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PART I
ENGINEERING METALLURGY

A. Development and Fabrication Programs for EBR-II

1. Fuel Materials

The fuel for the Core I loading of EBR-II is an U-5 w/o Fs* alloy jacketed in stainless steel and bonded with sodium. The reference fuel material for the Core II loading is U-20 w/o Pu-10 w/o Fs proposed to be jacketed in a refractory metal jacket. Development work on the U-Fs material was continued during this period toward termination. Development work on the plutonium-bearing fuel continues at an increasing level.

Properties of Uranium-Fissium Alloys (H. Savage)

The thermal conductivity of an U-5 w/o Fs-2.25 w/o Zr alloy has been measured in the apparatus described by S. T. Zegler (ANL-5611).** The standard bar method yielded a heat conductivity described by the equation $0.0464 + 3.3975 \times 10^{-5} T + 3.9068 \times 10^{-8} T^2$ cal/sec-cm-°C, with T in degrees centigrade, from 0 to 800° C, with an accuracy of $\pm 8\%$.

As may be seen from Table I, the enthalpy of this alloy is somewhat higher than that of the uranium up to approximately 350°C. From 350 to about 550°C, the enthalpy of the alloy increases very little, whereas the enthalpy of uranium continues to increase. Contrary to what would be expected from density considerations, the overall effect is that of a lower enthalpy at higher temperatures for the U-Fs alloy when compared to uranium. The accuracy of these measurements vary from 1.5% at 200°C to 2.3% at 750°C. The lower figure is valid to 600°C. These accuracies were determined on a silica tube in which no transformations occurred.

The data reported in Table I were obtained using a room-temperature, stirred water bath, isothermal drop calorimeter. This calorimeter, in addition to being used to procure data for the U-5 w/o Fs alloy, was the basis for design of a second, more elaborate, high-temperature model. The major design change in the new calorimeter was the conversion to an elevated-temperature calorimeter block. This change was made in an attempt to reduce the error due to sluggish transformations. The new, improved calorimeter will be installed and operated in a glovebox so that measurements can be made on plutonium-containing materials.

* The term "fissium" (Fs) denotes an aggregate of fission-product elements that remain in a spent fast reactor fuel after pyrometallurgical refining. These elements which are present in fixed ratios, are Mo, Ru, Rh, Pd, Zr and Tc. Increased additions of Mo and Ru were substituted for Tc in this investigation.

** Argonne National Laboratory reports to which reference is made are listed on p. 270

Table I

ENTHALPY OF URANIUM AND URANIUM -
5 w/o FISSION ALLOYS

Temp (°C)	Enthalpy (cal/gm-atom)		Remarks
	Uranium ^a	U-5 w/o Fs	
25	0	0	
35	67.0	106.5	Alloy ΔH above that of pure U
50		265.7	
100	514.2	574	
150		873	
200	1232.0	1260	Accuracy approx 1.5%
250		1660	
300	2006.7	2050	
350		2395	
400	2847.8	2705	Alloy ΔH below that of pure U
450		2845	
500	3766.2	2875	
550		2915	Accuracy approx 1.5%
600	4786.5	3320	
650		4260	
700	6340.0	4755	
750		4855	Accuracy approx 2.3%

^a Calculated from Ginnings, D.C., and Corruccini, R. J., J. Res. Nat. Bur. Stand., 39 309 (1947).

Phase Studies of Uranium-Plutonium-Fission Alloys
(O. L. Kruger)

The phases occurring in U-20 w/o Pu-Fs alloys are being studied to expand the knowledge on the plutonium-bearing fuel loading for the second core of EBR-II. As part of this investigation, any alloying trends which could be of interest in the measurement of properties will be noted. An attempt will be made to correlate the phase transformations with those present in the uranium-fission and/or the uranium-plutonium-molybdenum systems.

In order to avoid an extensive study of a complex system, certain isotherms occurring in quench specimens were selected for phase identification by metallograph and X-ray diffraction. Alloys of U-20 w/o Pu-Fs with 5-, 10- and 15-w/o Fs and the same alloys with 1.5-, 3- and 4.5-w/o Zr added to the basic fission have been prepared by arc melting.

Metallographic and X-ray diffraction needle specimens were taken from the more ductile homogenized and quenched material because the low-temperature phases are hard and brittle. Hardness data and densities of the as-cast material and solidus temperatures of these alloys have been reported.¹ Heat treatments at 775, 700, and 625°C for 74, 115 and 434 hours, respectively, have been completed. All alloys contain a primary phase which has not yet been identified (see Figure 1a). The amount of this phase increases with increasing fissium content.

The 75 w/o U-20 w/o Pu-3.5 w/o Fs-1.5 w/o Zr alloy was found to be body-centered tetragonal from 775 to 625°C. The lattice parameters for the 775°C heat-treated material are $a_0 = 6.99 \text{ \AA}$, $c_0 = 6.78 \text{ \AA}$ and $c/a = 0.970$. This phase is isostructural with the U-Nb tetragonal phase reported by Dwight and Mueller² and an unidentified phase in the U-Pu-Mo system with a composition of 77 w/o U-20 w/o Pu-3 w/o Mo.³ The 75 w/o U-20 w/o Pu-5 w/o Fs alloy is b.c.c. when quenched from 775°C. Quenching from 700°C produces a slightly distorted cubic cell, whereas, quenching from 625°C produces the tetragonal structure. It is not known whether this structure is due to ordering of the cubic gamma phase during quenching or whether it is a true phase change.

The 70 w/o U-20 w/o Pu-10 w/o Fs alloy has a Widmanstätten precipitate within the grain (Figure 1b) and a grain boundary phase when quenched from 700°C. When this alloy is quenched from 625°C, the grain boundary phase is no longer present.

The 65 w/o U-20 w/o Pu-15 w/o Fs diffraction patterns indicate the presence of the U_2Ru compound. This phase, which is shown in Figure 1c, increases in quantity with decreasing temperature.

Alloys containing additional zirconium have an identifiable concentration of the CsCl-type phase, ZrRu (see Figure 1d), which has been studied by Dwight. This additional primary phase increases in quantity with increasing fissium content.

The homogenized and quenched alloys of 65 w/o U-20 w/o Pu-3.5 w/o Fs-1.5 w/o Zr and 65 w/o U-20 w/o Pu-15 w/o Fs were somewhat brittle even though they were given the same heat treatment as the other alloys. The only apparent difference between the low fissium alloy with additional zirconium and the other ductile fissium alloys is the difference in the matrix structure. These matrix structures are tetragonal and b.c.c., respectively. The 15-w/o Fs alloy contains the U_2Ru phase, which is not present in the 10 w/o Fs alloy.

¹Annual Report for 1959, Metallurgy Division, ANL-6099, p. 9.

²A. E. Dwight and M. H. Mueller, Constitution of the Uranium-rich U-Nb and U-Nb-Zr Systems, ANL-5581 (1957).

³F. Anselin, Grenoble Conference Paper No. 20 (1960), to be published.

Figure 1. Photomicrographs of Several U-20 w/o Pu-Fs Alloys.

1-a.

Micro 27948 500X
 70 w/o U-20 w/o Pu-10 w/o Fs alloy
 heated at 775°C and quenched. Un-
 identified primary phase in b.c.c.
 gamma matrix.

1-b.

Micro 27985 200X
 70 w/o U-20 w/o Pu-10 w/o Fs alloy
 heated at 700°C and quenched.
 Widmanstätten precipitate in b.c.c.
 gamma matrix.

1-c.

Micro 27970 500X
 65 w/o U-20 w/o Pu-15 w/o Fs alloy
 heated at 700°C and quenched. U₂Ru
 type phase + unidentified primary
 phase in b.c.c. gamma matrix.

1-d.

Micro 27947 500X
 65 w/o U-20 w/o Pu-10.5 w/o Fs-4.52
 w/o Zr alloy heated at 775°C and
 quenched. ZrRu (light) + unidenti-
 fied primary phase (dark) in b.c.c.
 gamma matrix.

The X-ray diffraction patterns of heat-treated specimens indicate a relatively large grain size for the 5-w/o Fs alloys, a medium grain size for the 10-w/o Fs alloys, and a fine grain size for the 15-w/o Fs alloys. Increasing additions of fissionium apparently further retard grain growth.

