (1963).

110818

500×

FIG. 222. Photomicrograph Showing Clear Areas of Unre-crystallized Material and Areas of Recrystallized Material with Bubbles on Grain Boundaries in a Specimen Beta-quenched Before Irradiation, Irradiated to 0.17% Burnup, and then Annealed 75 hr at 620°C.

120428

12000×

FIG. 223. Photomicrograph Showing Bubbles on Grain Boundaries in a Specimen Beta-quenched Before Irradiation, Irradiated to 0.17% Burnup, and then Annealed 75 hr at 620°C.

anneal at 620°C (Figure 224). The largest bubbles (Table 81) in the latter specimen are mainly located on grain boundaries in recrystallized material. The

75-hr anneal at 620°C following the brief anneal at 720°C did not significantly alter the microstructure, which is characteristic of beta heat-treated uranium, nor the bubble distribution and bubble diameter (Table 81). A few cracks were visible in the micro-

120416

8000×

FIG. 224. Photomicrograph Showing Bubbles on Grain Boundaries in a Specimen Deformed and Recrystallized Before Irradiation, Irradiated to 0.17% Burnup, and then Annealed 75 hr at 620°C.

120473

8000×

FIG. 225. Photomicrograph Showing Uniform Distributi of Small Bubbles in a Specimen Deformed and Recrystallized before Irradiation, Irradiated to 0.17% Burnup, Pulse Annealed at 720°C, and then Annealed 75 hr at 620°C.

TABLE 81. DISTRIBUTION OF POROSITY IN IRRADIATED AND ANNEALED SPECIMENS

Specimen Heat Treatment	Number of Pores per cm ² in Given Size Range (microns)							Burnup (%)	$\pi/52n_i d_i^2 \dagger$ (%)	Density $\ddagger$ Decrease (%)
	0.02 to 0.06	0.06 to 0.15	0.15 to 0.3	0.3 to 0.6	0.6 to 1.3	1.3 to 2.5	2.5 to 5.1			
75 hr at 620°C	1×10^9 *	1×10^7	6×10^6	4×10^6	5×10^6	2×10^6	2×10^6	0.17	10.9	13.60
Pulse Anneal at 720°C**	1×10^8	3×10^8	2×10^7					0.17	2.7	1.54
Pulse Anneal at 720°C and 75 hr at 620°C**	3×10^8	2×10^8	7×10^6					0.17	1.8	1.77

* The estimated number of pores.

** The same specimen used for both of these observations.

† The ratio of the change in density to the initial density determined from the number of pores per cm², n_i , and pore diameters, d_i , observed in replicas. (Ref 255 with 4/5 correction factor from Ref 257).

‡ The ratio of the change in density to the density after irradiation determined by the buoyancy technique.

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FIG. 226. Apparatus for Study of Irradiation Growth.

structures of specimens with 0.17% burnup heated at 720°C, but cracks were not visible in the as-irradiated material nor in such specimens after being heated only at 620°C. The microstructures of specimens with other burnups were not examined.

The effect of the different preirradiation heat treatments on the swelling of uranium can be understood on consideration of the greater stability against irradiation growth of uranium quenched from the beta region comparison with deformed and recrystallized uranium.⁽²⁵⁶⁾ Since the specimens for this study were

⁽²⁵⁶⁾ Foote, F. G., *Progress in Nuclear Energy*, (Pergamon Press, 1956) Vol. I, 137.

irradiated at about 275°C in tight-fitting capsules, the strain induced in the specimens by growth during irradiation was less for the uranium quenched from the beta phase than for the deformed and recrystallized uranium. Consequently, recrystallization on annealing the irradiated specimens was more extensive for specimens with the preirradiation heat treatment of deformation and recrystallization than of quenching from the beta phase. Since recrystallization was more extensive in specimens of the former heat treatment, large gas-filled bubbles on grain boundaries were more prevalent and resulted in more swelling.

The lesser swelling of irradiated specimens that had

FIG. 227. Growth of Uranium Single Crystal in the [010] Direction during Irradiation.

TABLE 82. PREIRRADIATION AND POSTIRRADIATION MEASUREMENT OF LENGTH, DIAMETER, AND DENSITY OF URANIUM SINGLE CRYSTALS

	Crystal 16D-1 ~ [010]	Remarks
Burnup	0.002%	Calculated from the Neutron Flux
Preirradiation Length	2.101 cm	Micrometer Measurement
Postirradiation Length	2.275 cm	Micrometer Measurement
ΔL (Total Length Change)	0.174 cm	Micrometer Measurement
ΔL (Total Length Change)	0.173 cm	Transformer Output
Preirradiation Diameter	0.376-0.381 cm	Micrometer Measurement
Postirradiation Diameter	0.317 cm top 0.358-0.377 cm bottom	Micrometer Measurement
Preirradiation Density	19.038 ± 0.005 gm/cc	Buoyancy Technique with CCl_4
Postirradiation Density	18.790 ± 0.005 gm/cc	
Increase in Volume	1.33%	From Density Determination

received a brief anneal in the beta phase before annealing at 620°C is due in part to rapid heating to the alpha-beta transformation temperature whereby the

strain induced in the material by irradiation is replaced with material relatively free of strain and irradiation damage. Although the mechanism of the alpha-beta transformation is not completely understood, it is clear that the transformation does not lend itself to movement through relatively large distances of either fission-product gas atoms or bubbles. The bubbles in the irradiated uranium given a short anneal in the beta phase were fairly uniformly distributed with no obvious preference for grain boundaries or other microstructural features, in contrast to the preference for sites on grain boundaries exhibited by large bubbles in irradiated uranium that had been recrystallized in the alpha phase. It has been hypothesized that the bubbles on grain boundaries result from the sweeping of gas atoms by moving boundaries during recrystallization.⁽²⁵⁵⁻²⁵⁸⁾ The results of this study tend to support this hypothesis. The stability of the bubbles formed in the beta phase against further growth on annealing at 620°C can be attributed to the attainment of equilibrium between the gas pressure in the bubbles and the restraining pressure of surface tension.⁽²⁵⁹⁾

⁽²⁵⁷⁾ Bierlein, T. K., Mastel, B., and Leggett, R. D., "Metallographic Observations of Swelling in Uranium," HW-63848, USA (1960).

⁽²⁵⁸⁾ Bierlein, T. K., Leggett, R. D., Mastel, B., and Kosut, B. S., "Swelling in Uranium—Quantitative Metallography," *Fifth International Congress for Electron Microscopy*, (Academic Press, 1962) Vol. I, G-10.

⁽²⁵⁹⁾ Greenwood, G. W., Foreman, A. S. E., and Rimmer, D. E., *Nucl. Mat.*, **1**, 305 (1959).

Growth of Uranium during Neutron Irradiation

The growth of a uranium single crystal on thermal neutron irradiation at approximate temperatures of 100°K and 450°K was studied. The rod axis of the crystal was near to the [010] crystal direction. The change in length of the specimen was measured *in situ* by means of a linear differential transformer manufactured with ceramic insulated wire. The apparatus shown in Figure 226 (p. 235) is a schematic arrangement of the measuring apparatus that was calibrated with Johansson Blocks at 77°K and at room temperature. This apparatus was placed in the cryogenic facility located in Hole 44 of the CP-5 reactor.

The change in length of the crystal along the rod axis during irradiation is shown in Figure 227. The data were obtained from a single specimen, and the change in length of the specimen on irradiation is shown to commence at zero value with each change of irradiation temperature. The preirradiation and post-irradiation measurement of the length, diameter, and density of the specimen is presented in Table 82. The growth coefficient G , which relates the change in length to the number of fission events, is shown in Table 83 for various periods of bombardment.

TABLE 83. GROWTH COEFFICIENT G FOR IRRADIATED URANIUM SINGLE CRYSTAL

Crystal Orientation	Irradiation Temperature (°K)	Time of Irradiation (hours)	G^*
[010] 7° from rod axis	120	Fig. 227, Curve A, 0-40	150
[010] 7° from rod axis	440	Fig. 227, Curve B, 44-94	22,000
[010] 7° from rod axis	440	Fig. 227, Curve B, 94-440	2,100
[010] 7° from rod axis	130	Fig. 227, Curve C, 452-510	3,500
[010] 7° from rod axis	475	Fig. 227, Curve D, 514-542	2,100
[010] 7° from rod axis	100	Fig. 227, Curve E, 564-654	4,800
[010] 7° from rod axis	460	Fig. 227, Curve F, 659-818	1,500

(Change in length per unit of length at the irradiation temperature)

$$* G = \frac{\text{(Change in length per unit of length at the irradiation temperature)}}{\text{(Fraction of total atoms fissioned)}}$$

The interpretation of these results must await the irradiation of crystals that have a rod axis near to the [100] and [001] directions.

2. Migration and Coalescence of Gas Bubbles in Solids (Theoretical) (E. E. GRUBER)

The motivation for the interest shown in bubble migration and coalescence has generally been the problem of swelling of nuclear fuel materials due to the presence of fission gas bubbles. However, with growing understanding of the behavior of bubbles in solids, bubbles may be considered also as a means of understanding basic properties of materials, particularly since it is a rather simple matter to inject inert gases into pure metals. The primary objective during the past year has been to expand our understanding of the phenomenon of bubble coalescence. Particular emphasis has been on bubble coalescence by random walk; this problem was treated in an approximate fashion in the 1963 Annual Report.⁽²⁶⁰⁾ A considerably more elegant treatment, based on the discussion of colloid coagulation given by Chandrasekhar,⁽²⁶¹⁾ has recently been completed and is presented below. It includes a detailed analysis of the effects of random coalescence on the

frequency distribution of bubble sizes, as proposed in the preceding annual report.

Analysis of Brownian Motion Coalescence

Chandrasekhar, in his discussion of colloid coagulation, gave the number of "collisions" of colloid particles in the time increment Δt the relation⁽²⁶¹⁾

$$J_{ij}\Delta t \cong 4\pi D_{ij}R_{ij}G_iG_j\Delta t \quad (1)$$

In taking bubble coalescence as analogous to colloid coagulation, it is convenient to associate i and j with particular values of n_i , the number of gas atoms per bubble. D_{ij} is the appropriate diffusion coefficient, shown by Chandrasekhar⁽²⁶¹⁾ to be given by $D_{ij} = D_i + D_j$, the radius R_{ij} is just the sum of the bubble radii r_i and r_j , and G_i represents the concentration (number per cm³) of bubbles containing n_i gas atoms.

The bubble diffusion coefficient is given by⁽²⁶⁰⁾

$$D_i = 0.301 D_s(a_0/r_i)^4 \quad (2)$$

⁽²⁶⁰⁾ Annual Report for 1963, Metallurgy Division, ANL-6868, p. 404-5.

⁽²⁶¹⁾ Chandrasekhar, S., Rev. Mod. Phys., 15, No. 1 (1943).

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FIG. 228. Normalized Bubble Size Distributions for Several Values of Reduced Times τ .

where D_s is the surface diffusion coefficient and a_0 is the lattice parameter (the system is assumed to be f.c.c.).*

The approximation that all bubbles can be represented by one value of i greatly simplifies the solution of Equation (1). It can be shown by a procedure similar to that given in Reference 260 that the mean radius is given by

$$\bar{r}_{\text{appx.}} = 1.30 \left[\frac{MkTa_0^4 D_s t}{\gamma} \right]^{1/5} \quad (3)$$

where M is the dosage (number of gas atoms per cm^3) and γ is the surface tension. The bubble volume or change in sample volume based on this approximation is

$$\Delta V_{\text{appx.}} = 0.65 \frac{MkT}{\gamma} \left[\frac{MkTa_0^4 D_s t}{\gamma} \right]^{1/5} \quad (4)$$

The approximate result (Equation 3) agrees very well with the expression obtained by Speight⁽²⁶²⁾ by an approximate treatment based on the summation of a geometric series of pairwise coalescence times.

However, it would be expected that a range of bubble sizes would be present, and that since the larger bubbles contribute more to the volume change than the smaller ones, Equation (4) would give a conservative estimate of the volume change even if Equation (3) were perfectly correct. It was therefore considered worthwhile to undertake a more accurate treatment based on finite difference methods. A digital computer program was devised to calculate the change in an assumed initial

bubble size distribution according to Equation (1). The calculations will be described in greater detail elsewhere. The resulting distribution for three particular times are shown in Figure 228. The expected behavior is observed; that is, smaller bubbles disappear ($g(n, t)$ decreases with increasing τ for small n), forming larger ones ($g(n, t)$ increases for large n), the most probable size increases with time (the peak shifts toward larger n), and the total number of bubbles decreases (the area under the curve decreases). A "reduced" time τ is defined for convenience in calculation by

$$\tau \equiv 91.5M(\gamma/kT)^{3/2}a_0^4 D_s t, \quad (5)$$

which is dimensionless. The distribution function $g(n, \tau)$ has also been normalized by dividing the number of bubbles $G(n, \tau)$ per unit volume by the dosage M .

The important features of the distribution function $g(n, t)$ for our purposes are the appropriate mean values of n to give the mean radius (n_1), the mean number of atoms per bubble (n_2) and the mean value (n_3), the zeroth moment $\langle n^0 \rangle$, which gives the total number of bubbles per cm^3 , the ratio $\langle n^{1/2} \rangle / \langle n^0 \rangle$, which gives the mean radius, and the moment $\langle n^{3/2} \rangle$, which gives the change in volume of the sample. Figure 229 is a plot of these parameters as a function of reduced time, τ . The calculated slopes of these plots, after a short time required for the initial distribution (a delta function) to assume the proper shape, varied within about 0.5% of 2/5 for n_1 , n_2 and n_3 . The same accuracy was found for the other slopes, which were about $-2/5$ for $\langle n^0 \rangle$, $-1/5$ for $\langle n^{1/2} \rangle$, 0 for $\langle n^1 \rangle$ and $1/5$ for $\langle n^{3/2} \rangle$. As a check on the calculation, the total number of atoms $\langle n^1 \rangle$ was calculated. After 400 finite-difference steps, or a range in τ of more than 6 powers of 10, the initial normalized value of unity had decreased only to 0.99998.

It was possible from these results to standardize the distribution curve as shown in Figure 230. The theoretical distribution function $G(n, t)$ can be calculated for any set of experimental parameters from this

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FIG. 229. Dependence of Some Parameters of the Bubble Size Distribution on the Reduced Time τ .

* The previously given numerical coefficient was incorrect. (262) Speight, M. V., J. Nucl. Matl., **12**, 2 (1964).

single curve by multiplying the values on the ordinate by $M\tau^{-4/5}$ and those on the abscissa by $\tau^{2/5}$ (i.e., $G(n,t) = M\tau^{-4/5} f(u)$ and $n = \tau^{2/5} u$).

It can be shown from the results that

$$\bar{r} = 1.30 \left[\frac{MkTa_0^4 D_s t}{\gamma} \right]^{1/5} \quad (6)$$

and that

$$\Delta V = 0.75 \frac{MkT}{\gamma} \left[\frac{MkTa_0^4 D_s t}{\gamma} \right]^{1/5} \quad (7)$$

As an example of the predicted results, consider the case of copper annealed at 1000°K after irradiation which produces $M = 10^{20}$ atoms/cm³, with $\gamma = 1.7 \times 10^3$ ergs/cm², $a_0 = 2.55$ Å and $D_s = 10^{-5}$ cm²/sec. The term in brackets is about $3.3 \times 10^{-42} t$. For $t = 3 \times 10^6$ sec., or about one month, the calculated values are $\bar{r} \cong 42$ Å and $\Delta V \cong 0.006$ %. For $t \approx 10^5$ months these values are increased by a factor of ten.

It may appear that the results of this analysis are almost entirely negative; the swelling predicted for the assumed conditions is completely negligible for any reasonable length of time, the average bubble size is practically unobservable, and furthermore the rather expensive computer solution to the problem gives hardly any information beyond that obtained by the approximate solution. However, these negative results are not without value. The limited effect of random coalescence emphasizes the need for more quantitative consideration of other mechanisms of swelling, such as grain boundary sweeping,^(263,264) dislocation effects,⁽²⁶⁵⁾ thermal gradients and other external effects, and perhaps bubble interactions.

The computer solution to the problem is not of great value in this particular case. However, the re-

⁽²⁶³⁾ Loomis, B. A., and Pracht, D. W., *J. Nucl. Matl.*, **10**, 4 (1963).

⁽²⁶⁴⁾ Speight, M. V., and Greenwood, G. W., *Phil. Mag.*, **9**, 100 (1964).

⁽²⁶⁵⁾ Barnes, R. S., *J. Nucl. Matl.*, **11**, 2 (1964).

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FIG. 230. Standardized Bubble Size Distribution.

sults clearly show that it is a valid approach to the problem, and it is noteworthy that even though the results for $\bar{r}$ are identical to the approximate solution, the more accurate treatment predicts an increase of about 15 % in ΔV .

For the case of a thermal gradient as a driving force for migration approximate treatments are more tenuous because of the dependence on the shape of the distribution curve. Some approach similar to that used here it necessary for a quantitative theoretical treatment. Since our particular interest is in the migration and coalescence of bubbles in a thermal gradient, attention has also been given to this problem, and quantitative results are expected soon. Experiments to be analyzed in terms of the results are also planned for the coming year. Immediate interest lies in the relationship between bubble velocity and applied force, as given in the previous report.⁽²⁶⁰⁾ According to irreversible thermodynamics, a thermal gradient is expected to exert a force on a bubble proportional to the "heat of transport" (Q^*) and to the thermal gradient.

3. Fission Tracks in Evaporated Metal Films (K. L. MERKLE)

Publication

K. L. Merkle, *Heavy Ion Tracks in Films of Isolated Particles*, Proceedings of the Third European Regional Conference on Electron Microscopy, Prague 1964, Vol. A, 195.

The basic mechanisms of track formation in evaporated films can be understood in terms of the isolated

particle model.^(266,267) This model⁽²⁶⁶⁾ predicts tracks in films with a particle size that is smaller than a certain critical size. This critical size is also a function of the energy loss per unit path length of the fragment.

⁽²⁶⁶⁾ Merkle, K. L., *Phys. Rev. Letters*, **9**, 150 (1962).

⁽²⁶⁷⁾ Goland, A. N., and Paskin, A., *J. Appl. Phys.*, **35**, 2188 (1964).

39506

27000×

FIG. 231. Gold Films on Carbon Substrate Irradiated with Fission Fragments. The thicknesses indicated refer to equivalent continuous films.

In general

$$N_{cr} = \frac{1}{E_v} \frac{dE}{dX} l \quad (1)$$

where N_{cr} is the maximum number of atoms contained in a particle with an atomic heat of vaporization of E_v if it is to be vaporized by a fragment of energy loss $\frac{dE}{dX}$

whose path inside the particle is of the length l . Early experiments⁽²⁶⁶⁾ established that there is an upper limit of particle size that can be vaporized. During the past year experiments on a number of films consisting of gold particles on a suitable substrate were performed and the tracks were studied as a function of the film thickness. Figure 231 gives an example of fission tracks in films of various thickness of gold. The determination of the limiting particle size can be done in a number of ways:

- a) Individual particles are observed before irradiation and after irradiation. The trajectory of the fragment is established from the track. The intersection of the trajectory with the particle allows the determination of the energy input.

Comparison of values for particles that have been vaporized and for particles that have not been vaporized gives the maximum particle size.

- b) By measuring the width of tracks in films consisting of large particles. Knowing the amount of material removed from the track and the energy loss per unit path length one gets the critical size.

$$N_{cr}/l = N_0 a \cdot h \quad (2)$$

where N_0 is the number of gold atoms per cm^3 , a the width of the track, and h the thickness of the film. If we combine Equations (1) and (2) we get

$$\frac{1}{E_v} \frac{dE}{dX} = N_0 a \cdot h \quad (3)$$

We have written this equation in this simple form but in applying this equation to a particular film one has to bear in mind that the path of the fragment is not solely in the gold particles (see Figure 232). Therefore $\frac{dE}{dX}$ in Equation (3) is not the energy loss in gold but the average loss along the path of the fragment

which is given by

$$\left(\frac{dE}{dX}\right)_{\text{Au}} = \left(\frac{dE}{dX}\right)_{\text{Au}} \gamma$$

where γ is the fraction of the path that is in gold.

Testing Equation (3) by experiment we find that the limiting size is larger than given by this equation by about a factor of 2. More experiments are needed to establish accurately the limiting size. A tentative explanation of this larger than theoretical critical size is the following: The transfer of energy from the electrons to the atoms is fairly rapid, of the order of 10^{-13}

sec. The heat of vaporization, however, is measured under equilibrium conditions from a semi-infinite body; therefore one has to apply a correction to the energy necessary to vaporize a small particle, which is smaller by the amount of the surface energy and can be a considerable fraction of the total energy. However, this correction is not large enough to account for the observed deviations. There is, however, the possibility that the atoms do not come off individually but come off in larger aggregates in which case the vaporization energy would be reduced by the binding energy between these clusters of atoms. This process is very well possible because the time for energy transfer from the electrons to the lattice atoms is only of the order of a few lattice vibrations and one has therefore certainly nonequilibrium conditions.

Another interesting result concerns the films that consist of very small particles. Figure 233 shows an example of a track produced by a fission fragment from the spontaneous fission of Cf^{252} in a film of this nature. As pointed out before,⁽²⁶⁶⁾ not only particles in the direct path of the fragment are vaporized but also

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FIG. 232. Fission Fragment Passing through Film of Isolated Gold Particles.

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160,000X

FIG. 233. Fission Track from Spontaneous Fission of Cf^{252} in Film of Gold Particles on Carbon Substrate. Average film thickness is $18\text{\AA}$.

neighboring particles. This can be explained in terms of electrons escaping from one particle and being trapped in another one.^(268,269) If a fission fragment travels parallel to the surface as in Figure 232 one can determine the average energy loss per unit path length by considering the geometrical arrangement of the particles. Comparing this value with the energy necessary to vaporize the material in the track shows that practically all the energy available is used for vaporization. This means that the energy is originally concentrated only in one particle is transferred to its neighboring particles in a very efficient way. If the electrons were to come off isotropically, only a small fraction would intersect a neighboring particle because of the small solid angle subtended. Some deviation from the isotropic case can be expected due to image forces. The more energetic electrons, however, should not be

affected by this too much. The very efficient energy transfer can, however, be explained by means of the isolated particle model (see for example Figure 183, ANL-6677 (1962)). A potential is being built up around the particle through which the fission fragment has passed, the excited electrons will be retained in the vicinity of this particle by this potential. While the electrons move in the insulating substrate they have relatively small cross section for energy loss. However, as soon as an electron enters a metal particle, it will lose energy very rapidly via electron-electron collisions. Therefore the chance for it to escape is practically zero, unless it has a very high initial energy (>100 eV). The particles therefore act merely as trapping centers for electrons and the electrons move back and forth in the potential of the original particle until they encounter a neighboring particle and are trapped.

4. The Effect of Fast-Neutron Irradiation on Metals and Alloys (J. A. HORAK)

Irradiation capsules containing the following pure metals, copper, silver, gold, platinum, iron, nickel,

flux was 5×10^{11} n/cm² of energy greater than 1.0 Mev.^(270,271) The point-defect production in these

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FIG. 234a. Increase in Irradiation-Induced Electrical Resistivity as a Function of Irradiation Time for Copper, Silver, and Gold.

palladium, and the alloy Cu₃Au have been irradiated at 4°K in the CP-5 cryogenic facility. The neutron

materials was monitored by electrical-resistivity measurements during the irradiation. Preliminary results

⁽²⁶⁸⁾ ANL-6677, 360 (1962).

⁽²⁶⁹⁾ Merkle, K. L., *Heavy Ion Tracks in Films of Isolated Particles*, Proceeding of the Third European Regional Conference on Electron Microscopy, Prague 1964, Vol. A, 195.

⁽²⁷⁰⁾ Rossin, A. D., ANL-6826 (1964).

⁽²⁷¹⁾ Blewitt, T. H., "The Interaction of Radiation with Solids," in *Radiation Damage in Solids*, J. Wiley & Sons, New York, (1964).

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FIG. 234b. Increase in Irradiation-Induced Electrical Resistivity as a Function of Irradiation Time for Iron, Nickel, and Palladium.

as shown in Figures 234a and 234b indicate that the rate of point-defect production is linear with respect to neutron dose, at least for the doses employed thus far (10^{17} n/cm² of $E > 0.1$ Mev). No observation of saturation of defect production was observed. The initial transients that are evident in the two figures are thought to be due to internal heating in the specimens due to (n, γ) reactions when the reactor starts up. This same type of behavior occurred after the reactor was shut down after 1400 minutes of the experiment. The $\Delta\rho$ dose plot after the shutdown is also linear; however, it is displaced slightly from the initial line. This displacement is due to the transient after startup and to the method of adjusting the experimental time to a

power level of 4.4 Mw (normal operating power) while the reactor is up and down and operating at power levels between 0 and 4.4 Mw.

The data for the platinum exhibited much scatter, and at this time are not considered as representative. For the Cu₃Au, ρ was not computed, however the ΔR versus dose dependence was linear with a displacement of the two linear regions at 1400 minutes as for the other materials.

Other irradiation capsules are currently being prepared to further study the rate of point defect production during 4°K fast neutron irradiation; and to study the kinetics of the annihilation of irradiation-induced point defects on postirradiation isochronal annealing.

5. Recovery of Lattice Parameter and Electrical Resistivity in Low-Temperature Neutron-Irradiated Copper (T. H. BLEWITT, B. D. SHARMA,* AND J. A. TESK**)

Extensive investigations involving the recovery of various physical parameters of noble metals irradiated

* I.N.S.E. Affiliate, Indian Atomic Energy Establishment, Trombay, Bombay, India.

** University of Illinois, Chicago Circle, Consultant to Metallurgy Division.

at low temperatures have been reported in recent years. These studies, which include changes in electrical resistivity, volume, stored energy and lattice parameters, etc., show that the radiation damage recovers in discrete stages. These annealing stages are associated usually with "structural processes" involving anni-

hilation of interstitial atoms and lattice vacancies either by recombination or by individual migration to sinks. Since different defect configurations contribute differently to any two parameters, knowledge of the changes in more than one becomes essential to the understanding of the processes involved in the recovery spectrum.

Simultaneous changes in the length and electrical resistivity during annealing of neutron-irradiated, B¹⁰-doped copper have been reported by Blewitt *et al.*⁽²⁷²⁾ These studies show that though both length and resistivity changes have almost one to one correspondence in all stages, an exact linear relationship does not exist throughout the recovery. It is taken as evidence of the fact that different defects migrate in different stages. In contrast to this, Simmons and Balluffi⁽²⁷³⁾ have estimated a constant value for resistivity-lattice parameter change ratio, $\Delta\rho/\Delta a/a$, for the recovery of deuteron damage in copper, suggesting interstitial-vacancy recombination to be the predominant factor in all annealing stages. Theoretical calculations⁽²⁷⁴⁾ have shown that the lattice relaxation due to the presence of point defects can be expressed by $(\Delta a/a) = Ap$ where A is a constant and p is molar fraction of defects in the metal. Further, the values of A in copper have been found to be equal to 1.0 and -0.2 for interstitial atoms and vacancies respectively. The values of $\Delta\rho/\Delta a/a$, associated with the migration of interstitials and vacancies in copper should therefore differ significantly. Our studies are therefore aimed at measuring simultaneously the changes in resistivity and lattice parameters during low-temperature annealing in the hope of resolving the issue.

To date all the necessary equipment for the experiment have been constructed and tested. The setup for lattice-parameter measurement employs Bond's technique.⁽²⁷⁵⁾ This method, which is like the symmetrical back-reflection method, consists in mounting a highly perfect single crystal on a precision spectrometer and aligning it for a particular Bragg reflection on one side of the X-ray beam. Next, the crystal is rotated so that the same reflection can be picked up on the other side

of the beam. The rotation of the crystal equals $180^\circ - \theta$, where θ is the Bragg angle. The single crystals to be used in these experiments have to be free of subgrains and of as low dislocation density as possible. A liquid helium cryostat has been constructed and mounted on the precision X-ray spectrometer (reading up to a second of arc). A proportional counter with a wide window mounted on the spectrometer arm at a distance of 12" from the crystal acts as a detector. A pinhole collimator with maximum angular divergence of $15'$ is mounted on a cobalt target X-ray tube. With the tube operating at 50 KV and 7 mA and a 0.0009" Fe filter, a very high counting rate, 25,000 counts/sec, was obtained for (400) reflections of copper. A higher counting rate is preferred since in the postirradiation measurements the general background is expected to go up considerably due to γ -activity of the capsule. With the present setup an accuracy of 10^{-6} can be obtained in the value of $\Delta d/\Delta\theta$ for (400) reflections of copper at liquid helium temperature. This accuracy will be maintained throughout the experiment, as it is intended to pulse anneal the specimens and make all measurements at liquid helium temperature. This further obviates the necessity of highly accurate temperature measurements during the warmup.

The copper crystals for irradiation are mounted in a double-walled capsule which also acts as the liquid helium chamber of the X-ray cryostat. The single crystal is mounted in the outer chamber, which has a 0.25 mm thick (0.010") beryllium window for X-ray transmission and can be evacuated and sealed. The inner chamber is used for mounting the resistivity specimen, heater, carbon resistors, and lead wires, etc. Since the γ -activity of the capsule has to be kept as low as possible, 304 stainless steel, 14% Al-bronze and copper were selected for making various parts of the capsule (after some preliminary irradiation tests). The initial activity of the capsule after ten days of irradiation in Hole VT-53 is expected to be about 25 r/hr; it is expected to decrease to 1.5 r/hr after cooling for a week.

Single crystals of copper have been grown and cut for (100) orientation. Technique for aligning the crystal for any Bragg reflection has been standardized. A dry run has been made to determine the preirradiation lattice parameter of copper at liquid helium temperature and for standardizing the technique of pulse annealing. The value of the lattice parameter at 4.2°K was found to be $3.60288 \pm 0.00030 \text{ \AA}$. An irradiation test is in progress.

⁽²⁷²⁾ Blewitt, T. H., *Proc. of the Internat'l School of Phys., E. Fermi, XVIII Corso*, Academic Press, New York and London (1962).

⁽²⁷³⁾ Simmons, R. V., and Balluffi, R. W., *Phys. Rev.*, **109**, 1142 (1958).

⁽²⁷⁴⁾ Tucker, C W., and Sampson, J. B., *Acta Met.*, **2**, 433 (1954).

⁽²⁷⁵⁾ Bond, W. L., *Acta Cryst.*, **13**, 814 (1960).

6. Low-Temperature Energy Release in Irradiated Copper (M. LUCAS)

The energy release per unit change in resistivity is an important quantity in radiation-damage studies because it is sensitive to the type of bombardment, and because the contribution of a Frenkel defect to resistivity and to stored energy has received extensive theoretical study. The fast-neutron environment of the refrigerated Hole VT-53 in the CP-5 reactor provides a unique opportunity to measure $\Delta E/\Delta \rho$ after a bombardment expected to favor the production of clusters of displacement pairs more strongly than irradiations hitherto reported in the literature.⁽²⁷⁶⁻²⁸⁰⁾

The stored-energy release following reactor irradiation of a specimen at low temperature can be measured by studying the rate of warmup produced by a known heat input. During irradiation, the sample is cooled by keeping it in contact with the cryostat. Subsequently it must be isolated and the rate of rise of temperature measured as nuclear heating is supplied by the reactor. The nuclear heating is measured by warming the sample through the same temperature interval on a separate occasion when no stored energy is present—usually once before any irradiation and again in a third run made after the run in which energy release occurs. In practice, complete isolation of the sample is not possible and Blewitt *et al.*⁽²⁸⁰⁾ write the release E as:

$$E = \int \gamma' \left[\left(\frac{dT}{dt} \right)_B - \left(\frac{dT}{dt} \right)_A \right] dt \quad (1)$$

where T is the temperature, t the time, and the subscripts A and B refer to warming with and without stored energy, respectively. The effective heat input after losses through the switch is γ' . If the specific heat C_p is known independently:

$$\gamma' = C_p \left(\frac{dT}{dt} \right)_B \quad (2)$$

Because the heat released is small and occurs gradually, the thermometry and heat switch are basic to the success of the experiment. The heat switch described by Blewitt *et al.*⁽²⁸⁰⁾ will be used again, but a helium gas

thermometer has been designed and built to replace the thermocouple.

A cylindrical copper specimen of about 40 gm weight and 25 cc volume forms the thermometer bulb and is connected by a stainless steel capillary (0.028" OD, 0.019" ID) to a pressure transducer at the top of the reactor. The transducer is frictionless, of infinite resolution, and has an output of 1 mV/psia. The dead space of the thermometer is less than 2.5 cc, so when the system is filled with helium gas to a pressure of 300 psia at room temperature, the sensitivity is roughly constant at 1 mV/°K. With this sensitivity, changes of $\frac{1}{4}$ °K are easily followed on an extended range millivolt recorder. A rupture disc protects the bulb against overpressure.

Blewitt⁽²⁷⁶⁾ noted spurious emf's in the thermocouple due to changing temperature gradients in the lead wires as they passed through the reactor shielding. As the gas in the capillary is exposed to these fluctuating temperature gradients, the simple thermometer described above must be compensated. This requires provision of a dummy system which is an exact replica of the main thermometer save that the bulb is missing. If both systems are filled to a pressure p_0 at a temperature T_0 , and if p_0' denotes the pressure in the dummy when the main system reads p , the temperature of the bulb is given by:

$$\frac{T}{T_0} = \frac{p/p_0}{1 + N(1 - p/p_0')} \quad (3)$$

where N is the ratio of the volume of the dummy (and therefore of the dead space) to that of the bulb. Such a thermometer is compensated for temperature changes at the warm end as well as along the capillary. In the thermometer built for Hole VT-53 of the CP-5 reactor a second stainless steel capillary (0.040" OD, 0.034" ID) sheaths the first so that the cross sectional area inside the inner tube differs by <3% from the area between the tubes. The volumes at the warm end are also the same within 3%. If the thermometer is calibrated at the normal boiling points of hydrogen and nitrogen, it can be used for intermediate temperatures without correction for such effects as the imperfect nature of the helium gas.