Structure of Injection-cast U-20 w/o Pu-10 w/o Fs Alloy
(O. L. Kruger)

The injection-casting process is to be used to produce fuel pins of the U-20 w/o Pu-10 w/o Fs alloy, the reference fuel material for the second loading of EBR-II. This injection casting process will be similar to that which is being used to fabricate the first loading of U-5 w/o Fs. In the injection process, the top of the rod is cooled more quickly than the bottom, which is near the melt. The degree of formation of the primary dendritic phase, as shown in Figure 2, is evidence of the varying cooling rate. The primary dendrites in a specimen taken from the bottom of an injection-cast rod have a much greater degree of development than the dendrites in specimens taken from the center and top of the same rod. In fuel alloys which undergo sluggish phase transformation upon cooling, the high-temperature phase can be expected in regions of rapid cooling and the low-temperature phase in regions of slow cooling. This anticipated behavior was first made evident in the U-20 w/o Pu-10 w/o Fs injection-cast pins by the fact that the tops of the pins were relatively more ductile than the bottoms.

Metallographic specimens were taken from the top, center, and bottom of injection-cast pins and examined for evidence of phase changes. The photomicrographs of Figure 2 reveal that the structure of as-cast pins differs from top to bottom. The matrix of the top specimen is cored gamma while the matrix of the bottom specimen is transforming to an apparent low-temperature, two-phase structure. Thermal expansion curves⁴ show that this transformation takes place within the temperature range from 525 to 600°C.

The microstructures of specimens heat treated at 650 and 500°C for one hour and quenched did not change appreciably in this time, which indicates the sluggishness of the transformation. The low-temperature structure transforms to the gamma matrix on heating, as determined from thermal expansion curves.⁴ Cooling of cast alloys at a rate of about 20°C/min will retain the gamma structure to room temperature. The quenched structure will start to transform to the low-temperature phases after about eight minutes if held at 400 to 500°C.

The U-5 w/o Fs alloy, reference alloy for the first loading of EBR-II, has a solidus temperature of 1002°C,⁵ as compared with $820 \pm 10^\circ\text{C}$ for the solidus of U-20 w/o Pu-10 w/o Fs.

⁴Annual Report for 1958, Metallurgy Division, ANL-5975, p.15.

⁵H. A. Saller et al., Properties of Fissionium-Type Alloy, BMI-1123 (August 3, 1956).

Figure 7. Specimen Taken from the Top, Center and Bottom of an Injection-well (7000 U-2) on P-1 1000 Rd.

Top

Micro 20265

150X Micro 26264

75 X

Center

Micro 26270

150X Micro 26271

75 X

Bottom

Micro 26261

150X Micro 26260

75 X

Evidence of incipient melting was removed by heating at the same temperature for eight hours. From the curvature of the solidus,¹ incipient melting would not be expected below 780°C, even in a badly segregated cast structure.

Compatibility of Uranium-Plutonium-Fissium Alloy with Potential EBR-II Jacket Materials (D. B. Brown, J. J. Huet and L. R. Kelman)

The program to determine the compatibility of potential jacket materials with the EBR-II U-20 w/o Pu-10 w/o Fs reference fuel alloy has continued. Several materials were considered in addition to those being studied. To simulate thermal conditions anticipated in the reactor more closely, diffusion penetration studies, originally made at 700 and 800°C, were also made at 600° C for up to 60 days. High-temperature strength was a major criteria in selection of the materials tested in keeping with the requirement that the jacket must restrain irradiation swelling of the fuel. The materials under study include titanium, molybdenum, vanadium, tantalum, yttrium, niobium, niobium-5.3 w/o vanadium, zirconium, Zircaloy-2 and Types 347 and 430 stainless steel.

The depth of diffusion penetration between couples of these materials with the reference fuel alloy was determined by measuring the maximum diffusion band that could be developed metallographically. Considerable effort went into developing polishing and etching techniques to show these bands. The low solubility of uranium and plutonium into most of the metals tested permits the assumption that the edge of the observed diffusion band is a practical limit of penetration into the clad material. The exception is niobium, which has a relatively high solubility for uranium. Since gamma uranium can dissolve appreciable amounts of most of the investigated metals, the limit of diffusion into the fuel may be appreciably greater than indicated by the observed diffusion band.

Results to date are summarized in Table II, where times are given for diffusion penetration to depths of 1 mil as well as through the EBR-II can thickness of 9 mils. (Typical photomicrographs of diffusion zones for each type of couple are given in Figure 3.) From the data it is evident that only the stainless steels are useless as jacket materials for U-Pu-Fs alloys at EBR-II temperatures. The validity of some of the other test results must be checked to explain anomalies in the data.

The materials can be divided into four groups. The first group consists of titanium, molybdenum, tantalum, and vanadium, which can be considered for use well above the EBR-II fuel-clad temperature. At 700°C the penetration rates of the metals are relatively small, and, even at 800°C (only 20°C below the solidus of the fuel alloy), 9-mil jackets of titanium, molybdenum, and vanadium would not be penetrated in 90 days.

A hot pressure-bonding technique under vacuum was necessary to develop bonding of the vanadium to the fuel indicating that a protective film was present under normal conditions. Tantalum was the only metal tested that showed no penetration up to 700°C. However, the penetration at 800°C is unexpectedly high, indicating the need for further checking.

Table II

DIFFUSION PENETRATION OF POTENTIAL CLAD MATERIALS
BY U-20 w/o Pu-10 w/o Fs

U-20 w/o Pu- 10 w/o Fs vs	Time (days)							
	800°C		700°C		600°C		550°C	
	1 mil	9 mil	1 mil	9 mil	1 mil	9 mil	1 mil	9 mil
Ti	1.9	151	25.8	>1000	612	>1000		
Mo	3.1	251	21.6	>1000	52.2	>1000		
V	1.2	96.7	17.6	>1000	56.5	>1000		
Ta	<1	30.8	(b)	(b)	(b)	(b)		
Nb	<1	44.1	4.4	360	136	>1000		
Y	<1	60.5	6.0	484	51.0	>1000		
Zr-2	<1	10.1	14.2	>1000	19.8	>1000		
Zr	<1	4.9	6.8	555	14.3	>1000		
Nb-5.3 w/o V	<1	3.0	<1	72.5	15.8	>1000		
430 SS	(a)	(a)	(a)	(a)	(a)	(a)	10.0	806
347 SS	(a)	(a)	(a)	(a)	(a)	(a)	9.2	748

(a) Molten

(b) No detectable penetration

The second group consists of yttrium and niobium, which show appreciably more interdiffusion than did the metals in the first group, but are adequate under EBR-II conditions.

The third group includes niobium-5.3 w/o vanadium, zirconium, and Zircaloy-2, which show enough penetration under EBR-II conditions to make their use questionable. The penetration of zirconium and Zircaloy-2 at 700°C are unexpectedly low compared with that at 600 and 800°C, indicating the need for further checking.

The fourth group consists of Types 347 and 430 stainless steel, which showed such extensive diffusion that they cannot be considered for use as jackets under EBR-II conditions. Not only was solid diffusion excessive at 550°C but a liquid phase was present at 600°C.

Figure 3. Photomicrographs of Diffusion Zones in U-Pu-Fs Alloy Coupled with Various Materials.

3-a.

Micro 26728 350X
Titanium diffusion, 31 days
at 794°C.

Micro 29588 500X
Nb-5.3 w/o V diffusion, 10
days at 698°C.

3-i.

Micro 26731 120X
Zircaloy-2 diffusion, 9
days at 794°C.

3-b.

Micro 26816 350X
Molybdenum diffusion, 9 days
at 794°C.

Micro 26727 120X
Zirconium diffusion, 9 days
at 794°C.

3-j.

Micro 26817 350X
Stainless Steel diffusion,
11 days at 550°C.

During this study it was observed that the segregated cored cast structure resulted in a low-melting grain boundary phase which tended to react with some of the metals to form liquid at unexpectedly low temperatures. This tended to confuse the diffusion results, since the amount of the low-melting phase varied from top to bottom of the injection-cast pins. This variation was not anticipated when the specimens were made. As can be seen in Figure 4, heating to 800°C resulted in grain boundary melting; however, holding at 800°C for 10 days almost completely absorbed the grain boundary material.

Irradiation Behavior of Uranium-Fissium and Uranium-Plutonium-Fissium Alloys (J. A. Horak, W. N. Beck and J. H. Kittel)

Irradiations of 0.144-in.-diameter cast specimens of uranium-fissium and uranium-fissium-zirconium alloys continued during 1960, with all new irradiations during this period being made in temperature-controlled capsules in the CP-5 reactor. The critical swelling temperature of U-5 w/o Fs alloy, the Core I fuel for EBR-II, appears to be in the range from 650 to 700°C for burnups of 1 to 2 a/o. These postirradiation examinations confirmed observations made earlier on specimens irradiated in uninstrumented capsules in the MTR.

Additional experiments designed to explore more fully the irradiation behavior of the U-5 w/o Fs and U-5 w/o Fs-2.5 w/o Zr alloys at high temperatures are in progress. In these experiments a series of specimens are under irradiation with measured central temperatures controlled at 690 and 785°C. The corresponding surface temperatures of these specimens are 620 and 710°C, respectively. Estimated burnups in the specimens as of December 31, 1960, are approximately 2 a/o.

Specimens are also being irradiated at elevated temperatures in NaK-bonded jackets of yttrium, niobium, vanadium and Inconel-X. The jacket thickness of 0.009 in. and the NaK annulus thickness of 0.006 in. are identical to EBR-II fuel pin specifications. The irradiation is being concentrated with measured central temperatures of 650° and 700°C. The purpose of these experiments is to evaluate the ability of refractory metal cladding to restrain high-temperature swelling of these fuels.

Irradiations at MTR were completed on unclad uranium-plutonium-fissium alloys. Confirming earlier results, the swelling temperature of these alloys was found to be progressively lowered by increasing the plutonium content. These irradiation reference alloys for the EBR-II Core II, U-20 w/o Pu-10 w/o Fs, was found to swell in the temperature range from 350 to 400°C. Substituting molybdenum for part of the fissium did not improve performance. Zirconium substitutions, however, were helpful in specimens irradiated at higher temperatures.

Figure 4. Photomicrographs of Injection-cast,
and Heat-treated U-Pu-Fs Alloy.

4-a.

Micro 29587 250X
U-20 w/o Pu-10 w/o Fs
Injection cast, 3 days at
798°C.

4-b.

Micro 29589 250X
U-20 w/o Pu-10 w/o Fs
Injection cast, 10 days at
800°C.

Experiments with restrained and vented U-2 w/o Zr alloy specimens (see page 104) show that high-temperature swelling of metallic fuel can be restrained by strong cladding with dimensions comparable to that specified for EBR-II fuel elements. These experiments indicate that an effective solution of the swelling problem of uranium-plutonium-fissium alloy may be through the use of a strong jacket, compatible with fuel and coolant, to restrain this swelling. A series of irradiation experiments are in preparation to test this hypothesis.

Two-inch lengths of U-20 w/o Pu-10 w/o Fs alloy, 0.144 in. in diameter, have been made for irradiation in a variety of refractory metal jackets. The initial irradiations will be in controlled-temperature capsules in the CP-5 reactor. The most promising cladding materials from these tests will then be used to clad full-length (14.22 in.) pins for irradiation tests in an autoclave facility being prepared for MTR, or in the EBR-II reactor itself. Cladding components have been made of niobium, vanadium, niobium-1 w/o zirconium alloy, Inconel-X, and 304 stainless steel. A 0.001 in.-thick vanadium foil will be used as a barrier between fuel and the stainless steel and Inconel-X. Other cladding materials will be included in these experiments as they become available in tubular form.

Transient High-temperature Irradiations of EBR-II Fuel Elements (C. F. Reinke)

Six EBR-II-type fuel elements irradiated by Metallurgy in the TREAT reactor have been examined in the hot cells. Each element contained an U-5 w/o Fs alloy pin bonded with sodium to a jacket of Type 304 stainless steel. These elements were subjected to elevated-temperature transients in the TREAT reactor. The purpose of the experiments was to determine the behavior and course of possible alloying interactions between the fuel pin and its stainless steel jacket.

Each of the pins was found to have warped during the transient test. Warping was thought to be due to thermal stresses caused by temperature differences developed during and after the transient.

Dimensional and density measurements were made on three jacketed assemblies and their fuel cores after transients which did not produce jacket failure. The diametrical growth observed for the jacketed assemblies could not be accounted for on the basis of fuel core growth. It is believed that the observed increase in jacket diameter could have been caused by the differential thermal expansion of the fuel produced by temperature differences between fuel and cladding. During the transient, heat is very rapidly produced in the fuel, thereby initially established a high temperature differential between fuel and cladding. The greater thermal expansion of the fuel would plastically expand the cladding. On those assemblies which did not fail, the transients produced overall volume increases of 1.5 to 3%.

Examination of two failed elements indicated that molten fuel was initially expelled from the jacket under pressure of sodium vapor, after which the molten fuel continued to flow out of the jacket by gravity. One of the tests indicated that the stainless steel jacket may be capable of successfully containing molten fuel for a short period of time.

Fabrication of EBR-II-type Plutonium Irradiation Specimens (W. R. Burt, Jr. and A. G. Hins)

The Plutonium Fabrication Group's purpose in the program was: (1) to provide fuel specimens for testing by the Engineering Irradiation Group, and (2) to make preliminary studies of fabrication methods and materials which may be employed for EBR-II Core II.

A series of fuel alloys and jacketing materials are to be fabricated and tested. The first of the fuel alloys containing 20 w/o Pu-10 w/o Fs was injection cast on December 28, producing the castings shown in Figure 5. Of the total of 30 pins cast in 18 in.-long molds, the shortest was $16\frac{11}{16}$ in. long. The surface quality was equal to that produced by the injection casting of uranium-fissium alloy and appears satisfactory for EBR-II-type fuel elements.

Thermal Cycling of EBR-II Blanket Material (W. N. Beck)

Thermal cycling tests have been completed for samples of unalloyed, depleted uranium blanket slugs received for EBR-II. Two additional groups of samples with alternative cooling rates from the beta phase were thermally cycled for comparative purposes. All specimens were cycled 500 times between 300 and 600°C. At intervals of 50, 150, 300, and 500 thermal cycles, the samples were examined and remeasured.

It appeared that the cycling behavior of the specimens was essentially unaffected by differing cooling rates from the beta phase. The amount of scatter was large, so that for a positive conclusion to be drawn large groups of samples would be required for better statistics. After 500 cycles, the average length increase for all specimens was approximately 0.2%; density decreases averaged approximately 0.6%.

On the basis of these results it was concluded that the production beta heat treatment used for the EBR-II blanket stock is adequate, and that no significant changes in cycling (or irradiation) behavior would be expected to result from variations in cooling rate from the beta phase. Based on earlier work, it is expected that irradiation behavior would parallel thermal cycling behavior of this material.

Figure 5. Uranium-2₃₈ w/o Plutonium-10 w/o
Plutonium Film Coatings.

ANT. Neg. No. 50-5100

2. The Development of Methods and Equipment for the Refabrication of Irradiated Fuel

The purpose of the program was (1) to investigate techniques for the refabrication of irradiated reactor fuel and (2) to develop processes and equipment to refabricate melt-refined irradiated EBR-II fuel into fuel elements suitable for return to the reactor.