Another important consideration is the response time of the thermometer. If this is too long, the inevitable heat leak allows the energy release in the specimen to disappear before it can produce a measurable temperature change. Granato and Nilan⁽²⁷⁸⁾ discuss this from the point of view of the maximum permissible heat leak in the differential method of measuring stored

⁽²⁷⁶⁾ Blewitt, T. H., *Proc. International School of Physics, E. Fermi, XVIII Corso*, Academic Press, N. Y. and London (1962).

⁽²⁷⁷⁾ Holmes, D. K., *Radiation Damage in Solids*, J. Wiley & Sons, New York (1964).

⁽²⁷⁸⁾ Granato, A. V., and Nilan, T. G., *Phys. Rev.*, **137**, A1233 (1965).

⁽²⁷⁹⁾ Meechan, C. J., and Sosin, A., *Phys. Rev.*, **113**, 422 (1959).

⁽²⁸⁰⁾ Blewitt, T. H., Coltman, R. R., and Klabunde, C. S., *J. Phys. Soc. of Japan* **18**, Suppl. III (*Proc. of Internat'l Conf. on Crystal Lattice Defects*, 1962 288-9 (1963)).

energy. Their analysis can be applied to this method provided we talk about warming the same specimen twice rather than two specimens once. It shows that the energy release must occur in a time Δt not much greater than the time constant mC_p/P associated with the heat leak, where m is the mass of the specimen, P the heat loss rate coefficient, and C_p is assumed constant. Further, Granato and Nilan⁽²⁷⁸⁾ point out that if C_p increases with the cube of the temperature, the system behaves as if an effective heat loss coefficient of $(3mC_p/T)(\Delta T/\Delta t)$ were present, even if P were zero. Thus the thermometer must be able to follow a heating rate given by:

$$\Delta t \leq \frac{mC_p}{P + \frac{3mC_p}{T} \frac{\Delta T}{\Delta t}} \quad (4)$$

or

$$\frac{\Delta T}{\Delta t} \geq \frac{P}{mC_p \left(\frac{1}{\Delta T} - \frac{3}{T} \right)} \quad (5)$$

and P can be estimated from the expected heat leak down the capillaries and helium gas column. Also there will be a contribution from two No. 40 copper wires and one No. 30 constantan wire needed to measure the resistivity change associated with the energy release. A small copper wire within the bulb forms the resistivity specimen. If the capillaries, gas column and lead wires reach 300°K at 30 cm above the specimen, they contribute about 12 μ cal/deg sec to P . The radiant heat loss to the walls of the switch opposes this but only contributes at the higher temperatures, about 10 μ cal/deg sec at 80°K. The gas conduction across the

switch also contributes about this amount. We take $P = 60 \mu$ cal/deg sec as the largest probable heat leak.

The main peak in the energy release is expected to be at $T = 40^\circ\text{K}$, and of width $\Delta T = 10^\circ\text{K}$; so for 40 gm of copper of specific heat 0.015 cal/gm°K

$$\frac{\Delta T}{\Delta t} \geq 4.10^{-3} \text{ deg/sec.} \quad (6)$$

Trial experiments near 80°K have indicated that the thermometer can respond one hundred times more rapidly than this and still maintain reproducibility within $\frac{1}{4}^\circ\text{K}$. Holten's⁽²⁸¹⁾ results indicate it may be necessary to fill the bulb with loosely packed copper wire to facilitate rapid heat transfer to all the gas if the present response time of 0.4 deg/sec is to be retained at lower temperatures.

A heat leak not yet discussed is that associated with the expulsion of helium gas from the bulb during warming. At 40°K the gas in the bulb has a heat capacity about 20% that of the copper and during warming gas expelled from the bulb carries heat with it. Of the heat supplied by stored energy the proportion carried away by the gas is not available to produce a rise in specimen temperature. It is thought that one week's irradiation in Hole VT-53 of the CP-5 reactor will give about 3 calories of stored energy to be subsequently released from about 25 to 50°K. At these temperatures and the corresponding thermometer pressures the density of the gas changes by about 10^{-3} gm/cc. Consequently 25×10^{-3} gm with specific heat 1.25 cal/gm are ejected and the heat leak is only a little more than 1 % of the energy release.

Pending satisfactory completion of leak testing and thermometer calibration, the system will be placed in Hole VT-53.

7. Irradiation and Solid Solution Strengthening (T. J. KOPPENAAAL)

Publications

- T. J. Koppenaal and D. Kuhlmann-Wilsdorf, *The Effect of Prestressing on the Strength of Neutron-Irradiated Copper Single Crystals*, Appl. Phys. Ltrs. **4**, 59 (1964).
- T. J. Koppenaal and P. R. V. Evans, *Microstraining in Polycrystalline Niobium*, J. Inst. Metals **92**, 238 (1964). (Not based upon ANL work).
- R. M. J. Cotterill and T. J. Koppenaal, *Effects of Type and Density of Defects on Yield Strength of Neutron-Irradiated Cu and Cu-14 at. % Al Alloy*, Appl. Phys. Ltrs. **4**, 156 (1964).

T. J. Koppenaal, *The Effect of Neutron Irradiation on the Strength of $\alpha\text{Cu-Al}$ Single Crystals*, Acta Met. **12**, 487 (1964).

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T. J. Koppenaal, *The Microstrain Yield Stress*

⁽²⁸¹⁾ Holten, D. C., *Advances in Cryogenic Engineering*, **9**, Ed., K. D. Timmerhaus, 406 (1963).

Neutron-Irradiated Copper Single Crystals, J. Metals **16**, 85 (1964). (Abstract).

T. J. Koppenaal and R. M. J. Cotterill, *Annealing Studies in Neutron-Irradiated Copper Alloys*, J. Metals **16**, 771 (1964). (Abstract).

*The Effect of Aluminum on the Type of Defects in Neutron-Irradiated Copper**

The addition of 14 a/o Al to copper was shown to suppress the formation of the large interstitial loops found in neutron-irradiated copper. For samples simultaneously irradiated at $\sim 100^\circ\text{C}$ to 1.1×10^{19} fast neutrons/cm², interstitial loops up to 500 Å are found in pure copper whereas the largest defects in a Cu-14a/o Al alloy are only 75 Å. The most plausible explanation for this behavior is that a considerable amount of interstitial-solute atom binding occurs in the alloy. The number of free interstitials might then be so low that loops either cannot be nucleated, or, having been nucleated, cannot grow. The details of this research are given in publication Number 3 listed above.

Strength-Annealing Studies in Neutron-Irradiated Copper Base Alloy Single Crystals

Isochronal annealing studies in neutron-irradiated copper and $\alpha\text{Cu-Al}$ single crystals containing 0.5 to 14 a/o Al have shown that the relative amount of strengthening annealed out at a given temperature increases with increasing aluminum concentrations. The same general behavior is observed with gallium of germanium as the solute. Isothermal annealing studies show that the activation energy for this process is not unique, but rather increases as the degree of recovery increases. Because of this, it is difficult to assign a specific mechanism to the annealing process, since several different types of processes are evidently taking place (each with its own activation energy). A complete description of this investigation is given in publication Number 6.

Neutron-Irradiation Strengthening in Copper and Copper-Alloy Single Crystals

A determination of the activation energy for plastic deformation (assuming that a thermally activated process is involved) is not simple, since the presence of an applied stress as well as thermal energy contributes to the overall energy needed to achieve plastic strain. It thus becomes necessary to distinguish between the amount of energy supplied by thermal energy and that supplied by the applied stress. This is illustrated in the force-distance curve shown in Figure 235. Under an effective stress, τ^* (corresponding to a force $F' =$

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FIG. 235. Schematic Force-Distance Curve for a Thermally Activated Plastic Deformation Process.

$\tau^* b l^*$), a dislocation takes the position x_0 . The amount of thermal energy (activation energy) required to overcome the energy barrier is H , according to Basinski.⁽²⁸²⁾ Conrad and Wiedersich⁽²⁸³⁾ have shown that

$$H = -kT^2 \left(\frac{\partial \ln \dot{\gamma}}{\partial \tau^*} \right)_T \left(\frac{\partial \tau^*}{\partial T} \right)_{\dot{\gamma}}, \quad (1)$$

where k is Boltzman's constant, T the absolute temperature, $\dot{\gamma}$ the strain rate, and τ^* the effective stress (the effective stress is defined as the thermally activated portion of the applied stress and is therefore given by the applied stress minus the athermal component of the stress). The energy involved in moving the dislocation from x_0 to x'_0 is defined as H^* and is given by,

$$H^* = H + \tau^* b l^* (x_0 - x'_0), \quad (2)$$

where b is the Burger's vector and l^* the effective obstacle spacing on the glide plane. By defining a quantity v^* , termed the effective activation volume, as

$$v^* = b l^* (x_0 - x'_0), \quad (3)$$

equation (2) can be expressed as,

$$H = H^* - \tau^* v^*. \quad (4)$$

Conrad and Wiedersich showed that v^* can be experimentally obtained by the relationship,

$$v^* = kT \left(\frac{\partial \ln \dot{\gamma}}{\partial \tau^*} \right)_T. \quad (5)$$

Thus, by experimentally measuring $\left(\frac{\partial \tau^*}{\partial T} \right)_{\dot{\gamma}}$ and $\left(\frac{\partial \ln \dot{\gamma}}{\partial \tau^*} \right)_T$ we can obtain H and v^* . However, the

⁽²⁸²⁾ Basinski, Z. S., Phil. Mag., **4**, 393 (1959).

⁽²⁸³⁾ Conrad, H., and Wiedersich, H., Acta Met., **8**, 128 (1960).

* In collaboration with R. M. J. Cotterill, ANL Metallurgy Division.

magnitude of these properties are of only limited use since Figure 235 shows that H and v^* are stress dependent. The activation energy one would like to be able to determine is H_0 , the area under the entire force-distance curve. The only method of accomplishing this is to determine H as a function of stress and extrapolate the results back to zero effective stress. At $\tau^* = 0$, Figure 235 shows $H = H^* = H_0$. The activation volume under zero effective stress is defined as v_0^* and is determined in a similar fashion.

We have determined experimentally the activation energy (H) and activation volume (v^*) for neutron-irradiated copper and a series of Cu-alloy single crystals

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FIG. 236a. Flow Stress (τ) versus Testing Temperature (T) for Crystals Neutron Irradiated to 1.6×10^{18} nvt.

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FIG. 236b. Flow Stress, τ , versus Testing Temperature, T , for Crystals Neutron Irradiated to 3.4×10^{19} and 9.0×10^{19} nvt.

from the data shown in Figures 236a and 236b. Figure 236a shows the flow stress, τ , as a function of testing temperature for a dose of 1.6×10^{18} nvt. Solutes are seen to have little effect on the flow stress between 77 and 373°K, but produce a decrease at 4.2°K. A fairly large amount of solute is necessary to produce the decrease since 0.5 at. % Al seems to have little, if any, effect.

Figure 236b shows τ versus T for crystals irradiated to 3.4×10^{19} and 9.0×10^{19} nvt. The decrease in the flow stress at 4.2°K in the Cu-14 at. % Al crystals as compared to the copper crystals is noted for each dose. The flow stress at 4.2°K in both the copper and the Cu-14 at. % Al crystals appears to have reached a saturation value at 3.4×10^{19} nvt, since no significant increase is noted with 9.0×10^{19} nvt. The flow stress at room temperatures has increased over the same dose range in both the copper and the Cu-14 at. % Al crystals. Thus, our results are similar to those of Blewitt, *et al.*⁽²⁸⁴⁾ in that saturation is first observed at the lowest temperatures. One possible reason for the strength reduction at 4.2°K in the high solute alloys is that the slip mechanism may not be the same. We are currently planning deformation-electron microscopy studies to help clarify this.

A number of the copper crystals irradiated to 9.0×10^{19} nvt were annealed to produce roughly $\frac{3}{4}$, $\frac{1}{2}$ and $\frac{1}{4}$ of the as-irradiated strength at 373°K. The flow stress was then measured from 4.2 to 373°K after each anneal and the results are shown in Figure 237. As the flow stress at 373°K is lowered by annealing, the temperature dependence of the flow stress at low temperatures is greatly reduced. In the crystal annealed at 475°C for 70 minutes, the flow stress at 4.2°K was only ~ 20 per cent larger than that at 373°K; in the as-irradiated condition the flow stress is much more temperature dependent (the dashed line in Figure 237 shows the behavior for as-irradiated copper for a dose of 1.6×10^{18} nvt from Figure 236a).

From measurements of $\left(\frac{\partial \ln \dot{\gamma}}{\partial T}\right)_\tau$ at 1.6×10^{18} and 3.4×10^{19} nvt, activation volumes (v^*) were calculated by equation (5) and are shown in Figure 238 as a function of the applied stress under which they were made. When presented in this manner, the activation volumes are seen to be a continuous function of stress and are independent of solute concentration.

From these values of activation volume and measurements of $\left(\frac{\partial \tau}{\partial T}\right)_{\dot{\gamma}}$ obtainable from Figures 236a and 236b, activation energies, H , were calculated w equation (1) and are shown versus applied stress

⁽²⁸⁴⁾ Blewitt, T. H., Coltman, R. R., Jamison, R. E., and Redman, J. K., *J. Nucl. Mat's*, **2**, 227 (1960).

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FIG. 237. Flow Stress, τ , versus Temperature, T , for Copper Crystals Neutron Irradiated to 9.0×10^{19} nvt and Given Various Annealing Treatments after Irradiation. The dashed line is for the as-irradiated copper crystal shown in Figure 235 (1.6×10^{18} nvt).

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FIG. 238. Activation Volume, v^* , versus Stress, τ , for Crystals Neutron Irradiated to 1.6×10^{18} and 3.4×10^{19} nvt.

Figure 239. As shown, H , like the activation volume, is independent of solute concentration and can be represented as a continuous function of stress. Makin's⁽²⁸⁵⁾ values of the activation volume obtained with copper single crystals after a dose of 2.5×10^{18} nvt are shown in Figures 238 and 239 along with the present data for 1.6×10^{18} nvt; his values are in agreement with ours.

Since both H and v^* are independent of solute additions, we are led to the conclusion that solutes do not affect the neutron irradiation strengthening in copper. Having determined H and v^* as a function of stress,

⁽²⁸⁵⁾ Makin, M. J., *Phil. Mag.*, **9**, 81 (1964).

39671

FIG. 239. Activation Energy, H , versus Stress, τ , for Crystals Neutron Irradiated to 1.6×10^{18} and 3.4×10^{19} nvt.

we are able to determine H_0 and v_0^* by extrapolation to zero effective stress. To do this, however, we must also know τ^* . As noted earlier, τ^* refers to the temperature-dependent portion of the applied stress, τ . At each dose investigated, $\tau_{373^\circ\text{K}}$ is still quite temperature dependent. Therefore, the athermal component of the flow stress might vary from zero to value near the observed flow stress at 373°K . If $\tau^* = \tau - \tau_{373^\circ\text{K}}$, Figures 238 and 239 show that for 1.6×10^{18} nvt, H_0 is about 1.1 eV and v_0^* is about $1 \times 10^{-20} \text{ cm}^3$. On the other hand, if one were to assume that $\tau^* = \tau$, extrapolation of the data in Figures 238 and 239 to zero stress would yield values of about 5 eV and about $4 \times 10^{-20} \text{ cm}^3$ for H_0 and v_0^* respectively.

Figures 238 and 239 show that both the activation energy, H , and the activation volume, v^* , are stress dependent as predicted. Similar observations have been made in magnesium by Conrad, *et al.*,⁽²⁸⁶⁾ and in iron by Conrad and Frederick,⁽²⁸⁷⁾ and Arsenault.⁽²⁸⁸⁾

The question still remains as to whether or not H and v^* are also temperature dependent. The problem of whether or not H is temperature dependent is important in current analyses of neutron irradiation strengthening. Application of Seeger's⁽²⁸⁹⁾ model for neutron irradiation strengthening necessitates the use of an assumption of a temperature-dependent activation

⁽²⁸⁶⁾ Conrad, H., Hays, L., Schoeck, G., and Wiedersich, H., *Acta Met.*, **9**, 367 (1961).

⁽²⁸⁷⁾ Conrad, H., and Frederick, S., *Acta Met.*, **10**, 1013 (1962).

⁽²⁸⁸⁾ Arsenault, R. J., *Acta Met.*, **12**, 547 (1964).

⁽²⁸⁹⁾ Seeger, A., *Proc. Second International Conf. on Peaceful Uses of Atomic Energy*, **6** (New York: United Nations) 250 (1958).

39886

FIG. 240. H versus τ^* Comparison of Theory (Solid Line) and Experimental Data Points (Filled Circles).