The EBR-II fuel consists of fissium alloy pins, 0.144 in. in diameter by 14.22 in. long, sodium bonded in stainless steel fuel tubes and assembled in 91 rod elements (subassemblies). Because the residual zirconium, molybdenum, (technetium), ruthenium, palladium, and rhodium, not removed in melt refining, are highly radioactive, refabrication must necessarily be by remote control. Self-heating is a problem due to the absorption of radioactive energy. An inert atmosphere is essential to prevent ignition of the alloy. By the end of 1959, the proposed flow diagram for refabricating the EBR-II fuel elements was fairly well established, and a plant to manufacture the initial loading from a synthesized fissium alloy had been constructed.⁶

A gas pressure-injection casting in precision high-silica glass molds was selected as the method for fuel fabrication because of its comparative mechanical simplicity, high precision, and adaptability to production of varied shapes. The equipment consists of a bell-jar vessel which may be either evacuated or pressurized. The bell-jar houses an induction melting zone in which the crucible is positioned for melting. As many as 160, precision, glass mold tubes are suspended vertically above the crucible. The molds are closed at the top and coated with a refractory wash and are held in a pallet in the resistance-heated zone about 7 in. above the crucible. The metal is melted under inert gas, the furnace evacuated, and the crucible raised to immerse the open lower end of the molds. The furnace is then pressurized to force the metal into the tubes, where it solidifies while cool argon gas is circulated through the mold array. The crucible is withdrawn just before the remaining metal heel solidifies in the crucible.

After a programmed interval, the furnace is opened and the pallet of molds is transferred to a depalleting station, where the gravid molds are fed one at a time into feeder trays. The feeder trays are transferred to the pin-processing and inspection station where the gravid molds are fed through a mold-stripping operation into a shear which cuts the castings to length. The castings are then progressively fed to a length gage, onto a balance, through a pneumatic diametral gage, and through an eddy current coil for determination of the internal voids. Each value is reduced to electrical signals which will be fed into a data-processing unit outside the cell, which prints numerical and graphic data for each pin.

The fuel pins are transferred to a station where they are loaded into stainless steel fuel tubes containing a measured quantity of sodium and inserted into a magazine. This circular magazine is transferred to a furnace

⁶ Annual Report for 1959, Metallurgy Division, ANL-6099, p. 13

Figure 6. Radiation Intensity of Various Sources Versus Distance from Source to Receptor.

ANL Neg. No. 106-5740

where the sodium is melted under gentle vibration which immerses the fuel pin under the sodium surface. The magazine is then moved to a welding station where the fuel rods are capped and the stainless steel cap restrainer and tubes are fused together by an arc discharge from a capacitor welder. To prevent oxidation or ignition of the fuel, the above operations will be carried out in the argon atmosphere-supplied shielded cell.

Subsequent operations on the fuel rods will be performed in the air-atmosphere cell to allow the use of master-slave manipulators. These operations consist of vibratory heat treatment for bonding, leak detection, bond testing, and gaging. Acceptable fuel rods are then transferred to a subassembly construction machine. Hexagonal arrays of 91 fuel rods are assembled with 18 upper and 18 lower blanket elements and enclosed in hexagonal tubes as the reactor fuel element (subassembly).

Experimental equipment to test the process was installed and production tested. The lessons of these tests were then applied to the design of remote-control equipment for installation in the EBR-II Fuel Cycle Plant.

Criteria for the design of the Fuel Cycle Plant equipment includes the following: (1) a desired production capacity of 400 finished fuel rods per week, (2) choice of construction material to withstand 20,000 hours of exposure to prevalent process cell radiation or easy replacement of short-lived components, (3) equipment should be of modular, componentized design with plug-in submechanisms adapted to crane and manipulator replacement, (4) the largest component shall be capable of being passed through the air lock doors and vestibules, (5) routine fuel pin movements must be mechanized while bulk transfer movements may be made by crane and manipulator, (6) the equipment must be adaptable to changes in the fuel composition and, to reasonable dimensional and shape changes, (7) the equipment must be totally removable from the process cell for replacement or major product change.

Radiation and Self-heating Calculations (J. E. Ayer, M. J. Feldman,* and N. M. Lazar**))

An engineering analysis was made to estimate the levels of gamma-radiation intensity from the various fuel sources in the Fuel Cycle Plant Process Cell. This was done by calculation of radiation intensity from a number of fuel geometries and conditions versus distance from the source to the receptor. The results of these calculations are plotted on Figure 6. Consideration was given to overlapping gamma fields and the assumption was made that the argon-cell processes are functioning at their maximum rated

* Idaho Division.

**Resident Research Associate, Summer 1960.

capacity and with all machinery except one pin-processing machine in operation, but with a mold pallet being depalleted for loading this machine.

One of the problems of processes involving the refining and refabrication of irradiated reactor fuel is self-heating of the fuel due to absorption of beta and gamma energy from the fission products. This self-heating may be such as to influence significantly the design of processes and equipment and to require induced cooling. To resolve this problem and rationally to design equipment for the reprocessing of partially decontaminated reactor fuel, it was necessary to know, with fair reliability, the temperatures which various configurations of radioactive fuel will reach. The self-heating effects were calculated and data were developed for the cooling requirements through the various refabrication and reassembly operations of the proposed EBR-II Fuel Cycle.⁷ In this study the heating effect attendant to self-absorption was considered for a number of actual cases which occur during the operations of decanning the spent fuel element and of refabricating the active material into new fuel elements. The results of this study are summarized below.

A fuel element (subassembly), after 15 days of cooling, will generate 3350 BTU per hour and will require forced cooling of 25 ft/sec to maintain a temperature of 121°C. A 30-pin tray of disassembled fuel elements will have an equilibrium temperature of 153°C under free convective cooling in the air cell. In the air lock the same array will have an equilibrium temperature of 271 to 366°C under radiant cooling, and in the argon cell it will have an equilibrium temperature of 171°C under free convective cooling. The 10-kg billet can attain a surface temperature of 535°C when carried by the manipulator with free convection and radiation heat losses. The cast pins encased in Vycor and placed in the barrel unloader in close stacking will have an equilibrium surface temperature of 393°C. With 100 ft/sec of forced cooling, the pins will reach an equilibrium temperature of 111°C. The bare fuel pins placed in a single layer tray will reach a temperature of 176°C with free convective cooling. The clad reprocessed fuel in the vacuum chamber of the helium leak detector will reach a temperature of 274°C. Finished fuel rods, housed in the bonding magazine, will have an equilibrium temperature of 208°C and with 10 ft/sec of forced cooling the equilibrium temperature will be 56°C. After assembly, the subassembly will require forced cooling of 10 ft/sec to maintain a temperature of 98°C.

Injection-casting Furnace (H. F. Jelinek and G. M. Iverson*)

Figure 7 shows the Model III injection casting furnace design for use in the EBR-II Fuel Cycle Plant. It is of the same dimensions and capacity as the Model II furnace used for the initial loading, but radiation-resistant components have been used throughout.

⁷ Shuck, A. B. et al., Development of Methods, Equipment and Plant for Production of EBR-II Core I, to be published.

* Central Shops Department

Figure 7. Injection-casting Furnace

ANL Negative No. 1-177

The upper heating zone is suspended from the furnace bell and an electrical connection is made through the top of the furnace. An internal shell is provided to support the molds, to distribute the heat received by the molds, and also to serve as an internal baffle for the flow of argon cooling gas. The induction coil assembly is supported on two taper-end spindles which engage taper sockets in the legs on the bottom of the coil and in the furnace base. These serve as the connectors for the 10,000-cycle induction-power leads. Compliance is built into the furnace socket legs to compensate for thermal expansion and contraction of the assembly. The crucible actuator is a folded cylinder design which has been successfully tested on the Model II furnace.

It will be noted that all major furnace components are held together by gravity alone. There are no bolts or locks necessary in order to secure the items which will be removed by the manipulator. Standardized lifting lugs designed for the double-hook manipulator tool have been used where possible. The crucible assembly will be handled by a clam-shell fixture held in the double hook manipulator.

A freeze seal has been employed to secure the bell to the lower assembly, and experimentation has indicated that the seal may be relied upon as a closure device at several times the pressure to be employed in the furnace. Four parallel-connected resistance elements are used to heat the freeze seal, and these are of such capacity that if any two should fail the remaining two are capable of melting the freeze seal. For normal use they will be derated by operation at reduced voltage.

Originally a solid-bar copper coil was used outside of the Lava coil forms for inductive heating. A molybdenum heat shield was employed within the form in an attempt to reduce the amount of heat which was conducted to the copper coil. But even with these precautions the coil tended to operate dangerously close to the melting point of copper with rather frequent incidence of failure.

To circumvent this problem, the experimental induction coil was wound from solid $\frac{3}{8}$ in.-diameter molybdenum bar. The outside diameter of the coil allowed it to be placed inside of the heat shield and ceramic cylinders. It was supported on three Lava pieces with milled slot spacers. This coil balanced out at nine turns, four turns more than were required for the copper coil. The amperage required for melting fuel with the molybdenum coil was one-third that required with the copper coil as a result of the increased number of turns, better coupling, and improved thermal efficiency. Because the molybdenum coil is within the heating zone, it reaches approximately the same temperature as the crucible, and the hot coil tends to be a barrier to heat losses from the crucible to the external furnace parts. The coil has now been used nearly 100 times and is still in use in the Core I manufacture.

Determination of the crucible or melt temperature is, and continues to be, a problem. High-temperature thermocouples have a

limited life. For this reason the crucible base thermocouple was incorporated with the crucible pedestal and insulator stack, since it is expected that these subassemblies must be changed at frequent intervals. Wiping spring contacts were previously used between the movable crucible support and the furnace base. These have broken contact at elevated temperature. In the new design, contact is maintained by allowing the weight of the crucible to be taken on sharpened spindles which are made of thermocouple alloy, but reinforced with high-speed steel. These spindles are in turn supported on contact buttons attached to the thermocouple leads.

Fuel Pin Process and Inspection Machine (N. J. Carson, Jr.,
S. B. Brak,* and A. B. Shuck)

The equipment described in the previous annual report (ANL-6099) consisted of a series of operating stations on an inclined plane to which the fuel pins were fed by gravity down a longitudinal transfer chute. The individual operations of demolding, shearing, diametral inspection, eddy current testing, weighing, and length measurement all worked satisfactorily. However, the longitudinal, gravity slide transfer of pins from station to station was unsatisfactory. The pins jammed in the restricted passageways, particles of glass found their way into the slideways, and equipment components were inaccessible for effective manipulator maintenance.

The Model II pin-processing and inspection machine shown in Figure 8 was designed to correct the deficiencies in Model I. Several changes were made. The depalleting operation was removed from the fuel pin process station and relocated in a separate sector of the process cell; this will eliminate broken glass and pin ends which found their way into the fuel pin-process and inspection machine from the depalleting operation. Longitudinal sliding transfer from station to station has been eliminated. In the new equipment the pins will be fed down parallel rails in removable magazine trays. Gravity is still used as the main motive force for transfer, but loose glass and casting fragments will fall free and are collected by trays and hoppers below the inclined rails. A rotary, single-pin delivery gate was designed so that each of the inclined trays becomes a magazine for in-process storage of the fuel pin. Since the pins were spread out in a two-dimensional array, natural convection is sufficient to prevent overheating.

The miniature, jaw crusher, demolder was replaced by one in which the gravid mold was dropped from the inclined feeder tray into a slot between two parallel hard-faced bars spaced slightly closer than the diameter of the mold. A single flat-edge blade brought down by a pneumatic ram pushes the mold between the parallel bars, breaking the glass from the fuel pin.

* Central Shops Department

Figure 8. Fuel Pin Manufacturing Machine.

ANL Neg. No. 106-5742

This unit was tested and it was found that with repeated blows of the blade the equipment was self-clearing. The fragmented glass falls through a "grizzly" down a chute into a collecting receptacle. A working model was constructed to test the principle and several hundred pins were demolded without jamming. A few pins were broken, but most of these were the result of internal flaws in the castings.

The shear station has been completely redesigned. The pin enters the shear from the top and is dropped between the spring-loaded horizontal pressure pads and a pair of movable shear tools. The shear tools are mounted on a movable platen which is pushed forward by means of two pneumatic-cylinder-powered bell crank actuators. The pin is gripped between the three pressure pads and the four shear tools and, as the platen is moved forward, the two ends are simultaneously sheared, leaving a center section 14.22 in. long. An important feature of the new shear design is the accessibility of all moving parts to the manipulator. The cutting tools are square and designed to be rotated, presenting four cutting edges to the work. Since the fixed and moving sockets are at different elevations, the cutting tools may be exchanged so that each tool may present a total of eight cutting edges to the work.

After shearing, the fuel pin rolls down the inclined feeder tray to a length-measuring station. Length is measured by forcing the pin longitudinally against a dimension-measuring transducer by means of a pneumatic ram. A stop on the pneumatic ram serves as a second reference point.

Reversal of the ram releases the pin, which rolls down the inclined tray and is placed on the balance platform by a movable section of the tray. The deflection of the balance platform is measured by the movement of a radiation-resistant microformer. After weighing, the fuel pin is elevated by the movable tray section and rolled down onto the longitudinal feeding device which moves it through the pneumatic diametral gage and eddy current flaw detector.

Each of these units is designed to fit a 24 x 12-in. modular mount. They are locked to a five-module "staircase" frame. The height of the "risers" is five inches; the mounting frame consists of a heavy, fabricated plate frame with one side open for access and for the collector chutes. The "stair treads" consist of two heavy rails and are open at the center. A standardized maximum number of pneumatic connections are provided in one rail; similarly, a standardized maximum number of electrical contacts are provided in the second rail. Three ogive-tipped locating lugs are provided for each module and are designed to position the base frame kinematically. Thus this modular mount can accommodate a large variety of equipment stations with connection being made to the electrical controls and pneumatic lines on the outside of the process cell.

Data Process and Recording (J. E. Ayer and G. J. Pokorny)

Data-processing equipment was required so that the accept-reject decision may be made on a flowing stream of pins. The data-processing equipment consists, in part, of a two-channel recorder which plots porosity and diameter. Porosity is plotted as a unitless function of the eddy current signal output versus point locus on the pin. Diameter is plotted in 0.0001-in. units versus point locus on the pin.

Coupled with this recorder section is an integrating device which sums the area below the curve of the pin diameter over the measured length of the pin, yielding a calculated volume. This calculated volume, expressed in cubic centimeters, is stored for future calculation and presented to the print-out system. Fuel pin length is expressed in inches to the nearest 0.001 in.; fuel pin weight is expressed in grams to the nearest 0.01 gram. A total of four digits are employed for expression of weight between 67.00 and 71.00 grams.

The stored signals representative of the calculated volume which results from the integration of the diameter curve and the fuel pin weight are fed into a computer which calculates the density of the fuel pin. The result of this calculation, expressed in grams per cubic centimeter, is then included in the print-out presentation of data. Acceptable pins are delivered to one tray at the end of the eddy current transfer device. Reject pins are delivered to a second tray for transfer to a pin chopper for recycle to the melt-refining or pin-casting operation.

Fuel Rod Assembly and Welding (A. P. Grunwald, T. C. Cameron and N. F. Hessler^{*})

An equipment station has been designed by J. Martich to push the fuel pin into stainless tubes which have been preloaded with sodium and then push the tubes into a cylindrical magazine. The magazine is transferred to a meltdown station where the temperature of the tubes is increased to melt the sodium while the pin is settled beneath the sodium surface under gentle vibration.

The welding machine was redesigned to incorporate a cap-restrainer loader and to adapt the mechanism for remote maintenance and removal of components. The principle of welding developed by C. Stone for the original machine has been retained. A cam-type indexing device operated by a push-pull cylinder has replaced the vane-type pneumatic motor and Geneva mechanism used to index the Model I equipment.

^{*} Reactor Engineering Division

Sodium Level Control (T. C. Cameron)

Control of the level of sodium presents two problems: (1) to obtain the specified sodium level, and (2) to inspect the sodium level obtained. Sodium level is a function of the volume of the fuel tube, the displacement of the fuel pin, and the accuracy of metering a sodium volume to match the variables. For the Core I production, the fuel tubes are measured at two diameters at five different loci along the length of the tube. The average diameter is converted to volume and the tubes are classified in accordance with this volume. Fuel pins are rejected when the diametral variation is greater than 0.001 in.