39887

FIG. 241. v^* versus τ^* Comparison of Theory (Solid Line) and Experimental Data Points (Filled Circles).

energy. Our results contradict this, since we can interpret our deformation data without making such assumption, as discussed below.

Fleischer^(290,291) has developed a strengthening model based upon tetragonal distortions, and he successfully applied it to strengthening due to magnesium-vacancy pairs in lithium fluoride. By modifying the theory to neutron-irradiation strengthening, Makin⁽²⁸⁸⁾ showed

(290) Fleischer, R. L., *Acta Met.*, **10**, 835 (1962).

(291) Fleischer, R. L., *J. Appl. Phys.*, **33**, 3504 (1962).

that

$$H = H_0 \left[1 - \left(\frac{\tau^*}{\tau_0} \right)^{1/2} \right]^2. \quad (6)$$

Conrad, *et al.*⁽²⁸⁶⁾ show that

$$\frac{dH}{d\tau^*} = -v^*. \quad (7)$$

Thus we obtain from equation (6),

$$v^* = \frac{H_0}{\tau^*} \left[\left(\frac{\tau_0}{\tau^*} \right)^2 - 1 \right]. \quad (8)$$

Equations (6) and (8) are shown in Figures 240 and 241, respectively, for our copper crystals irradiated to 1.6×10^{18} nvt. For the calculations we have assumed $\tau^* = \tau$, and therefore $H_0 = 5$ eV. The agreement between the theory (solid line) and experimental values (filled circles) is remarkably good. Thus, the Fleischer theory predicts the correct stress dependence for H and v^* , and hence the temperature independence of the activation energy.

As a continuation of this investigation, we are planning a rather conclusive experiment. This involves a measurement of $\left[\frac{\partial \ln \dot{\gamma}}{\partial (1/T)} \right]_{\tau^*}$, which permits H to be determined solely as a function of temperature (under constant effective stress). It is interesting to note that such measurements in magnesium single crystals by Conrad, *et al.*⁽²⁸⁶⁾ and polycrystalline iron by Arsenaault⁽²⁸⁸⁾ have shown that H is temperature independent. In both cases, H was a function of stress alone.

Fleischer's theory also predicts a $\gamma^{1/2} \propto T^{1/2}$ relationship; our data plotted in Figure 242 show this to be the case.

39670

FIG. 242. $\tau^{1/2}$ versus $T^{1/2}$ for the Copper Data in Figures 236a and 236b.

8. Displacement Cascades (K. L. MERKLE)

From a study of the energy dependence of the black spot damage in gold, we have previously reached the conclusion that the black spots are produced directly at the site of displacement cascades and are not due to long-range diffusion and clustering of point defects. Irradiations at liquid-helium temperature inside an electron microscope by Howe and McGurn⁽²⁹²⁾ have

confirmed this. They find black spots are produced at liquid-helium temperature and do not change noticeably on warmup to room temperature.

104362

480000×

FIG. 243. Single Crystalline Gold Film at (001) Orientation, 820 Å Thick, Irradiated with 0.7 MeV Protons. Dose: 1.4×10^{16} Protons/cm².

confirmed this. They find black spots are produced at liquid-helium temperature and do not change noticeably on warmup to room temperature.

Nature of the Spots

Studies of the influence of the primary displacement energy (T_m) on the nature of the spots have been made by utilizing charged particles of different masses and energies. The results of these studies show that the primary displacement energy determines the size of the spots, the defect structure of the spots, and the distribution of the spots. Figures 243 and 244 illustrate that the spot size increases with increasing displacement energy.

⁽²⁹²⁾ Howe, L. M. and McGurn, J. F., Appl. Phys. Letters, **4**, 99 (1964).

104771

480000×

FIG. 244. Single Crystalline Gold Film of (001) Orientation, 820 Å Thick, Irradiated with 4 MeV α -particles. Dose: 1.2×10^{15} α /cm².

Figure 247 illustrates that high-energy primary displacements result in the clustering of spots, whereas low-energy primary displacements result in a relatively random distribution of spots.

The results can be summarized as follows:

1. Small vacancy clusters, about 20 Å in diameter at a primary energy $E_p = 3 \times 10^4$ eV.
2. Medium size clusters (20–100 Å) at $E_p > 3 \times 10^4$ eV, vacancy and some interstitial.
3. Spot clusters (up to 300 Å) at $E_p \gg 3 \times 10^4$ eV of vacancy and interstitial type.

Earlier work has shown that the dependence of a spot yield on the energy of the primary displacement suggests that a threshold energy exists for the production of visible spots. A least squares fit of the experimental

106010

160000X

FIG. 245. Dark Field Micrograph Taken from (220) Reflection. Gold film irradiated with 0.7 MeV protons. Dose: 1.4×10^{16} Protons/cm². A light shadow in the direction of *G*, the reciprocal lattice vector, signifies vacancy structure; in the reverse direction, interstitial structure.

data expressed in terms of the reduced cross section σ'_s as a function of energy to the theoretically derived curve

$$\sigma'_s = C \frac{1}{T_m} \int_{E_d}^{T_m} \frac{W(E)}{E^2} dE$$

$$= \frac{C}{T_m \Omega \sqrt{2\pi}} \int_{E_d}^{T_m} \left(\frac{1}{E} - \frac{1}{T_m} \right) \exp \left[-\frac{(E - \bar{E}_T)^2}{2\Omega^2} \right] dE \quad (1)$$

where $W(E)$ is the probability function for spot formation,

E_d is the displacement energy,

T_m is the maximum primary displacement energy,

$\bar{E}_T$ is the average threshold energy,

yields values of the parameters E_T and Ω . The least square fit of the experimental data to Equation (1) is shown in Figure 248. E_T is found to be $3.15 \pm 0.12 \times 10^4$ eV and Ω to be $1.13 \pm 0.06 \times 10^4$ eV.

An approximation for Equation (1) can be utilized

when $T_m \gg E_T$. In this case the function $W(E)$ of E shown in Figure 249 would be replaced by a step function with a threshold energy $E_T = 2.8 \times 10^4$ eV that would correspond to the energy required to produce a spot 20Å in diameter. Under these circumstances, Equation (1) would reduce to

$$\sigma'_s = C \frac{1}{T_m E_T}; \quad T_m \gg E_T; \quad E_T = 2.8 \times 10^4 \text{ eV.} \quad (2)$$

Let us now consider displacement energy-size relationship in terms of defect concentration. It should be recalled that diffraction effects observed in dark-field microscopy indicated that the defects were arranged in planar array, probably in a dislocation loop, rather than in spherical array. According to displacement theory the number of pairs is given by $n_f = (E_i/2E_d)$; in the case discussed here there are $(3 \times 10^4)/(7 \times 10^1) = 4.3 \times 10^2$ interstitial vacancy pairs. It turns out that between 80% and 90% of the defects produced at liquid-helium temperature anneal out on warming up to room temperature. We should therefore expect

105996

160000X

FIG. 246. Dark Field Micrograph Taken from (220) Reflection. Gold film irradiated with 26.1 MeV α -particles. Dose: 2×10^{15} α /cm². A light shadow pointing in the direction of G, the reciprocal lattice vector, signifies vacancy structure; in the reverse direction, interstitial structure.

2151

24000X

FIG. 247. Gold Film Irradiated with 2.5×10^{11} Fission Fragments per cm².

37000

FIG. 248. Reduced Cross Section for Black Spot Formation as a Function of the Maximum Knock-on Energy T_m .

38998

FIG. 249. The Probability for Spot Formation on $W(E)$ as a Function of the Primary Knock-on Energy.

about 4.3×10^4 defects to form. This corresponds to a dislocation loop of $20\text{\AA}$ in diameter, which is in reasonably good agreement with the spot size.

Fast Neutron Irradiation

Previous results indicated that the number of spots produced by fast-neutron irradiation were in discrepancy with the number of spots to be expected from the theoretical concept of an energy threshold. Agreement within experimental error can be attained by modifying the calculation to include inelastic collision events and incorporating the probability function $W(E)$ in place of the step function used earlier. A brief outline of this computation is now shown.

We obtain the neutron spectrum in Hole VT-14, which was used for the irradiation from a 20 group reactor physics calculation (see Figure 250). The dose is determined via threshold activation detectors.⁽²⁹³⁾ The number of recoils per second and atom that have an energy between E and $E + dE$ is given by

$$L(E) = \int_0^\infty K(E_n, E) \varphi(E_n) dE_n$$

if $K(E_n, E)$ is the differential cross section for a neutron of energy E_n to produce a recoil whose energy lies between E and $E + dE$. $\varphi(E_n)$ is the neutron flux for neutrons of energy between T and $T + dT$. The recoils are produced by elastic and inelastic encounters of neutrons with gold atoms:

$$K(E_n, E) = K_{el}(E_n, E) + K_{inel}(E_n, E).$$

The recoil energy in elastic collisions is given by

$$E_{el} = \frac{2M}{(M+1)^2} (1 - \cos \theta) E_n$$

where θ is the scattering angle in the center of mass

⁽²⁹³⁾ Seeger, A. K., *Proc. 2nd Inter. Conf. Peaceful Uses Atomic Energy* (United Nations: New York) 6, 250 (1958).

system. Most of the inelastic cross section in the energy range 1 to 10 MeV is due to (n, n') reactions. We therefore neglected (n, γ) reactions and reactions which involve the emission of charged particles. In the (n, n') reactions we can assume isotropic emission of the neutron from the compound nucleus. In this case the average recoil energy that a nucleus receives in this process is approximately given by

$$\bar{E}_{el} = (1/M)(E_n + E'_n)$$

where E_n is the energy of the absorbed and E'_n the energy of the emitted neutron. Figure 251 shows the elastic and inelastic recoil spectrum. We find that the median spot-producing recoil energy is 27.3 keV, the average is 30.5 keV. If one considers the elastic and inelastic collisions separately, one finds that the average elastic recoil energy $\bar{E}_{el} = 35.8$ keV is considerably higher than the inelastic one $\bar{E}_{inel} = 24$ keV. As can be seen from Figure 251 the elastic-recoil energy spectrum is not necessarily a monotonically increasing function with decreasing E_n , as is always the case in the Rutherford region of charged particle irradiations, even in irradiation with monoenergetic particles. The calculations have shown that inelastic collisions are of importance at neutron energies above 1 MeV; inelastic collisions produce 45 percent of the total number of spots. Generally one finds that the inelastic

39001

FIG. 250. Neutron Spectrum in Hole VT-14 of CP-5 Reactor.

39307

FIG. 251. The Recoil Spectrum for Elastic (n,n) and Inelastic (n,n') Collisions of Neutrons with Gold Atoms in Hole VT-14 of the CP-5 Reactor.

collisions contribute more and more to the energetic recoils, the higher the neutron energy. This is due to the increased forward scattering at high neutron energies.

Inelastic collisions have always been neglected in the past in radiation damage calculations. As we have shown, this contribution is not negligible, particularly if one investigates property changes that are specifically caused by energetic cascade events (as for example black spot damage or radiation hardening). Dark-field micrographs indicate that the spots consist mainly of vacancy clusters, but some interstitial clusters are also present (see arrow in Figure 252) after fast neutron irradiation.

Low-Energy Bombardments

If one irradiates gold with charged particles of such an energy that T_m , the maximum primary energy, is small compared to E_T , one generates only single displacements and small cascades, whose energy is not large enough to enable the spontaneous formation of a visible defect. Therefore one would not expect to see any electron microscopically visible effects at low doses. However, if one introduces a high enough concentration of defects they will be able to interact with each

other, and this might possibly lead to the formation of clusters that are large enough to be visible by the transmission electron microscope technique. Furthermore the defects that are mobile at the temperature of irradiation will migrate to sinks or form their own sinks by clustering. Typical of irradiation experiments is that always the same number of vacancies as interstitials are formed. If the spatial distribution would be completely homogeneous one would expect that the main annealing mechanism would be mutual annihilation of interstitials and vacancies. The initial distribution of defects can be assumed to be homogeneous in low-energy irradiations except near the surface and at discontinuities in the lattice, as for example at stacking faults. Focusing collisions will be able to separate vacancies and corresponding interstitials by distances of the order of 100 lattice distances. When a dynamic crowdion is defocused by a stacking fault, an inter-

106183

290000X

FIG. 252. Fast Neutron Irradiated Gold Film. Dark field Micrograph. Note direction of asymmetric dark-white contrast at loops.

FIG. 253. Dislocation Loops on Stacking Faults in Proton-Irradiated Gold Films.

stitial will be generated at the stacking fault or close to it. Consequently, a high concentration of interstitials will be generated at a stacking fault, and in a region limited by the focusing length, there will be a correspondingly higher concentration of vacancies than interstitials. The single-crystalline gold films of (100) orientation that we use in our irradiations invariably contain a large number of stacking faults. In irradiations with fission fragments no increased defect production at stacking faults was found by us that could have been indicative of focusing effects. Ruedl *et al.*⁽²⁹⁴⁾ have observed a high concentration of defects at coherent twin boundaries in fission-fragment irradiated platinum and have interpreted this in terms of focusing collisions. In the light of our observation on gold, however, it seems very unlikely that this interpretation is correct.

About two years ago, we observed the formation of dislocation loops on stacking faults after proton irradiation (see Figure 253). We did not report this at the time because we had difficulties in duplicating the result. During the past year we were able to perform a number of irradiations that were designed to explore the conditions for the formation of the loops. In some

experiments the films were oriented with respect to the beam in such a way that focusing chains from primaries ended up preferentially on one set of stacking faults. However when loops were observed on stacking faults they seemed to appear with equal frequency on all sets of stacking faults. Apparently focusing from secondaries was important enough to mask the effect completely. There was a marked influence of the temperature of irradiation on the defect structure. Figure 254 and Figure 255 show a film that was irradiated at 50°C. Figure 254 shows an excess concentration of defects near the stacking faults. The squares in this picture represent tetrahedra of stacking faults. This can be seen from Figure 255 where the gold film has been tilted by approximately 35° in order to look at a stacking fault edge on. In this orientation the tetrahedra appear as triangles. Observation on a number of micrographs shows that they appear preferentially within approximately 250Å of the stacking faults. This is just what one would expect if the tetrahedra are formed by clustering of vacancies in the zone of excess vacancies that is formed by the focusing mechanism. We consider this observation as a direct evidence for focusing collisions and as an indication that the focusing length is of the order of 100 lattice distances in agreement

⁽²⁹⁴⁾ Ruedl, E., Delavignette, P., and Amelineckx, S., *Phys. Rev. Letters*, **6**, 530 (1961).

105072

240000X

FIG. 254. (001) Gold Film Irradiated with 100 keV Protons at 50°C.

105409

120000X

FIG. 255. (001) Gold Film Irradiated with 100 keV Protons at 50°C. Film tilted for observation 35° around (110).

with theoretical estimates. It should be mentioned that the type of focusing observed here is of the dynamic crowdion type where a whole row of atoms is moved by one atomic distance. If we have momentum focusing,

that is, if only energy is transferred, the defocusing at the stacking fault would produce Frenkel pairs within a few atomic distances from the fault. Under our experimental conditions these would be expected to an-

105101

126000×

FIG. 256. (001) Gold Film Irradiated with 100 keV Protons at 150°C. Note large loops on stacking faults.

neal out; in any case the effect would be limited to a region within a few interatomic distances of the fault plane. It is interesting to note that the tetrahedra seem to exist as such at very small sizes. See Figure 254. Also, nonequilibrium shapes can be observed in the stacking fault region where the tetrahedra have grown largest. Preliminary experiments have shown that growth of tetrahedra is observed in the temperature range of 40–50°C. At higher temperature formation of loops on stacking faults is observed. See Figure 256. The nature of the loops has not been determined as yet. Presumably they would also be vacancy loops, formed by vacancies migrating to the stacking fault. It seems unlikely that the interstitials generated at the stacking fault are bound to the fault strongly enough not to become mobile until temperatures $>50^{\circ}\text{C}$. We presume that the interstitials have annealed out and have gone to the surface. However, more experiments are needed to verify this.

A more complete series of irradiations has already been performed at the Cockcroft-Walton accelerator. The specimens are kept at -78°C and will be examined as soon as the installation of the new electron microscope is completed. One major problem in irradiating thin films with charged particles has been the surface contamination that builds up during irradiation. We have now completed the construction of a target chamber which hopefully will eliminate this problem. This facility can also be used to irradiate at low temperatures down to the temperature of liquid helium.

9. Studies of Lattice Defects in Quenched and Irradiated Metals (R. M. J. COTTERILL)

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2. R. M. J. Cotterill and T. J. Koppenaal, *Effects of Type and Density of Defects on Yield Strength of Neutron-irradiated Copper and Cu-14 at% Alloy*, Appl. Phys. Letter, **4**, 156 (1964).
3. R. M. J. Cotterill, "Vacancy Clusters in Pure and Impure F.C.C. Metals," *International Conference on Lattice Defects in Quenched Metals*, ANL, June 1964. (Abstract).
4. R. M. J. Cotterill and M. Doyama,* "Small Vacancy Clusters in F.C.C. Metals," *International*

Conference on Lattice Defects in Quenched Metals, ANL, June 1964. (Abstract).