The quantity of sodium is normalized to the tube volume, but, because of process difficulties and delays which would result, matching of tube and sodium volume to individual fuel pin volume should be avoided. Using the pneumatic gage volumes of fuel pins and normalizing the sodium volume with tube volume as described above, the standard deviation of sodium level was computed to be ± 0.055 in. Since this computation did not include the inaccuracies of sodium measurement and tube gaging, a batch of 1,000 fuel pins were very carefully X-rayed, turned 90° and re-X-rayed, and the average sodium level of each pin was measured. The standard deviation for the lot was found to be 0.068 in., with 15% of the sample out of specification. Since process dimensional limits are triple the standard deviation, both of the above studies indicated that the sodium level specification of ± 0.100 in. is not consistent with the tolerances on the fuel pins and fuel tubes.

X rays have been used to measure sodium level for the Core I loading. This will not be practical for the radioactive fuel elements. Eddy current measurement using an encircling coil gives an extremely vague indication of the sodium level. This is partly because the level of the solidified sodium is not flat but is irregular and deeply indented by the liquid-solid shrinkage. A twelve-coil, differential, point probe, described below, gives results which may be averaged to indicate the sodium level in close agreement with the X-ray measurements, but the delicacy of the instrument may be judged from the fact that the twelve probes surround the $\frac{3}{16}$ -in. diameter fuel pin with a clearance of 0.010 in. Work on this type of probe is continuing to develop a satisfactory, remote production instrument. Sodium-level measurement, therefore, continues to be an area without a totally satisfactory solution.

Measurement of Sodium Level (K. Ono)

A pulsed-eddy current instrument has been built for inspecting the sodium level in EBR-II fuel elements. Five EBR-II fuel elements were tested with this equipment, radiographed, and destructively tested. To check the accuracy of measuring sodium level with the eddy current equipment, a

destructive test was carried out by means of an electron discharge machine which made narrow slots longitudinally through the wall of the canning tube, thereby making visible the end of the uranium and the sodium level through the slot. Thus the sodium levels were directly measured. The result has proved that four fuel elements out of five have sodium levels varying around the peripheries of the fuel elements with the largest variance of 0.08 in., and the sodium levels on four points of periphery of the fuel elements determined by the eddy current method coincide with those determined by destructive test with errors within ± 0.03 in., while those determined by radiography have errors within ± 0.05 in. Since some of these errors come from the fact that points measured were slightly different on the periphery in each method, it is more reasonable to compare the average values.

The following data show average sodium levels determined by each method.

Pin Identification Number	Sodium Level, in.		
	Radiography	Eddy Current	Destructive Test
14A-5	0.648	0.660	0.660
14A-42	0.705	0.720	0.714
14A-48	0.759	0.746	0.750
14A-49	0.721	0.745	0.740
14A-50	0.715	0.730	0.730

Another similar experiment was conducted with seven rejected EBR-II fuel elements. In this case, the destructive test was made in a different way, as mentioned above. The fuel elements were cut crosswise above the sodium levels and the sodium levels were measured from the cross section.

The comparison of the average values has shown that the values measured by the eddy current method have a largest difference of 0.028 in. from those measured by destructive test, while those measured by radiography have largest difference of 0.032 in. from those measured by destructive testing. These differences are considered to be due to the fact that these fuel elements have larger irregularities and this destructive test is not as accurate as the former one.

Bond Testing (T. C. Cameron and N. F. Hessler)

The encircling coil eddycurrent probe produces satisfactory results in the detection of void areas in bonds. Production studies made on cold rods indicate a varying number of rods with voids which do not appear

to contain gas. T. Cameron was asked to investigate this phenomenon by means of the eddy current technique on molten sodium. He was able to demonstrate that the major percentage of the voids disappear as the sodium becomes molten, and that new voids tend to reappear as the sodium solidifies. These were thought to be shrinkage voids. Gas-filled voids, on the other hand, persist through the change of state and may be traced by the eddy current method as they migrate to the surface of the sodium.

These hot pin eddy current studies were extended to investigate the bonding operation. It was demonstrated that a low-frequency jolting action was an effective means of moving sodium bubbles, whereas some modes of vibration at 30 and 60 cycles per second were relatively ineffective in causing the gas bubbles to move or may introduce gas voids. These studies have influenced the design of the new bonding furnace and eddy current testing equipment. The bonding furnace incorporates low-frequency fuel element jolters, while inspection will be done on hot pins with the sodium in the molten state.

Leak Detection (A. P. Grunwald)

The mass spectrometric method of detecting leaks in closed containers, in which the specimen is placed in a pressure vessel under helium at several atmospheres and then is quickly transferred to a vacuum vessel connected to a mass spectrometer leak detector, was applied to the Core I manufacture.

It was found that neither very small nor very large leaks were detected in the EBR-II fuel elements by this method for the following reasons:

- a. The ratio of void space in the fuel elements to the volume of the evacuated leak detection vessel was very small, so that an extremely sensitive setting on the leak detector was required to detect the leaks.
- b. Large leaks were evacuated during the pumpdown and did not persist long enough to be detected.
- c. The sensitivity of the helium leak detector was reduced below the required level when the tubulation between the test chamber and spectrometer was increased to 15 ft or more, as required in the fuel cycle plant.

A leak detector developed by A. Grunwald and G. Blazek has been tested and found to be satisfactory for detection of large leaks and at least as sensitive as the mass spectrometer with a short tube connection for the detection of small leaks in the EBR-II fuel elements. This equipment consists of a steel frame with a swing-out fuel element carrier. A

gasketed bushing was placed over the top of the fuel element and the carrier raised by means of a pneumatic cylinder. A cam causes the carrier to move to the vertical position and the top of the fuel element to be inserted into a chamber of small volume. The ferrule seals the chamber which, with the fuel rod in place, has a void volume approximately $\frac{1}{20}$ of the void space within the fuel rod. High pressure (up to 500 psig) is now bled into a prefill chamber which is valved from the filling line and the gas admitted to the detector chamber by momentarily opening a special valve in the head. A sensitive radiation-resistant pressure transducer registers the resulting pressure and any change in pressure due to leakage through a small hole in the fuel element welds. Leaks are indicated by two means: (1) a very large hole is indicated as an increased volume by a markedly depressed pressure reading, (2) a small leak in the fuel element is indicated by a drift in pressure which is asymptotic at the lower value, and (3) a leak in the valves or gaskets is indicated by a drift which is not asymptotic.

Careful design of the gaskets and valves has resulted in a measuring system with insignificant leakage. Although the instrument measures only one pin at a time, it may be cycled quite rapidly and has the advantage that extra operations are not required to sort the leaking fuel elements from the nonleakers, as was done in the batch testing mass spectrometer leak detection system.

Very small leaks detected by any method (including direct mass spectrometric detection) were found to be very elusive. This elusiveness was traced to condensable vapors, water, alcohol, acetone, etc., which would block a capillary porosity completely with little relationship to the pressure applied, and then would suddenly break through. It was found that heating of the welds, just before leak detecting, to drive off these condensable vapors, allowed a greater percentage of the leakers to be detected, but with further handling or exposure to moist air some of the porosity would be temporarily plugged up. This is a factor which must be considered in the design of any leak detection system.

Fuel Element (Subassembly) Construction (R. H. Olp*)

The Model I fuel element construction machine was developed into an effective means of assembly of the 91-element fuel rods using Model 8 manipulators. A set of 0.020 in. deep restraining indentations were impressed into the hexagonal tubes to hold the fuel rod pack in tight compression. Since the hexagonal tube must be forced over the elements with a slight interference fit, it was necessary to heat the hexagonal tube to 370°C and melt the sodium in the fuel rods before assembly. Since the hexagonal tube must be pushed over the fuel bundle with a force of 120 to 175 pounds and be held in very close alignment during this operation, an aligning jig was designed using two motor-driven lead screws to close the assembly and

* Reactor Engineering Division

to provide a steady closing motion. A force-limiting switch was incorporated to prevent overloading of the element.

The Model II machine designed for the Fuel Cycle Plant is similar to the Model I machine but incorporates replaceable components which allow assembly, on the same machine, of the 91-rod fuel element, of the 61-rod control element, and of the blanket region fuel elements with blanket-type lower adapters.