5. R. M. J. Cotterill, "A Liquid Helium Stage for the Siemens Elmiskop I," *Proceedings of the Third European Regional Conference on Electron Microscopy*, Prague, Czechoslovakia, 1964, Vol. **I**, p. 63 (1964).
6. M. Doyama* and R. M. J. Cotterill, *The Energy and Atomic Configuration of an Edge Dislocation in an F.C.C. Metal*, Phys. Letters, **13**, 110 (1964).
7. T. J. Koppenaal and R. M. J. Cotterill, *Annealing Studies in Neutron-irradiated Copper Alloys*, J. Metals, **16**, 771 (1964). (Abstract).
8. M. Doyama* and R. M. J. Cotterill, *Discrete Atom Model of an Edge Dislocation in Copper*, Bul Amer. Phys. Soc., **9**, 742 (1964). (Abstract).

* With the Solid State Science Division, ANL.

107002

67000X

FIG. 257. Thin Film of Quenched Gold Containing Stacking-fault Tetrahedra.

Neutron-irradiation-induced Removal of Stacking-fault Tetrahedra in Gold (Experimental)

It has been shown^(295,296,297) that when gold containing stacking-fault tetrahedra is subjected to 1.0 and 3.5 meV alpha-irradiation the tetrahedra eventually disappear. One also observes the simultaneous appearance of the spot defects, which are characteristic of radiation damage experiments. The explanation of these effects was that the interstitials generated by the irradiation migrate to the tetrahedra and annihilate them, while the less mobile vacancies stay localized at their point of generation, cluster, and form the spot defects. More recent experiments of this type by Howe and McGurn,⁽²⁹⁸⁾ which are discussed later, have been taken to indicate that the annihilation process is due mainly to close pair recovery. The author does not subscribe to this viewpoint but believes instead that the rate-con-

trolling process is the long-range migration of interstitial atoms. The experiments of Howe and McGurn, and also all previous experiments of this nature, have involved the irradiation of thin foil specimens. This is not an ideal setup for the detection of long-range migration processes because the foil surfaces are the predominating sinks and are able to absorb the large majority of point defects generated by the irradiation. Because of this, it was felt advisable to work with bulk specimens, and therefore to use neutrons rather than alpha-particles for the irradiation.

It was first established that the irradiation-induced annihilation effect observed with alphas could also be obtained with neutrons. Figure 257 shows a thin-foil electron-microscope specimen of quenched gold before irradiation. Figure 258 shows the same area after irradiation with neutrons. The tetrahedra are, in fact destroyed as in the case of the alpha irradiation. The results of the bulk experiment are shown in Figures 259, 260, and 261. A capsule was loaded with specimens of gold 5.0 cm $\times$ 0.5 cm $\times$ 0.0075 cm some of which had been quenched from 1000°C and annealed at 100°C for 5 hours. The specimens were neutron irradiated to

⁽²⁹⁵⁾ Cotterill, R. M. J., and Jones, M. W., *J. Phys. Soc. Japan*, **18**, 158 (1963).

⁽²⁹⁶⁾ Hirsch, P. B., Cotterill, R. M. J., and Jones, M. W., *Proc. Fifth Int. Conf. on Electron Microscopy*, **1**, F3 (1962).

⁽²⁹⁷⁾ Cotterill, R. M. J., and Jones, M. W., *Phil. Mag.*, **10**, 535 (1964).

107003

67000×

FIG. 258. Thin Film of Quenched Gold Containing Stacking-fault Tetrahedra after Neutron Irradiation.

107000

67000×

FIG. 259. Typical Area of a Specimen of Quenched Gold

107001

67000X

FIG. 260. Typical Area of Specimen of Quenched Gold After Neutron Irradiation in Bulk Material. Note the presence of spot defects and the absence of interstitial loops.

105810

67000X

FIG. 261. Typical Area of Specimen of Annealed Gold After Neutron Irradiation in Bulk Material. Note the spot defects and interstitial loops.

a total dose of 5×10^{17} nvt. On the basis of the results of the thin-film experiment, and allowing for the correction due to loss of interstitials to the surfaces in that experiment, the dose in the bulk experiment was calculated to give about 80 percent completion of the

annihilation process. This is confirmed by the results. Figure 259 shows an area of a quenched specimen that was not irradiated. It contains a high density of tetrahedra. Figure 260 shows an area of a quenched specimen that was irradiated. Few tetrahedra remain, and

one notes the appearance of the black spot defects that are characteristic of neutron-irradiated material. It is also important to note that no interstitial loops are observed in Figure 260. For comparison, Figure 261 shows an area of a specimen that was annealed (but not quenched) before irradiation. This contains both spots and loops. The accepted interpretation of pictures of the type shown in Figures 259, 260, and 261 is that the spots are vacancy clusters, which are mainly formed at the displacement spikes, while the loops, which are larger but less numerous, are formed from interstitials. This model is consistent with the view that the interstitials have a lower migration energy than the vacancies. The difference between Figures 260 and 261 lead to the following conclusions: (1) The defect that in an annealed-irradiated specimen produces the large loops is the same defect that in a quenched-irradiated specimen is responsible for the annihilation of tetrahedra. (Since it is clear that tetrahedra are composed of vacancies, and because only interstitials could annihilate them, this proves that the large loops in the pre-annealed specimens are of the interstitial type.); (2) Because the loops are larger and less dense, they are formed as a result of long-range interstitial migration, and the annihilation of the tetrahedra must also be a result of this long-range migration. The second conclusion is in direct opposition to the model proposed by Howe and McGurn.⁽²⁹⁸⁾

A Liquid-Helium Stage for the Siemens Elmiskop I (Experimental)

The liquid-helium stage is one of a series of components designed to permit low-temperature irradiation studies *in situ* in the Siemens Elmiskop I electron microscope.

The helium stage and cryostat assembly are shown in Figure 262 (which is not drawn to scale). The dewar system, which was constructed from 0.38mm thick stainless steel, consists of an outer vacuum jacket, a liquid nitrogen shield, an inner vacuum jacket, and the liquid helium container. A 6.4mm stainless steel tube extends from the bottom of the helium dewar to the copper specimen holder. To facilitate the passage of this tube through the microscope wall, a new specimen chamber was built to replace the standard airlock. The specimen holder fits into a Teflon cartridge, and the latter fits into the standard specimen translation device. The specimen holder is connected to the 6.4 mm stainless steel tube via a nickel bellows (which has a 0.025 mm wall thickness). This affords easy adjustment of specimen position. (It would also permit tilting of the holder,

⁽²⁹⁸⁾ Howe, L. M., and McGurn, J. F., Appl. Phys. Letters, 4, 99 (1964).

38331

FIG. 262. Helium Stage and Cryostat Assembly. (Not to scale.)

38332

FIG. 263. Details of the Specimen Holder.

although this has not been attempted with the present model.)

Details of the specimen holder are shown in Figure 263. The holder itself was fabricated from OFHC copper. When in place in the holder, the specimen is at the center of a cylindrical hole, which is 1.0 cm long and only 0.1 cm in diameter. The specimen therefore receives thermal radiation only through a quite small solid angle. No supporting grids are used for the speci-

107005

67000X

FIG. 264. Quenched Gold Specimen under Observation in the Helium Stage Operating at about 30°K.

men. Instead the specimen shape recommended by Venables⁽²⁹⁹⁾ is employed. A sheet of the specimen material is first indented with a ball bearing and then electropolished until a hole appears at the center of the indentation. A disc of the required diameter with this hole at the center is then punched out of the sheet.

The bleeder line shown in the figures has two functions. During the precooling and filling of the helium dewar, it is used to purge the lower part of the system. This is achieved by blowing cold helium gas (at about 78°K) through the line. During operation of the stage, the line is connected to a rotary vacuum pump to remove helium vapor. Some control over the position of the gas-liquid interface, and hence of the stage temperature, is obtained by varying the pumping rate. At a sufficiently high pumping rate, the liquid helium reaches into the specimen holder itself. This condition is detected by means of the carbon resistor shown in Figure 263. The carbon resistor, which has been previously calibrated, is used to measure the stage temperature. The latter is also measured by condensing various gases on the specimen. Presence of the condensate is detected by direct transmission in the manner discussed by Piercy *et al.*⁽³⁰⁰⁾

⁽²⁹⁹⁾ Venables, J. A., *Rev. Sci. Instrum.*, **34**, 585 (1963).

⁽³⁰⁰⁾ Piercy, G. R., Gilbert, R. W., and Howe, L. M., *J. Sci. Instr.*, **40**, 487 (1963).

A typical micrograph of a specimen under observation at low temperature is shown in Figure 264. In this case the specimen is a thin film of quenched gold. The excellent resolution obtained with the stage is demonstrated by the sharpness of the fringes observed in the defects.

The Clustering of Vacancies during the Quenching of Pure and Impure F.C.C. Metals (Theoretical)

It is now a well-established fact that impurity atoms can have a marked influence on the clustering of vacancies in quenched metals. This effect has been studied quite extensively in gold, for instance, and the most important direct observations have been as follows. One observes spot defects⁽³⁰¹⁾ rather than stacking-fault tetrahedra when 99.999% pure gold is quenched from 800°C or below, and subsequently annealed at 100°C. When it is quenched from around 800°C one observes both tetrahedra and spot defects, while a quenching temperature of 750°C produces only the spot defects. These defects have an average diameter of about 25Å and are not clearly resolved in the electron microscope. The formation of spot defects is therefore favored at lower quenching temperatures. It was also found that an increase in impurity content, at a given quenching

⁽³⁰¹⁾ Cotterill, R. M. J., *Phil. Mag.*, **6**, 1351 (1961).

temperature, T_q , favors the formation of spot defects.⁽³⁰²⁾ In particular, it was found that 99.98 % gold, quenched from 1000°C, contains spot defects. Finally, it may be noted that if 99.999 % gold is quenched from a temperature well above 800°C (i.e., from a temperature that would produce only tetrahedra) and then observed in the electron microscope before appreciable annealing has occurred at room temperature, spot defects are observed rather than tetrahedra.

It was found that the concentration of spot defects observed in this way is approximately equal to the concentration of tetrahedra observed in a specimen quenched from the same temperature and then fully annealed at 100°C prior to observation. The results of this last experiment strongly suggest that the spot defect is an intermediate stage in the growth of the tetrahedron. In fact, one cannot rule out the possibility that the spot defects are themselves tetrahedra. A recent model^(303,304) suggests that elementary tetrahedra can be formed from a relatively small number of vacancies, and that they can grow continuously by the absorption of further vacancies and the simultaneous passage of jogs across the stacking-fault faces. The dependence of the type of defect observed on T_q and specimen purity has been considered by Cotterill and Segall.⁽³⁰²⁾ It was suggested that the parameter that determines the type of cluster observed is the ratio C_v/C_i where C_v is the concentration of vacancies at the quenching temperature, and C_i is the impurity concentration. It was recognized that the value of C_i appearing in this ratio might not be the total impurity content. Impurities having a negligible binding energy with a vacancy would not be expected to have much influence on vacancy clustering. For large values of C_v/C_i homogeneous nucleation should predominate, whereas heterogeneous nucleation (i.e., nucleation on complexes containing a proportion of impurity atoms) might be important for low values of this ratio. If the large tetrahedra are formed as a result of homogeneous nucleation and the spot defects (or very small tetrahedra) by heterogeneous nucleation, this would be in agreement with the experimental results, because C_v decreases with T_q while C_i remains constant in a given specimen. Similarly the ratio is decreased if, for a given T_q , a less pure specimen is used. The temperature below which heterogeneous nucleation becomes important was referred to by Cotterill and Segall as T_{CRIT} . Thus in the 99.999 % gold $T_{\text{CRIT}} \cong 800^\circ\text{C}$, and for the 99.98 % gold one might infer that T_{CRIT} is above the melting

point. Cotterill and Segall were able to show reasonable quantitative justification for this simple model. The study described here aims at giving a complete quantitative description of a quenched noble metal in terms of the concentration of each type of vacancy cluster immediately after the quench. It also investigates the influence of impurity atoms on these concentrations.

As has been appreciated for several years,^(303,305,306) the concentration of any and every type of vacancy cluster can, in principle at least, be determined by solving the appropriate kinetic equations. In general, these kinetic equations take the form

$$dC_{jv}/dt = \sum_{m,n} A_{mn} C_m^m C_n^v \exp(-E_{mn}/KT) \quad (1)$$

where C_{jv} is the concentration of the cluster which contains j vacancies. A_{mn} incorporates three factors; the atomic vibration frequency, an entropy factor, and a coordination factor (of which only the latter is known with any certainty). The E_{mn} are activation energies of migration or a combination of both migration and binding. To appreciate what other difficulties are involved in the use of Equation (1) we single out one of the expressions. Let us consider the case where j is four. One of the terms on the right-hand side will be that for which m is three and n is one. In choosing a value for C_n , one has to distinguish between the various types of trivacancy (as has been emphasized by deJong and Koehler⁽³⁰³⁾). An exact solution will only be obtained if a separate term is included for each type of trivacancy. Moreover, all three components of A_{mn} may depend upon the configuration of the trivacancy so three different values of this parameter will be required. Similarly, because the tetravacancy may be able to break up into a vacancy and a trivacancy in several different ways forming a variety of different trivacancies, the term for which m is four (and C_n is made equal to unity) will also have to be split into several parts. There will be as many of these parts as there are trivacancies, and each will involve a different value of the energy, E_{mn} . For larger clusters the situation may become even worse because one might expect that the number of possible forms of a cluster containing a given number of vacancies is in some way related to that number.

At the present time, the possibility of measuring the binding energies of the various states of the trivacancy, for instance, seems fairly remote. Calculations of these energies have been reported,⁽³⁰⁷⁾ but the absolute values obtained thus far are not to be taken too seriously.

⁽³⁰²⁾ Cotterill, R. M. J., and Segall, R. L., *Phil. Mag.*, **8**, 1105 (1963).

⁽³⁰³⁾ deJong, M., and Koehler, J. S., *Phys. Rev.*, **129**, 40 (1963).

⁽³⁰⁴⁾ Kimura, H., Kuhlmann-Wilsdorf, D., and Maddin, R., *Appl. Phys. Letters*, **3**, 4 (1963).

⁽³⁰⁵⁾ Koehler, J. S., Seitz, F., and Bauerle, J. E., *Phys. Rev.*, **107**, 1499 (1957).

⁽³⁰⁶⁾ Kimura, H., Maddin, R., and Kuhlmann-Wilsdorf, D., *Acta Met.*, **7**, 145 (1959).

⁽³⁰⁷⁾ Cotterill, R. M. J., and Doyama, M., *Lattice Defects in Quenched Metals*, Academic Press, New York, (1965) p. 653.

Since the values of the A_{mn} are also not known with any certainty, it seems that any solution of Equation (1) can only be very approximate. Before describing one specific attempt to obtain a solution by the use of an analog computer, it will be convenient to consider the broad features of the equations.

To make things as simple as possible, let us first consider the case where only single vacancies and divacancies exist. Equation (1) then simplifies to

$$\begin{aligned} dC_{1V}/dt &= -2A_{11}C_{1V}^2 \exp \left(-\frac{E_V^M}{KT} \right) \\ &\quad + 2A_{22}C_{2V} \exp \left[-1 \left(\frac{E_V^M}{KT} + \frac{E_{VV}^B}{KT} \right) \right] \\ dC_{2V}/dt &= A_{11}C_{1V}^2 \exp \left(-\frac{E_V^M}{KT} \right) \\ &\quad - A_{22}C_{2V} \exp \left[-\left(\frac{E_V^M}{KT} + \frac{E_{VV}^B}{KT} \right) \right] \end{aligned} \quad (2)$$

We consider the time dependence of C_{1V} and C_{2V} during quenching and make the further assumption that no vacancies escape from the specimen. The last assumption is written formally

$$C_V = C_{1V} + 2C_{2V} \quad (3)$$

For a so-called "linear" quench we have

$$T = T_q - \alpha t \quad (4)$$

where T_q is the quenching temperature and α is the quenching rate. Figure 265 shows schematically the time variation of C_{1V} and C_{2V} during quenches at three different rates. For an infinite quenching rate there is no time for the vacancies and divacancies to migrate and collide or break up. C_{1V} and C_{2V} therefore stay constant throughout the quench. For $\alpha = 0$, an infinitely slow quench, there is sufficient time for equilibrium to be maintained throughout and the left-hand sides of Equations (2) tend to zero; giving the relationship

$$C_{2V} = C_{1V}^2 \exp \left(\frac{E_{VV}^B}{KT} \right) \quad (5)$$

From this expression it is not difficult to show that as the temperature falls, the ratio C_{2V}/C_{1V} increases (as long as condition 9 holds). This behavior is indicated in Figure 265. For a finite quenching rate a behavior somewhere between that of the two extreme cases is to be expected. The number of jumps m made by a vacancy in time t is⁽³⁰⁸⁾

$$m = Z\nu A t \exp \left(-\frac{E_V^M}{KT} \right) \quad (6)$$

where Z is the coordination number, ν the atomic vibration frequency, and A is an entropy factor. This shows that the vacancy jump rate decreases with decreasing temperature. For a finite quenching rate the vacancies and divacancies are able to maintain the equilibrium values derived from Equations (2, 5) during the early

40912

FIG. 265. Schematic Time Variation of the Concentration of Single and Divacancies during the Quenching of a Specimen from which No Vacancy Loss Occurs.

part of the quench. As the temperature falls, however, a point is reached where the jump rate is not high enough to allow sufficient collisions for the vacancies to attain equilibrium during the time that the specimen is at that temperature. Each curve then deviates from the equilibrium curve and levels off. The temperature at which the separation occurs is referred to as T^* . In the general case, when not only single vacancies and divacancies but also trivacancies, tetravacancies, etc., are taken into account, one would expect the same broad features to be observed. For $\alpha = 0$, the more tightly bound clusters will predominate at lower temperatures, while a finite α will prevent equilibrium from being maintained below T^* . It might be expected that T^* will be different for different clusters, however.

We will now discuss the results of a study in which the Equation (1) was solved by an analog computer for the case in which single vacancies, divacancies, trivacancies, tetravacancies, impurity-atom-vacancy complexes, and impurity-atom-divacancy complexes were considered. The time dependence of the concentrations of these clusters is given by Equation (1) with only those terms indicated in Table 84 included in the calculation.

Several assumptions were made for this study. One, which is apparent from an inspection of the equations, is that all forms of a given type of cluster have been lumped into one averaged configuration with an av-

⁽³⁰⁸⁾ Cottrell, A. H., *Vacancies and other Point Defects in Metals and Alloys*, (Inst. Met. Monograph No. 23, 1958) p. 10.

TABLE 84. ACTIVATION ENERGIES USED IN THE ANALOG COMPUTER CALCULATIONS

$E_V^F = 0.97 \text{ eV}$	$E_{VV}^B = 0.2 \text{ eV}$
$E_V^M = 0.82 \text{ eV}$	$E_{V_2V}^B = 0.3 \text{ eV}$
$E_{2V}^M = 0.57 \text{ eV}$	$E_{V_3V}^B = 0.4 \text{ eV}$
$E_{3V}^M = \infty$	$E_{2V-2V}^B = 0.5 \text{ eV}$
$E_{4V}^M = \infty$	$E_{iV}^B = 0.25 \text{ eV}$
$E_{iV}^M = \infty$	$E_{iV-V}^B = 0.35 \text{ eV}$
$E_{i_2V}^M = \infty$

39014

FIG. 266. Variation of the Concentration of Various Small Homogeneous and Heterogeneous Clusters during Quenching. $T_q = 1000^\circ\text{C}$, $C_i = 10^{-6}$.

39013

FIG. 267. Same as Figure 266 Except That $C_i = 5 \times 10^{-5}$.

eraged binding energy and an averaged value of A_{mn} . In addition to this rather sweeping assumption, and because the magnitudes of the various components of the A_{mn} are known only to within an order of magnitude or so, all the A_{mn} were made equal. The study was applied to a "typical" noble metal, and the values of the various activation energies used in the calculations were as given in Table 84. The study investigated the effects of three parameters on the formation of clusters: impurity atom concentration, quenching temperature and quenching rate. The first results of this project are shown in Figures 266–272.

Figure 266 shows the variation of the C_{jV} as a function of time during a quench from 1000°C at a rate of $5 \times 10^4^\circ\text{C sec}^{-1}$. The impurity concentration, C_i , is 1×10^{-6} . The dotted lines show the equilibrium concentrations (for no vacancy loss from the specimen). These curves indicate that if thermal equilibrium could be maintained throughout, the trivacancies would predominate over the divacancies immediately after the quench. The trivacancies would in turn be predominated over by the tetravacancies, and so on. The same thing would occur for the impurity-vacancy clusters. The figure shows that in practice equilibrium is not maintained below a certain temperature (the T^* referred to earlier) and that this temperature varies with the cluster size. Below T^* the curves tend to continue to rise slightly, and then level off. It can be seen that T^* increases with increasing cluster size, as might be expected. If this trend is maintained for larger clusters, this would mean that such clusters are present at the quenching temperature (in concentrations which are always quite small, and which get smaller with increasing cluster size) and that they show only a slight increase in concentration during the quench. With the binding energies given in Table 84, the concentration of trivacancies existing in the specimen immediately after the quench actually exceeds that of the divacancies. Figure 267 differs from Figure 266 only in respect to the impurity concentration, which has been increased by a factor of 50. One obvious consequence of this change is to increase the initial concentrations of the impurity-vacancy complexes by the same factor. It can also be seen that the concentrations of these clusters immediately after the quench is raised by a similar factor. These increases are not accompanied by a corresponding decrease in the number of homogeneous clusters. The increase appears to be at the expense of the single vacancies. The increase in impurity content does not appear to have much effect on the various values of T^* . We now consider the dependence of quenching temperature by comparing Figures 266, 268, 269, 270, and 271.

Figures 268 and 269 show the situation for a lower

39012

FIG. 268. Variation of the Concentration of Various Small Homogeneous and Heterogeneous Clusters During Quenching. $T_q = 800^\circ\text{C}$, $C_i = 10^{-6}$.

39011

FIG. 269. Same as Figure 268 Except that $C_i = 5 \times 10^{-5}$.

quenching temperature (800°C) for the same two impurity levels. Figure 268 shows the same general features as Figure 266. For instance, T^* is again found to increase for increasing cluster size. The effect of changing the impurity content is also roughly the same as for a quench from 1000°C . Comparison of Figures 268 and 269 shows that if C_i is increased by a factor of 50, the concentrations C_{iV} and C_{12V} , both at the quenching temperature and also immediately after

the quench, are increased by about the same factor. Figures 270 and 271 correspond to a still lower quenching temperature (600°C). Again one obtains the same general features shown by the earlier plots. For example, an increase in C_i produces a corresponding increase in the initial and final concentrations C_{iV} and C_{12V} by the same factor.

Although the sets of curves corresponding to the three quenching temperatures do have certain similarities, as discussed previously, there are also important

39009

FIG. 270. Variation of the Concentration of Various Small Homogeneous and Heterogeneous Clusters during Quenching. $T_q = 600^\circ\text{C}$, $C_i = 10^{-6}$.

39008

FIG. 271. Same as Figure 270 Except that $C_i = 5 \times 10^{-5}$.

39010

FIG. 272. Same as Figure 269 Except that $\alpha = 5 \times 10^5 \text{ } ^\circ\text{C Sec}^{-1}$.

differences between them. Consider, for instance, the initial values of C_{2V} and C_{iV} shown in Figures 267, 269, and 271. At $T_q = 1000^\circ\text{C}$, C_{2V} is about three times as large as C_{iV} . For $T_q = 800^\circ\text{C}$, C_{iV} is slightly larger than C_{2V} , and at $T_q = 600^\circ\text{C}$, it is about twenty times as large as C_{2V} . A similar thing holds for the relative values of C_{3V} and C_{i2V} . The importance of heterogeneously nucleated clusters therefore increases with lower quenching temperature. It is not difficult to see why this should be. The initial concentration, C_{mV} , of a particular homogeneous cluster containing m vacancies is proportional to $(C_{1V})^m$, whereas, the concentration, $C_{i(m-1)V}$, of the corresponding heterogeneous cluster, which contains the same number of point defects, one of which is an impurity atom, is proportional to $(C_{1V})^{m-1}$. As the quenching temperature is lowered, C_{1V} decreases and this has a greater numerical effect on $(C_{1V})^m$ than it has on $(C_{1V})^{m-1}$. Another parameter which appears to depend upon the quenching temperature is the ratio of initial and final concentrations of a given type of cluster. This effect can be seen by comparing the initial and final values of, say, C_{3V} in Figures 266, 268, and 270. For $T_q = 1000^\circ\text{C}$, C_{3V} rises by a factor of 10^3 during the quench. For $T_q = 800^\circ\text{C}$ the factor is only 5×10^2 , and for $T_q = 600^\circ\text{C}$, it falls to 10^2 . This means that the value of C_{3V} at the end of the

quench is a more rapidly decreasing function of T_q than is the value of C_{3V} at the start of the quench. This is not unexpected because the number of jumps made by a vacancy during the quench is a function of T_q and the same is true of the number of attempts to break up (and the chance of success) that a cluster makes during the quench.

A dependence on quenching rate can be seen by comparison of Figure 272 with Figure 269. The only difference in the quenching parameters of these two figures is that $\alpha = 5 \times 10^4 \text{ } ^\circ\text{C sec}^{-1}$ for Figure 269 and $\alpha = 5 \times 10^5 \text{ } ^\circ\text{C sec}^{-1}$ for Figure 272. One obvious consequence of increasing α is to raise the individual values of T^* . The rise of T^* for C_{iV} is particularly marked. It increases from about 300°C to over 400°C . This increase in T^* is accompanied by a decrease in the final concentrations of the various clusters. This is just the behavior that would be expected from the simple arguments put forward in connection with Figure 265.

As was mentioned earlier, the studies outlined beforehand are still at an early stage. More runs must be made with different binding energies. It is useful, however, to list the trends that have been established thus far. These are:

- 1) An increase in impurity content causes an increase in the concentration of impurity-vacancy complexes, mostly at the expense of the single vacancy concentration.
- 2) Impurity-nucleated clusters become more important at lower quenching temperatures.
- 3) For quenches from close to the melting point the concentration of some of the smaller clusters (divacancies and trivacancies) reaches a maximum at some time during the quench and then decreases as the concentration of larger clusters builds up.
- 4) For small clusters at least, T^* , the temperature below which equilibrium ceases to prevail, increases with cluster size.
- 5) T^* increases with increasing quenching rate.
- 6) T^* is fairly insensitive to changes in quenching temperature and impurity content.
- 7) The increase in the concentration of a given type of cluster increases with T_q .

For the binding, migration and formation energies given in Table 84, one also finds that:

- 8) The concentrations of some of the smaller clusters (trivacancies, tetravacancies) might increase by factors as large as 10^3 or more during the quench.

10. Theoretical Studies of Lattice Defects in F.C.C. Metals (R. M. J. COTTERILL*)

The Energy and Atomic Configuration of a Dislocation—Edge Dislocation

The elastic continuum treatment of dislocations in metal crystals suffers from difficulties associated with the dislocation core. Expressions for the stresses around a dislocation, derived by this method, have a singularity at the center of the dislocation. This is usually overcome by effectively cutting out of the crystal a small cylindrical hole whose axis is the dislocation and whose radius is r_c , say. The elastic theory breaks down inside this radius. The integrations that are involved in calculations of dislocation energy have r_c as a lower limit of the radius. This procedure is unsatisfactory in that, without knowing the exact arrangement of atoms in the core, one has difficulty in choosing a value of r_c . Moreover, even when a value of r_c has been chosen, there is no satisfactory way of dealing with that part of the crystal which lies inside this radius.

Several rough estimates of the core energy have been published⁽³⁰⁹⁻¹²⁾ for metals; the generally accepted estimate is about 1 eV per atom plane. In recent years calculations of the energies and atomic configurations of clusters of point defects have been facilitated by application of computer techniques and the use of discrete atom models. This method is extended to the case of a three-dimensional edge dislocation in copper (Burgers' vector, $a/2\langle 110 \rangle$). A crystal containing 2184 atoms was made effectively infinite along the direction of the dislocation line by the use of periodic boundary conditions. A Morse potential function,

$$V(r_j) = D\{\exp[-2\alpha(r_j - r_0)] - 2[\exp - \alpha(r_j - r_0)]\},$$

truncated at 54 neighbors, was used to represent the interaction between atoms. The constants were $D = 0.34353$ eV, $\alpha = 1.2704\text{\AA}^{-1}$, and $r_0 = 2.8496\text{\AA}$. The atoms in the crystal were first located at the positions given by the elastic theory and then allowed to relax, one by one, until equilibrium prevailed.

Figures 273 and 274 show the positions of the atoms around the dislocation. The dislocation lies along a $\langle 112 \rangle$ direction normal to the plane of the figures. In this orientation there are six different resolved atomic

positions on the plane of the figure, so the figure is given in two parts, for clarity. The displacements normal to the slip plane are very small, being less than 5 percent of the distance between $\{111\}$ planes even for atoms near the center. The largest displacements were in the direction normal to the dislocation line and parallel to the slip plane. It was also found, in marked contrast to the elastic theory, that the displacements parallel to both the dislocation line and the slip plane were not zero (at some positions they are about 9 percent of the near-neighbor distance). These displacements have both positive and negative signs. The edge dislocation is not very wide. The region of appreciable displacement extends only four or five near-neighbor distances either side of the dislocation, in agreement with the estimates of Foreman *et al.*⁽³¹³⁾ According to the elastic theory, the dislocation energy should increase linearly with $\ln(r)$, where r is the radial distance from the dislocation line. We find that this linear dependence holds only down to a distance of about 1.5 near-neighbor distances. Inside this core the elastic theory underestimates the dislocation energy. The radius of 1.5 near-neighbor distances corresponds to an energy of approximately 1.0 eV. This core energy is in good agreement with the estimates discussed earlier.

Screw Dislocation

The previous section describes a method by which the core of an edge dislocation can be treated atomistically. The core energy of a $\langle 112 \rangle$ edge dislocation in copper was found to be 1.0 eV per $\{112\}$ plane. This section presents the results of similar calculations on a $\langle 110 \rangle$ screw dislocation in copper (Burgers' vector $(a/2)\langle 110 \rangle$).

A crystal containing 282 atoms per $\{110\}$ plane, and which was made infinite along the direction of the dislocation line by use of periodic boundary conditions, was fed into a CDC 3600 computer. The atoms were first located at the positions given by the elastic theory and were then allowed to relax, one at a time, until atomistic equilibrium prevailed. Pairwise interaction between atoms was represented by the Morse potential function discussed in the previous section.

Figure 275 shows the positions of atoms around the screw dislocation in planes parallel to a slip plane. Even for atoms near the center it is found that the displacements parallel to the direction of the dislocation line are in good agreement with those calculated by elastic

* In collaboration with M. Doyama, ANL Solid State Science Division.

⁽³⁰⁹⁾ Bragg, W. L., *Symposium on Internal Stresses*, (London, Inst. of Metals), 222 (1947).

⁽³¹⁰⁾ Hasiguti, R. R., and Doyama, M., Japan Inst. of Metals, Oct. 1952, Bull. Phys. Soc. Japan, April (1953).

⁽³¹¹⁾ Cottrell, A. H., *Dislocations and Plastic Flow in Crystals*, (Oxford, Clarendon Press, 1953) p. 39.

⁽³¹²⁾ Huntington, H. B., Dickey, J. E., and Thomson, R., Phys. Rev., **100**, 1117 (1955).

⁽³¹³⁾ Foreman, A. J., Jaswon, M. A., and Wood, J. K., Proc. Phys. Soc., London, **64A**, 156 (1951).

125-1443

FIG. 273. Positions of the Atoms Around an Edge Dislocation in a F.C.C. Lattice. The plane of the figure is $\{112\}$. It is drawn to scale.

theory. The isotropic continuum elastic theory predicts that displacements in a slip plane normal to the dislocation line and also displacements normal to a slip plane are both zero. This was found to be not so on an atomistic scale. The displacements in these directions were found to have both positive and negative signs, and the maximum displacement was approximately 5 percent. Figure 276 shows a plot of dislocation energy as a function of radius from the center. Each point on the figure represents the addition of the energy of one atom to the total energy. According to the elastic theory, the dislocation energy should increase linearly with $\ln(r)$, where r is the radial distance from the dislocation line. As can be seen from Figure 276 this linear dependence holds only down to a distance of two near-neighbor distances. The difference between the atomistic and elastic energies inside this core is due mainly to the nonzero displacements discussed previously. Another interesting implication of these displacements is that there should be an interaction between point defects and a screw dislocation (even if the point defect has spherical symmetry).

Small Vacancy Clusters in F.C.C. Metals (Theoretical)

It is now well established that large aggregates of lattice vacancies generally find it energetically favorable to exist in the form of collapsed defects bounded by dislocations rather than in the form of open voids. The collapsed defects sometimes also contain stacking faults. When the aggregates contain several thousand vacancies, they can be observed directly by transmission electron microscopy, and this technique has afforded fairly precise determinations of their crystallographic character. The nature of the simplest forms, namely the single vacancy and the divacancy, is also known to a reasonable degree of certainty. It is the shape of the intermediate-sized clusters and the mechanisms by which they are formed that are not very well understood. The atomic configurations, binding energies, and migration energies of these clusters are still for the most part unknown. A more nearly exact knowledge of their properties might permit not only a more nearly complete interpretation of the quenching process (including the annealing by which it is invariably

125-1442

FIG. 274. Positions of the Atoms Around an Edge Dislocation in a F.C.C. Lattice. The plane of the figure is {112}. It is drawn to scale.

followed), but also a better understanding of such related processes as radiation damage, plastic deformation, and diffusion.