3. Refractory Metal Jacket Development (R. L. Salley and F. J. Karasek)

The use of stainless steel as a jacketing material for liquid metal-cooled fast flux reactors operating at elevated temperatures has decided limitations; including the relatively low yield and stress rupture properties, and the possibility of forming low-melting eutectics with uranium or plutonium fuels. The desired high operating temperatures and the use of the lower melting plutonium alloys require the development of new high-strength alloys to cope with the situation. Additional requirements for these alloys include compatibility with sodium coolant, good fabricability and weldability, and, if possible, good thermal conductivity. These requirements can best be met with certain refractory metal-base alloys. Most development work to date has been limited to available vanadium, niobium, and tantalum-base alloys.

Because of the potential uses of these alloys in supersonic aircraft, missiles, and space programs, laboratories throughout the country are carrying out exhaustive research programs in the development of refractory alloys. To evaluate these alloys for our needs, attempts have been made to procure samples for compatibility test with sodium and with plutonium fuels at elevated temperatures. To date, some 40 samples of refractory metals and their alloys have been obtained and submitted for tests. A number of samples were exposed to 650°C flowing sodium containing 1 - 5 ppm Na_2O for 504 hr. Samples which exhibited good corrosion resistance will be tested as before; however, the Na_2O concentration will be increased to 10 - 20 ppm, a figure which more nearly represents anticipated service conditions.

The availability of commercial refractory alloy tubing is extremely limited. The main reasons for this scarcity are: (1) the lack of knowledge, experience, and equipment - all prerequisites for the fabrication of materials having high strength at elevated temperatures, and (2) the size desired, (0.174 in. $\pm$ 0.001 O.D. x 0.009 in. $\pm$ 0.001 wall x 18 in.). The only tubing obtainable to date is pure Nb, pure V, Nb-1 w/o Zr, and Inconel-X.

Because of this scarcity of commercial tubing, efforts have been made to make tubing of alloys that are of primary interest at this time. Small lengths of sound tubing, approximately 3 in. in length, have been produced from Ta-0.1 w/o W and V-10 w/o Ti-3 w/o Nb alloys. These tubes will be used in the fabrication of irradiation specimens. Attempts have been made to produce welded tubing of other alloys; however, these were unsuccessful due to laminations of the sheet stock used.

Because of the little work done on the extrusion of wrought refractory alloys, some attention has been given to the fabrication of welded tubing. The most objectionable feature of this approach, particularly with the niobium-base alloys, is the cast structure resulting in the weld zones, which is difficult to fabricate until it is broken up. Two possible solutions to the problem of control of cast structure are: (1) electron beam welding, in which the fusion zone can be kept small and oxygen pickup low, and (2) resistance welding.

BMI is carrying out a research program for ANL to develop high-strength niobium-base alloys. The work proposed consists of: (1) cast two ingots each of the following compositions: Nb-2 w/o Cr, Nb-3 w/o Zr, and Nb-5.3 w/o V, (2) fabricate one ingot of each composition into sheet for tensile, annealing, and creep studies, (3) remaining sheet material to be sent to ANL for fabrication of welded tubing, and (4) the remaining ingots to be delivered to ANL for development of extruded tubing.

The initial objective of ARF was a substantial improvement in the properties of molybdenum for use as a fuel-cladding material in sodium-cooled fast reactors. Current work is now focused on vanadium. The three alloys of primary interest are V-5 w/o Ti-20 w/o Nb, V-10 w/o Ti-3 w/o Nb, and V-10 w/o Ti-3 w/o Ta.

4. Fabrication of EBR-II Core I Fuel Pins and Assembly of Fuel Rods and Elements (N. J. Carson, Jr., H. F. Jelinek, N. F. Hessler, E. L. Kimont* and T. C. Cameron)

The purposes of the above programs were: (1) to fabricate the uranium-fissium alloy fuel pins, (2) to assemble, weld, and bond these pins into stainless steel-jacketed fuel rods, (3) to construct the 91-rod fuel elements (subassemblies) and (4) to test the production methods to be used for remote fabrication of the EBR-II fuel.

The original order for the Core I loading of EBR-II consisted of 2,400 normal uranium fuel rods, 10,000 fuel pins, and 9,350 fuel rods.

*Reactor Engineering Division.

These were to be assembled with blanket rods fabricated by the Foundry and Fabrication Group into 24 natural uranium-core elements, 55 enriched uranium-core elements, 30 blanket region-core elements, 15 control rods, 3 safety elements, and 6 boron control elements. In December, the requirement for blanket region core rods was increased from 30 to 42, for control rods from 15 to 14, and for boron control rods from 6 to 3.

The fuel rod shown in Figure 9 consists of a fuel pin measuring 0.144 in. diameter x 14 in. long. It is jacketed in a stainless steel tube which is closed at the lower end by a precision-cast stainless steel T-slot fitting. The fuel pin is bonded to this tube by means of sodium which in solid condition is specified to be 0.65 ± 0.10 in. above the top of the fuel pin. The top of the fuel rod is closed by means of a plug, with an extension beneath the sodium level, which restrains the pin from rising above the sodium.

The methods employed to manufacture the Core I fuel elements were as described in the previous annual report (ANL-6099). Production of normal uranium fuel elements was started late in 1959 and was completed in February, 1960. Modification of the casting furnace was necessary, and production was resumed with enriched uranium in April 1960.

The monthly production rates are plotted in Figure 10, which also shows the number of castings, pins, fuel rods and elements completed by 30 December 1960. The furnace operations reached a maximum production rate of 2,500 acceptable castings per month during August, whereas 2,000 elements were produced during September, at which time 10,000 castings had been produced. Subsequent casting operations were mainly for the purpose of reclaiming reject fuel pins. During the period of maximum production, one injection-casting melt was made per day with a six-day work week.

Analysis of the process flow indicated that approximately 25% more molds have been used than produced full-length pins. In this figure, however, there were several low-yield or miscast batches due to mechanical difficulties and some experimental batches. Residues from the casting operation which were not reclaimable within the cycle (by recycle to melt-refining or injection casting) appear to be approximately 1.3% of the metal charged.

Pin processing and inspection met with equipment malfunctions, which were straightened out by July 1. After this period, the pin-processing operation was able to keep pace with the casting operation at its maximum production rate. Approximately 8% of the pins were rejected in the inspection operation. Of these, 4.5% were returned to process for internal defects or pipes, 1.8% sheared short, and 1.8% were rejected for improper diameter or surface imperfection.

Figure 9. EBR-II Fuel Element.

Figure 10. Production of EBR-II, Core I, Fuel Loading

ANL Neg. No. 106-5739

Assembly of the fuel rods was delayed until June because of nondelivery of the jacket components. The final inspection of the assembled fuel elements to date has resulted in rejection, stripping, and re-jacketing 22.5% of the fuel pins jacketed. Of these, 11.3% were rejected for improper sodium level, 6.0% for imperfect bond, and 2.2% each for sodium trapped in the void space and for gas trapped below the restrainer tip. Approximately 2% of the assembled fuel rods have not been recoverable by recycle within the jacketing and bonding operations. These have been returned to the melt-refining operation.

In order to obtain more complete figures on process yield, to clean up scrap as completely as possible, and to produce the maximum number of finished fuel rods for the reactor, scrap, residue and excess metal were salvaged by means of the process operation to make the maximum number of fuel elements from the EBR-II fuel allotment. This operation was in process at the end of 1960.

5. Blanket Rods for EBR-II Core I (R. L. Salley, C. H. Bean, R. D. McGowan and A. D. Zumbrennen)

Fabrication and Inspection of Depleted Uranium Blanket Slugs

The fabrication of depleted uranium slugs containing 0.22 ± 0.02 w/o U^{235} for the blanket loading of EBR-II was carried out in three basic steps:

- a. Conversion of UF_6 to uranium metal and casting of $7 \frac{1}{8}$ -in.-diameter, 1,000-lb ingots, performed by the Union Carbide Nuclear Company at Paducah, Kentucky.
- b. Hot breakdown of ingots, beta heat treatment of rolled $\frac{1}{2}$ -in.-diameter rod stock, machining to finished size and inspection for dimensions, surface quality and beta heat treatment, done by the National Lead Company of Ohio at Fernald, Ohio.
- c. Final inspection for internal defects, surface quality, density and grain size, carried out by the Metallurgy Division at ANL.