The atomic configurations and binding energies of trivacancies and tetravacancies in a face-centered cubic metal have been calculated.

There are four possible types of compact trivacancy; a "compact" trivacancy being one in which every vacancy is a near neighbor of at least one other vacancy. These four configurations, which have been briefly discussed by deJong and Koehler,⁽³¹⁴⁾ are the 60°, 90°, 120° and 180° trivacancies (see Figure 277). The last three of these are frequently referred to as "dog-leg" trivacancies. The angles referred to here are the angles which the outer two vacancies subtend at the middle vacancy. The 60° trivacancy has been investigated by Damask *et al.*,⁽³¹⁵⁾ who find that the atom located immediately above the three vacancies is able to relax

down towards the center of the triangle. This behavior is indicated in Figure 278. The atom 000, which is the common nearest neighbor of all the vacancies, relaxes in the direction indicated and reaches a stable position that is exactly at the center of the tetrahedron formed by position 000 and the three vacancy positions. This configuration is thus equivalent to an atom at the center of a symmetrical arrangement of four three-quarter vacancies. Damask *et al.* find that this relaxation leads to a considerable lowering of energy. The dog-leg trivacancies might not appear to permit large relaxations and therefore should not be so tightly bound. One of the objects of the present study was to test the truth of this point.

Calculations of some tetravacancy configurations have been reported by Vineyard and Gibson⁽³¹⁶⁾ although details of these calculations have not been published. These configurations are shown in Figures 279a and 279b. Other configurations of the tetravacancy are,

⁽³¹⁴⁾ deJong, M., and Koehler, J. S., Phys. Rev., **129**, 49 (1963).

⁽³¹⁵⁾ Damask, A. C., Dienes, G. J., and Wiezer, V. G., Phys. Rev., **113**, (1959).

⁽³¹⁶⁾ Vineyard, G. H., and Gibson, J. B., Bull. Am. Phys. Soc., **6**, 158 (1961).

125-1611

FIG. 275. Positions of the Atoms Around a Screw Dislocation in a F.C.C. Lattice. The figure shows atoms in three {111} planes immediately above the slip plane. It is drawn to scale.

125-1612

FIG. 276. The Energy of a Screw Dislocation Plotted as a Function of Radial Distance from the Center of the Dislocation.

of course, possible and Doyama and Koehler⁽³¹⁷⁾ have recently classified some of these. The configuration of Figure 279c is of particular interest because it would seem to be as compact as those of Figures 279a and 279b. The configuration of Figure 279a involves six nearest neighbor "bonds" (between vacancies). That of Figure 279b involves four such bonds. That of Figure 279c involves five bonds and should, therefore, have an energy before relaxation which is intermediate to the other two. Moreover it lies completely in a {111} plane, and such planes are known to be favorable to vacancy clustering.^(318,319) Finally it may be noted that configuration 279c is related to the 60° trivacancy discussed earlier.⁽³²⁰⁾ It permits two relaxations of the type that

⁽³¹⁷⁾ Doyama, M., and Koehler, J. S., *Phys. Rev.*, **134**, A522 (1964).

⁽³¹⁸⁾ Strudel, J. L., Vincotte, F., and Washburn, J., *Appl. Phys. Letters*, **3**, 148 (1963).

⁽³¹⁹⁾ Silcox, J., and Hirsch, P. B., *Phil. Mag.*, **4**, 72 (1959).

⁽³²⁰⁾ Cotterill, R. M. J., and Segall, R. L., *Phil. Mag.*, **8**, 1105 (1963).

occur in the 60° trivacancy. Atom 110 can relax towards the center of triangle 000, 101, 011 and atom

125-1288

FIG. 277. Configurations of the Trivacancies.

125-1246

FIG. 278. Positions of the Vacancies and the Relaxing Atom in the Tetrahedral Trivacancy. The three original vacancies are located at the corners of the triangle 011, 101 and 110, and the atom 000 relaxes towards the center of the triangle as shown.

125-1245

FIG. 279. Configurations of the Vacancies and Some of the Relaxing Atoms in the Tetravacancies Study.

0-11 can relax towards the center of 000, 101, 1-10. The configuration 279a will be referred to as the tetrahedral form, and those of 279b and 279c will be called the square form and the diamond form respectively (i.e., referring to the initial vacancy arrangement). One of the main objects of this study was the calculation of the binding energy of each of these tetravacancies to determine which is the most stable form.

The results given in Table 85 show that, contrary to

TABLE 85. "DOG-LEG" TRIVACANCIES

Type of Trivacancy	E_{R_3}	E_{3V}^B
60°	7.190 eV	2.119 eV
90°	7.657 eV	1.652 eV
120°	8.172 eV	1.137 eV
180°	8.006 eV	1.303 eV

TABLE 86. TETRAVACANCY

Type of Tetravacancy	E_{R_4}	E_{4V}^B
Diamond	9.430 eV	2.982 eV
Square	9.809 eV	2.604 eV
Tetrahedral	11.444 eV	1.069 eV

125-1247

FIG. 280. The Final Arrangement of the Vacancies and Relaxing Atoms in the Diamond Tetravacancy (compare with Figure 279c). All vacancies and relaxing atoms are in the plane of the paper, except for the vacancy 101, which is above, and the vacancy 000, which is below and which is hidden by 101.

what was anticipated, the binding energy of the 60° trivacancy is not appreciably greater than all three "dog-leg" trivacancies. The binding energy of the 90° type is smaller than that of the 60° type by only 22 percent. The present calculations do not give the height of the energy barrier between these two configurations. However, the similarity between the two binding energies does raise the interesting question of whether the 60° type can be easily transformed into the 90° type. If this is the case, it might be of considerable significance because the 90° trivacancy should be able to migrate rather freely. It can migrate without changing its shape. From Figure 277 we note that the middle vacancy, for instance, can change places with

one of the two atoms that is a near neighbor of all three vacancies. This process should have a very low activation energy because apart from the middle vacancy two other adjacent near-neighbor sites of the moving atom are vacant.

The 120° and 180° trivacancies have binding energies that are very close (see Table 85). Again the height of the energy barrier between these two configurations is not known at this time, but it does appear possible that the two configurations could interchange fairly easily. In so doing, the cluster would migrate. Moreover, since the two outer vacancies, in the 120° and 180° types, do not have much influence on each other (as is shown by the low binding energies of these two types) the migration energy of these two trivacancies should be close to the divacancy migration energy.

The results given in Table 86 establish that the diamond tetravacancy is the lowest energy configuration of the tetravacancy. (It is thought to be most unlikely that any of the less compact tetravacancies could have lower energies than those considered here.) In the diamond configuration the relaxing atoms 110 and 0-11 move towards the centers of the respective triangles, as was anticipated. The equilibrium positions of the moving atoms do not correspond exactly to the position occupied by the central atom in the tetrahedral trivacancy, however, because these atoms interact with each other. The final arrangement of the two relaxed atoms, the four original vacancies, and the two partial vacancies left behind by the relaxing atoms is shown in Figure 280 in which the plane of the paper is a {110} plane. It is to be noted that both of the relaxed atoms lie in this plane and that the final configuration thus has considerable symmetry. The symmetry is not so high, however, that either relaxed atom is equidistant from any two of the six partial vacancies (i.e., neither atom lies on the dashed line in Figure 280). As can be seen from the figure, the final distance between the two relaxed atoms is approximately equal to the nearest neighbor distance in the perfect crystal. Moreover, the component of this separation distance along the (111) direction normal to the plane containing the four original vacancies is approximately equal to the spacing between {111} planes in the perfect crystal. This is interesting because it suggests that even for a relatively small cluster such as the tetravacancy, there is a tendency for the relaxing atoms to move to the positions in the {111} planes that they occupy in a Frank sessile dislocation loop. It seems, therefore, that a cluster may be able to collapse at a very early stage of its growth, and continue to grow as a loop. Once a loop is formed the incoming vacancies will tend to join it on the outside because this region is under compression. A collapsed cluster will therefore tend to stay collapsed.

The square and tetrahedral tetravacancies must be metastable. Had they been unstable the computer would have allowed them to degenerate to the diamond form. The possible existence of these forms, as indicated by the results given in Table 86, raises the interesting question of whether they are produced in practice. The tetrahedral form, for instance, involves very little

40910

FIG. 281. Atomic Arrangement in a Twin Boundary in a F.C.C. Metal.

40911

FIG. 282. Atomic Re-arrangements Due to Vacancies in a Twin Boundary in a F.C.C. Metal.

41074

95,500X

FIG. 283. An Area of a Thin Film of Quenched Gold after Alpha-irradiation. Note that some partially annihilated tetrahedra remain.

relaxation. It could eventually lead to the formation of an uncollapsed void. To test whether this might be so, however, one would have to investigate the effect of adding further single vacancies at various points on the tetrahedral tetravacancy. The square form may also be of considerable significance. Yoshida *et al.*⁽³²¹⁾ and Kiritani⁽³²²⁾ have recently discovered a new type of vacancy cluster in quenched aluminum. This cluster has the form of an octahedron bounded by $\{111\}$ planes. It is observed in highly pure aluminum, quenched from close to the melting point at a relatively fast rate, and then annealed at 10°C . They believe that the defect is hollow. It is interesting to note that the square tetravacancy also produces an octahedral defect,

⁽³²¹⁾ Yoshida, S., Kiritani, M., and Shimomura, Y., "Formation of Secondary Defects in Quenched Aluminum," *Lattice Defects in Quenched Metals*, Academic Press, N. Y. (1965) p. 1.

⁽³²²⁾ Kiritani, M., *J. Phys. Soc. Japan*, **19**, 618 (1964).

39005

FIG. 284. Proposed Early Stage of the Annihilation of a Stacking-fault Tetrahedron.

when the relaxing atoms have reached their equilibrium positions. It is not yet known whether this tetravacancy would maintain its octahedral shape when joined by other vacancies, however, and even if it did it seems that the net results would be an octahedral arrangement of stacking faults rather than an octahedral void.

Annihilation of Vacancies at a Coherent Twin Boundary

Hirsch *et al.*⁽³²³⁾ have shown that when aluminum is quenched to produce dislocation loops the regions immediately adjacent to grain boundaries are denuded of these clustered-vacancy defects. This effect is a result of the fact that the severe misfit associated with grain boundaries makes them effective sinks for vacancies. More recently Segall⁽³²⁴⁾ has shown that twin boundaries are also capable of absorbing vacancies. Segall quenched gold and discovered denuded zones extending approximately 0.5 microns on either side of a coherent twin boundary. This observation was taken to indicate either that vacancies cluster preferentially at the twin boundary (by analogy with the segregation of impurities to stacking faults) or that they are annihilated at pre-existing monatomic steps in the boundary. In discussing the first of these possibilities, Segall states that removal of part of the boundary layer by insertion of a sheet of vacancies is energetically unfavorable. This note re-examines the possible occurrence of such a process.

The stacking sequence across a coherent twin boundary is, in the usual notation, C A B C A C B A C, and

⁽³²³⁾ Hirsch, P. B., Silcox, J., Smallman, R. E., and Westmacott, K. H., *Phil. Mag.*, **3**, 897 (1958).

⁽³²⁴⁾ Segall, R. L., *Acta Met.*, **12**, 117 (1964).

Segall suggests that the vacancies might remove part of one of the adjoining C planes and cause a localized movement of the boundary plane. In re-examining the possible removal of atoms in the A layer, it is convenient to consider the planes shown in Figure 281. The large white circles represent atoms in the C layer just below the twin boundary, the shaded circles are atoms in the A layer, and the small white circles are atoms in the C layer just above the boundary. As an example of the geometry involved one may consider the case in which four vacancies lie in a straight line in the A layer. The presence of these vacancies permits six of the atoms in the A layer to move into B positions as

39007

FIG. 285. Proposed Intermediate Stage of the Annihilation of a Tetrahedron.

39006

FIG. 286. Proposed Final Stage of the Annihilation of a Tetrahedron.

shown in Figure 282. We show below that this leads to a lowering of the energy. In the region where this movement occurs the local stacking sequence becomes C A B C B C B A C, and the net effect of the change is to produce a narrow region, five atomic layers deep, of hexagonal close-packed material (see Figure 282). The triangle XYZ which forms the boundary of the shifted region is a Shockley partial dislocation (Burgers' vector = $(a/6) \langle 112 \rangle$). Further growth of the untwinned region will occur as more vacancies arrive at the sides of the triangle.

It is interesting to note that when further vacancies arrive at the interior of the Shockley loop, they too can be absorbed. This secondary absorption allows atoms in the B layer to shift back into A positions, thus reverting part of the region back to the twin configuration. This process is energetically easier than the first process because the term involving γ_T now has the opposite sign. The successive absorption of vacancies at the coherent twin boundary may therefore produce a series of concentric Shockley partials any one of which separates layers of twin and five-layer hexagonal material. The Shockley partials need not be triangles. It seems likely that they would tend to be more circular. Geometrical considerations suggest that the smallest vacancy cluster that can be absorbed at a twin boundary in this manner is the divacancy.

Annihilation of Stacking-fault Tetrahedra

We have recently considered the removal of tetrahedra by interstitial absorption. We re-examined some of the results of the Cotterill-Jones experiment^(325,326) in which tetrahedra in gold are removed during alpha-irradiation, presumably by the accretion of interstitials generated by the irradiation. In particular, we scanned the pictures taken at about 80 percent completion of the process. Such pictures (see Figure 283) frequently show partially annihilated tetrahedra. One should note the shape of these defects. Some appear to still contain stacking faults, but the fault contrast is not the same as that observed with complete tetrahedra. Others ex-

hibit contrast in the form of thick straight lines, and these frequently appear in pairs, giving rise to V-shaped defects. Working backwards from these observations, we considered a mechanism of the type shown in Figure 284. Interstitials have clustered on one face of the tetrahedron and have created a tetrahedral jog. This jog involves the formation of three obtuse stair-rod dislocations which join intrinsic and extrinsic faults, three stair-rod dislocations joining pairs of extrinsic faults, and the three extrinsic faults themselves. A simple way to look at the indentation is to imagine a small interstitial tetrahedron arranged so that one of its extrinsically faulted faces coincides with a face of the tetrahedron and cancels it out. It seems that the smallest cluster of interstitials that could initiate this process is the tri-interstitial. The increase in energy due to the corresponding indentation is found to lie between about 2.0 and 4.0 eV, and it is interesting to note that this is in reasonable agreement with the value obtained by Koehler and Lund⁽³²⁷⁾ for the activation energy for tetrahedron annealing. In the case of the irradiation experiment, the process could easily proceed because the three interstitials would be able to give up to 12 eV between them in order to create the indentation. The interesting point is that the indentation might also be able to form spontaneously by thermal activation if the specimen is annealed at a high temperature. Presumably, once it is formed vacancy emission would proceed by the passage of the sides of the jog over the face of the tetrahedron.

Getting back to Figure 284 and the case of the irradiation-induced removal of tetrahedra, we might note that as more and more interstitials are absorbed the triangular indentations will grow. Figure 285 shows this process occurring on two faces (to simplify the diagram) and the indentations have interpenetrated. At a later stage one might have a defect of the type shown in Figure 286. There are, of course, numerous other possible configurations. One sees that faulted planes and also isolated "arms" may be formed in this way, and these may correspond to the defects shown in Figure 283.

⁽³²⁵⁾ Cotterill, R. M. J., and Jones, M. W., *J. Phys. Soc. Japan*, **18**, 158 (1963).

⁽³²⁶⁾ Hirsch, P. B., Cotterill, R. M. J., and Jones, M. W., *Proc. 5th Intern. Conf. Electron Microscopy*, **1**, F3 (1962).

⁽³²⁷⁾ Koehler, J. S., and Lund, C. A., "Non-equilibrium Situations Involving Point Defects in Metals," *Lattice Defects in Quenched Metals*, Academic Press, N. Y. (1965) p. 713.

APPENDIX A

PLANT MODIFICATIONS AND NEW FACILITIES

1. Plant Recirculating Water System for Cooling Scientific Equipment, Building 212 (B. J. KOPROWSKI AND W. H. LIVERNASH)

To satisfy the demand for the large quantity of water required for cooling scientific equipment, a separate recirculating water system was constructed as one of the building utilities for the Fuels Technology Center. This system, after operating satisfactorily for about three years, was revised to provide additional capacity and to correct certain minor deficiencies in the original system.

The revised system is shown in the schematic diagram, Figure A-1. Water is distributed to the scientific equipment by the four pumps, G-10, G-11, G-12 and G-13 through a network of supply and return pipe headers located in each wing of the building. The pumps supply water at a pressure of 5.3 kg/sq cm (75 psig) and a maximum flow rate of 100 liters/sec (1600 gpm). Before the water is distributed to the supply headers in the building it is first filtered to remove particulate impurities and then cooled by the refrigeration units to a temperature of 15.5°C (60°F). The water then flows to the supply headers, through the scientific equipment being cooled, back to the return headers and finally, back to the pump inlet line through the mixing tank, which acts as a reservoir for the system. The supply and return pipe headers located in each wing of the build-

ing are connected to the common manifold for the pump supply and return lines and are provided with isolation valves so that the piping in each wing of the building is essentially a separate "zone" of the system. By this arrangement, a "shutdown" can be made in one wing without affecting the distribution of water to other wings of the building. Figure A-2 is a detailed illustration of all of the components for control of pressure, temperature and flow for the system. For convenience of operation and maintenance these are located together in one room.

Engineering for the modification of the system was performed by the Plant Engineering Division at ANL. The P. Nacey Company, selected on the basis of competitive bids, performed the construction work. Inspection of the construction work was provided by the ANL Engineering Inspection Department. The construction work extended over a period of about six months. Because of the importance of this system to the operation of the scientific equipment, construction modifications to the water system were scheduled in a manner that allowed the system to remain in operation throughout the construction period except for one scheduled shutdown period of three weeks.

Fig. A-2. Recirculating Water Flow Diagram for Room G-1.

2. Helium Atmosphere System for a Single Vacuum Drybox (W. H. LIVERNASH, B. J. KOPROWSKI, AND H. A. LEVIN)

Transfer and loading operations involving small (<10 gram) amounts of high purity sodium are to be performed in a vacuum drybox recently installed in Building 212, DL-223. In order to maintain a high purity atmosphere during the operations, a purification-recirculation system has been installed and is now being tested. Since short duration (<20 minutes) manipulations are anticipated for this drybox, only a minimum purification unit (Figure A-3) has been provided. It is recognized that the ultimate purification system is much more sophisticated in design. With normal operation and careful transfer techniques, moisture and oxygen levels in the drybox are expected to be maintained below 1 ppm. The actual objective is to maintain a bright noncontaminated surface on solid sodium samples for periods of 30 minutes or more while the operator is working "through" the drybox gloves.

The system includes one vacuum drybox with a vacuum transfer lock, a vacuum system, an enclosed recirculating pump, a molecular sieve-liquid nitrogen helium purifier, pressure control devices, and an electrolytic moisture monitor. Provisions have been included to add oxygen monitoring equipment and additional purification equipment at a later date if necessary.

System Operation

Start-up of the system is accomplished by evacuating and backfilling the entire system with helium. Components subject to damage by excessive pressure differentials (Magnehelic pressure gauges, pressure switches, etc.) are isolated during evacuation. Cleanup of residual impurities is performed by the purification system.

Recirculation is achieved by a positive-displacement carbon-vane pump. When system pressure-drop characteristics have been established, a blower-type unit will be selected to eliminate maintenance problems associated with carbon-vane pumps operated in extremely dry atmospheres. System flow rates between 2.4 and 7 liters/sec (5 and 15 SCFM) are planned to accommodate from one to three dryboxes.

The purification unit consists of four chambers filled with molecular sieves immersed in liquid nitrogen and piped in a series-parallel arrangement. Regeneration will be accomplished by disconnecting the purifier assembly and lifting it from the liquid nitrogen bath. Back purging of the purifier at room temperature will complete the regeneration cycle. During regeneration the recirculating pump will be turned off but the pres-

FIG. A-3. Helium Atmosphere Drybox System.

sure controls will remain in operation. Liquid nitrogen consumption for continuous operation is expected to be about 400 l/week.

Operating pressure in the drybox will be maintained between +0.75 and +1.75 cm of water column (+0.3" and +0.7" W.C.) by a pair of pressure switches that operate solenoid valves for make-up from a helium manifold or bleed off to the room. Helium consumption has not been estimated, but will vary directly with the frequency of vacuum lock transfers, purifier regenerations and system start-ups.

A representative drybox atmosphere sample will be

taken from the box exhaust gas and monitored continuously for moisture content. System leakage or purifier efficiency may be established by monitoring for moisture at various other parts of the system such as the purifier inlet or outlet or the pump discharge.

Actual usage and operating experience during the next six months are expected to dictate minor modifications to the system. Automatic liquid nitrogen transfer and heat exchangers for liquid nitrogen economy are some of the items that have not been included in the system at this time.

3. Recirculating Argon Atmosphere for Glovebox System (W. H. LIVERNASH, B. J. KOPROWSKI, AND E. D. LYNCH)

The preparation and compaction of nonradioactive, but toxic, ceramic powders will be performed in a glovebox train recently installed in Building 212, G-124. An extremely dry inert gas atmosphere is required to prevent powder deterioration or contamination. Oxygen as an atmosphere impurity in the glovebox train is of secondary importance for the work anticipated in this facility. This system was designed and installed in a manner that will permit conversion to a facility for handling alpha active materials with relative ease.

A dry atmosphere is maintained by recirculating argon gas through a commercially available molecular sieve dryer. Oxygen level and glovebox pressure are controlled by the once-through pressure control system (Figure A-4). Three interconnected gloveboxes with isolation doors and vacuum transfer locks have been provided.

The following four basic units have been combined in this system:

1. A glovebox train composed of three gloveboxes, interconnected by means of sheet metal tunnels that are sealed with "O-rings" to the glovebox panels.
2. A low flow, once-through argon atmosphere and glovebox pressure control system.
3. A high flow rate argon gas recirculating and drying unit.
4. Oxygen and moisture monitoring equipment with sample lines connected to various points of the system.

Operation of the Systems

Glovebox Train

The three gloveboxes have been assembled to form a single unit. Extreme care was taken to minimize

water vapor transmission into the glovebox atmosphere. Hypalon coated neoprene gloves are the only permeable membranes in the system. Vacuum locks are located at each end of the train for the transfer of materials into and out of the system. "O-ring" sealed isolation doors have been installed in the center glovebox to permit the separation of operations that might cause atmosphere contamination (solvent vapors, etc.) within the gloveboxes. High efficiency filters are included at all inlet and outlet argon connections to each glovebox. All filters are changed from within the glovebox.

Once-through System

High-purity argon gas is supplied to the gloveboxes on demand from a commercial liquid argon converter. The argon gas is metered into the system at a constant flow rate of about 1.5 m³/hr (1 SCFM). The argon gas flows through the gloveboxes into the exhaust header which is maintained at a constant pressure of +1.75 cm H₂O (+0.5" W.C.) with respect to the room by a pneumatically actuated valve and valve controller. Glovebox pressure is essentially the same as the exhaust header pressure. The gas is then drawn from the system and discharged to atmosphere outside the building by the room air exhaust duct system.

Recirculating System

The three gloveboxes are connected in parallel with a dual tower gas dryer. The dryer is automatically regenerated. The maximum flow rate of 0.5 m³/min (3 SCFM) through the dryer can be piped through one glovebox, or distributed to any combination of gloveboxes.

106-8346

FIG. A-4. Recirculating Argon Atmosphere Glovebox System.

Gas Monitoring Systems

Continuously recording instruments that have been provided monitor oxygen and water-vapor concentrations in the glovebox atmosphere. Gas samples may be taken from various parts of the system as noted in Figure A-4. The moisture monitor is an electrolytic hygrometer with a multiple range of 0–10, 0–30, 0–100, 0–300, and 0–1000 ppm. The oxygen analyzer is a paramagnetic-type instrument with a dual range of 0–1000 ppm and 0–5000 ppm and automatic standardization. Individual sample lines terminate at manifolds near each instrument and an additional manifold has been installed on the moisture monitor system to permit continuous purging of all sample lines even though samples from some lines are not being analyzed.

Operating Experience

During installation of the equipment the dryer unit required complete repiping to attain helium mass spectrometer leak tightness. Initial "drying" of the system

required about six weeks of continuous recirculation. Moisture levels of 0.5 ppm are now being attained, however, the work load in the system has been light. Moisture concentrations from 2 to 5 ppm are expected in the gloveboxes as the work load increases. Oxygen concentrations under light and normal operating conditions vary between 20 and 35 ppm.

Planned Modifications

Conversion of the laboratory to a plutonium-handling facility is now in the engineering phase. Modifications to the room are required but will not be discussed here. Conversion of the glovebox system to plutonium work will be readily accomplished by:

1. operating the gloveboxes at a negative instead of positive pressure;
2. replacing the vacuum locks with bag rings and plastic pouches to permit alpha active materials to be transferred by the plastic transfer bag technique;
3. modifying the transfer tunnels to facilitate glovebox relocation or maintenance without violation of the alpha barrier.

4. Alpha-Gamma Hot Cell, Building 212 (F. L. BROWN)

The air-atmosphere service areas of the Metallurgy alpha-gamma hot cell were activated during the year, placing the entire facility in full operation. Thus it became possible to remove alpha contaminated wastes for disposal, to store contaminated equipment within the confines of the service area, and to make equipment repairs in the various service facilities. Complete remote operation of the nitrogen-gas-filled main working area was not realized, however, due to limitations posed by master-slave manipulators. Continuous remote decontamination remained a major operating requirement so that the main working area could be entered after only minimum delay for decontamination.

The changeover of the service area from a static to an air purge ventilation system greatly simplified the development of equipment and techniques for making transfers into the gamma shielded areas as completely tight seals were no longer required; small temporary openings in the alpha barrier could be tolerated. The introduction of large equipment items through an overhead pouch transfer system presented no difficult problems. Equipment was installed to effect removal of alpha contaminated wastes. Waste shipments requiring an excess of four inches of lead shielding for operator protection were sealed into disposal cans and then transferred to the shielded shipping container using completely remote methods. Intermediate level wastes (which comprised the main bulk of the waste material) were bagged into a cask with a split lid which closed to provide the operator with four inches of lead shielding while sealing the plastic disposal pouch.

Other transfer facilities, installed for special purposes, were sealed until special operating equipment is available. These facilities include a port for operation of a sealed remote metallograph now under construction, and two ports to be used for re-encapsulation techniques now being developed.

Additional equipment items were procured and in-

stalled in the main working area of the cell. Among the more important of these items were a postirradiation annealing furnace and vacuum system, a Tukon microhardness tester (also used for photomicrography) and metallography preparation equipment. The foregoing items were introduced and installed remotely in the cell main working area, although on several occasions personnel entries were made to effect rather extensive modifications. Air line plastic suits were worn to protect operators from alpha contamination. The suits were readily decontaminated in water-detergent showers before removal; a few garments worn under the suits were lost due to contact with smearable alpha contamination remaining on the suit exteriors following the shower decontamination.

Capability for macrophotography was greatly enhanced by the acquisition of a Lerma periscope and a camera which utilized a telephoto lens to take pictures through the zinc bromide viewing windows. Resolution was improved by the use of sodium illumination.

A procedure for control of materials introduced into the cell was programmed to keep track of radioactive samples as they were processed or stored within the facility and to prevent the inadvertent accumulation of a critical mass of fissionable material. The data system was designed for transformation to punch cards when the number of individual items reaches unwieldy proportions.

Operations performed during the year included annealing studies, metallographic preparation, microhardness testing, density determinations, physical dimensioning, and photography. The most difficult problem, that of waste removal, apparently was solved. The time devoted to remote decontamination, however, was a major factor in the operation of the facility and will continue to be until more effective techniques are developed.

5. Tube Fabricating Equipment, Wing H, Building 212 (R. M. MAYFIELD AND W. R. BURT, JR.)

The procurement of some light equipment items and alterations and/or modifications to existing equipment occurred during the year where necessary to improve overall operating efficiency. A brief review of certain of these details is discussed in the following paragraphs.

Straightener

A Model AY Macintosh-Hemphill tube straightener ($\frac{1}{8}$ "– $\frac{5}{8}$ " diameter) was received in January, 1964 (WP-2254—P.O. 424512). The unit was installed and made operable shortly thereafter. It has seen service for rod and tube straightening and to a limited extent for reel-

ing tubes from mandrels. It is a useful and versatile device for the group operations.

A cold-wall high-temperature heat-treating and annealing furnace was ordered from Centorr Associates, Suncook, New Hampshire, on July 24, 1964 (WP-2605—P.O. 458224). An inspection of the furnace by an ANL representative was completed on November 16, 1964. The unit was due to be shipped during December, 1964.

Annealing Furnace

This furnace has been needed for some time since the tungsten and tungsten alloys have stress-relieving and recrystallization temperatures above the capabilities of our existing resistance heated vacuum furnaces. The unit will be put into immediate service and hopefully the tungsten program work will be accelerated.

Tube Reducer

Toward the end of the year some effort was expended on the possible procurement of a tube reducer of a size suitable for our needs. None could be found except large scale production models that were priced far

above our budget (\$34,000 for a used model and \$185,000 for a new model).

Accordingly, a design has been proposed and studied based upon a unique principle developed by Krause and modified by Nosal. The design calls for a three roll configuration in contrast to the two rolls or dies used in conventional tube-reducing, or rocking. Work Project 2659, Rev. 1, has been approved to cover design, construction and installation. Drawings (MY-E-2200) should be completed in the early part of December, 1964, and a service request for shop construction will be issued shortly thereafter.

Extrusion Press Tooling

The 7.6 cm tooling and container for the 1150 tonne press was received during the early part of the year. Upon inspection it was noted that the container liner was improperly assembled and it had to be returned for correction. The tooling is now complete and ready to go except for a slight modification on the billet loader. The pressure of other program demands has forestalled testing of the tooling arrangement.

6. Extrusion Press Testing and Modification, Building 350 (G. BURTON, JR.,* N. CARSON, AND A. CARR)

The extrusion press was made operable and the glovebox atmosphere was established in late 1963. The work done during 1964 was directed toward (1) training the personnel on press operation, (2) shaking down the auxiliary systems, (3) testing extrusion and (4) developing safe operating methods that do not contaminate the equipment.

Instrumentation was added to the press to indicate extrusion pressure and ram speed. A pressure transducer was installed in the main cylinder line and circuitry was added to bring the electrical signal to the operating console. A two-pen, strip-chart recorder was installed to record extrusion pressure and ram speed.

The induction billet-heating furnace was tested. Additional capacitors were added to the motor-generator-powered tank circuit to improve the power factor. The bus bars carrying power to the furnace were not sufficiently cooled. The bus bars, originally cooled by the negative-pressure water system, were reconnected to the positive-pressure water system to obtain increased plant flow.

The hoist motor in the five-ton crane burned out as

a result of control circuit failure and was replaced during 1964. The crane was disassembled in the storage hood and the motor was removed from the glovebox line through a vinyl pouch. A new motor and limit switch were installed without introducing air to the helium atmosphere. The ram-travel limit switches were found to be reversed and were rewired to operate correctly. Billet closure-welding equipment was installed in the storage hood and connected to an external welding power supply.

An exploratory program was initiated to test extrusion concepts. Nonradioactive materials were substituted for costly plutonium-bearing fuels. A total of 22 billets were extruded, including (1) one piece metal billets, (2) metal slugs within metal shells, (3) shot-and-oxide-filled metal shells and (4) rod-and-oxide-filled metal shells. The shells were copper, iron, zirconium and titanium. Copper outer jackets were used over the last three shells to prevent die sticking. Dry colloidal-graphite and MoS₂ lubricants were also tried with marginal success.

The solid billets were extruded (with little trouble) while setting up, testing and calibrating press instrumentation. Composite bimetal billets were extruded to

* Now with Nuclear Materials and Equipment Corporation, Apollo, Pennsylvania.

develop die designs and determine the best extrusion ratios for coextrusion. Coextrusion of metals with comparable plasticity was accomplished with dies having a lead-in angle of 45° and a straight section and flared exit. Sharp edge extrusion dies were not satisfactory for coextrusion.

Preliminary tests were made on billet shells filled with compacted-copper shot and fine aluminum oxide. In extrusion the shot elongated to needle-like fibers with the oxide filling triangular-sectioned spaces between the needles. There was a tendency for clumping of the oxide at the ends of the needles. A subsequent billet was filled with copper wires and Al_2O_3 . The wires extruded to the full length of the extrusion with a uniform packing of oxide in full length stringers. Sections of this extrusion were inserted in a drilled copper block and re-extruded. The fibers were reduced to microscopic dimensions. Further investigation of this technique will be made with fertile metal and fissionable oxide composites.

An attempt was made to repeat the preceding experiment with metal shot and powdered glass. The experiment was not successful. Because of the high lubricity of the glass, the interior developed pressures that caused irregular swelling of the jacket beyond the dies.

Preliminary experiments were made with dry lubricants applied to the jacket shells before loading. Graphite and MoS_2 were partly successful, but were not as good as a thin shell of copper. Pickling to remove copper is undesirable with plutonium fuels because of contamination and nuclear criticality problems. A test was made with an alumina powder layer between the fuel jacket and the extrusion can. This permitted machining and mechanically stripping the jacket, but further development is required.

With the modifications made to the extrusion press and these tests, the equipment was judged ready for test fabrication of fuel materials. Further work on uranium, plutonium and thorium bearing materials is being carried out under Program 1.5.11.

APPENDIX B

PUBLICATIONS AND REPORTS

Publications

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- Baskin, Y., and Shalek, P. D., *Synthesis of Uranium Monophosphide by the Phosphine Reaction*, J. Inorg. Nucl. Chem. **26** (10) 1679-1684 (1964).
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