A total of 95,593 inner and outer blanket slugs (0.433 ± 0.0005 -in. diameter $\times$ 11.000 ± 0.005 in. long), were received at ANL. Prior to assembly into blanket tubes the uranium slugs were inspected as follows:

- a. visual examination of the surface for pits, laps, seams, cracks, or other defects;
- b. weight check to assure minimum density; and
- c. ultrasonic through transmission test to observe internal defects, such as cracks and to determine grain size.

Of the 94,676 slugs inspected, 80,742 (85.3%) were approved for blanket loading; 10,776 (11.4%) were rejected by the ultrasonic test; and 3,158 (3.3%) were visual rejects. The latter group was eventually ultrasonically tested, and 393 of these visual rejects were also sonic rejects.

Loading Uranium Slugs into Blanket Rods

The breeding blanket for EBR-II consists of a closely spaced network of stainless steel tubes containing depleted unalloyed uranium as fertile material. Due to the location of these tubes with respect to the core of the reactor, they are descriptively referred to as upper and lower, and inner and outer blanket rods.

During the past year, steady progress was made in the blanket rod loading phase of the EBR-II blanket element fabrication program. Initial production of the upper and lower rods was completed in June, 1960. Production of the inner and outer rods was completed in December, 1960. Prior to a permanent shutdown of equipment, however, the uranium from several hundred rejected upper and lower rods are to be salvaged and reloaded. The final production figure for upper and lower rods will then be somewhat greater than that shown in Table III.

Production Summary: A summary of blanket rod production figures as of December 31, 1960 is contained in Table III.

Table III

EBR-II BLANKET RODS

Type Rod	Number Assembled	% Rejected	Number Accepted	First Loading Requirement
Upper and lower	6,842	21.0	5,506	5,112
Inner and outer	15,722	4.48	15,019	11,780

As can be seen, a number of additional rods over initial requirements have been produced. These spares are to be placed in storage and will be available for use as the need arises.

Equipment: For information concerning the design, construction and operation of special equipment used in the EBR-II blanket loading program, the reader is referred to the Metallurgy Division Annual Report for 1959 (ANL-6099). This report gives a detailed account of important design problems that were considered with respect to equipment, as well as the actual procedures used in assembling the blanket rods. Suffice it to say that operations involving the loading of depleted uranium and sodium metal into the stainless steel jacket tubes were carried out in an inert atmosphere of 90 v/o argon and 10 v/o helium. Such operations were conveniently performed in a glovebox equipped with suitable access ports on the underside for inserting tube bundles, and transfer locks at either end for the movement of parts and materials in and out of the glovebox. The equipment was designed to handle the two sizes of blanket rods that are required for the reactor. Minor conversions must be made to the equipment, however, when making the changeover from one type to the other.

On a normal production day, 216 rods of either type were assembled, bonded, and inspected. This schedule was maintained with relative ease. The upper and lower rods were the first to be loaded. Production of these was completed in June, 1960, and the changeover then made to load the inner and outer blanket rods.

The volume of sodium that is loaded into the tubes is closely controlled by cutting to length an extrusion of known diameter of this metal; therefore it was necessary to modify the extruder to produce the desired incremental volumes of sodium. Also, due to the difference in length of the two types of rods, $62\frac{1}{2}$ in. for the inner and outer rods versus $21\frac{1}{2}$ in. for the upper and lower rods, appropriate conversions were made to the tube handling equipment, oil immersion bath furnaces, and bonding furnace.

Loading Procedure: The loading, welding, and testing procedures were virtually the same for both types of blanket rods. This report will be concerned primarily with the assembly of inner and outer blanket rods. Unless otherwise mentioned, the reader may assume that identical or analogous methods prevailed for the upper and lower blanket rods.

The stainless steel jacket tubing was first cut roughly to the desired length and then the ends of each tube machined to the finish dimension. After cutting and machining, the tubes were cleaned in a suitable solvent followed by soapy and clear water, and alcohol rinses. The inside diameter was then air-gage inspected. This test also revealed any ovality that might be cause for rejecting a tube.

Following air-gage inspection, a bottom end-plug was welded in place by means of inert-gas shielded-arc welding equipment and the weld leak-checked with a helium mass spectrometer-type leak detector.

Before the tubes were transferred to the glovebox, each was initially loaded with three slugs of uranium. The tubes were then placed in tube bundles of 36 rods each and inserted in access ports on the bottom of the glovebox. Before opening to the glovebox atmosphere, the tube bundles were evacuated and purged with inert gas.

The glovebox operations consisted of loading the sodium and two additional slugs of uranium into each tube. The sodium was melted, Inconel-X compression springs placed in the tops of the tubes, and top end plugs tapped into place. The plug was held in place by a rolled groove in the tube, which matched a corresponding groove in the plug.

After removal from the glovebox, the top end plugs were welded, thereby completely sealing the tubes. These welds were also leak checked with a helium mass spectrometer.

The rods were then placed in a bonding furnace and held at 450°C for $2\frac{1}{2}$ hr and mechanically vibrated to facilitate bonding the sodium to the uranium and the steel jacket. Amplitude and frequency of vibration were $\frac{1}{16}$ in. and 30 cycles per second, respectively.

Daily gas samples from the glovebox were analyzed to insure that the proper argon-helium mixture was being maintained and that the oxygen content of the glovebox atmosphere was sufficiently low.

Table IV contains a tabulation of production figures for inner and outer blanket rods, including a breakdown of rejected rods according to defects noted.

Table IV

EBR-II INNER AND OUTER BLANKET RODS

Total Rods Assembled	15,722	
Total Rods Accepted	15,019	
<u>Rejected Rods</u>		<u>%</u>
Inadequate or Leaking Welds	227	1.45
Damaged in Loading or Bonding	62	0.39
Insufficient Sodium Fill	342	2.18
Excessive Sodium Fill	56	0.36
Bonding Cycle Residue	16	0.10
Total Rejected	703	4.48

Upper and Lower Blanket Rod Inspection

After loading and bonding, the finished blanket rods were eddy current tested. This test served a dual purpose, namely, to locate areas where the sodium did not form a bond between the uranium slug and the inside wall of the stainless steel tube, and to determine the fill height of the sodium above the top slug. Rods containing voids with a nominal diameter greater than $\frac{1}{16}$ in. were recycled through the bonding furnace and reinspected.

Equipment used in the eddy current test consisted of the following components:

- a. a cyclograph which supplied power to an encircling coil and received a return signal from the coil;
- b. an encircling coil which served as an induction coil and through which the rod to be tested was passed by means of a pair of motor-driven rolls;
- c. an amplifier which magnified the eddy current losses that resulted from defective rods; and
- d. a strip chart recorder which gave a permanent record of each rod tested. The chart speed was synchronized with the rod drive rolls so that the recorded trace was equal in length to the rod, providing 1:1 correlation in locating defects.

The resulting trace was essentially a straight line and any downward deflection indicated a nonbond area. The upward deflection which

occurred on every trace represented the fill height of the sodium. The fill height was measured as being the horizontal width of this upward deflection. This measurement was verified by destructive tests of representative rods and actually measuring the fill height. Sodium fill height (distance above slugs) and fill tolerances were established by the Reactor Engineering Division. These dimensions were: 0.450 ± 0.200 in. for the upper and lower elements and 1.200 ± 0.500 in. for the inner and outer elements.

Of the 6,487 upper and lower blanket rods which were eddy current inspected, 6,343 (97.8%) were accepted; 107 rods were rejected because of low sodium level, 22 because of high sodium level and 15 for nonbond. However, it was discovered that the first 25% of these acceptable rods had too deep a groove at the top end plug. This was a groove rolled in the tubing to hold the top end plug in place mechanically until it could be welded. Hydraulic pressure tests were performed on six tubes containing grooves in excess of 0.009 in. deep. Failure occurred in the range of 8,400 to 10,000 psi gage, and in no case did the tubing rupture at the groove. The decision was made to accept rods which had a groove of 0.007 in. or less. The rolled groove in the remainder of the tubing was not allowed to exceed 0.004 in. Of the 1,712 deep groove rods, 55 had a groove of 0.007 in. or less and were accepted, 720 with a groove between 0.007 and 0.010 in. deep were loaded into assemblies containing natural uranium core material for the dry critical test only, and the balance were decanned, the uranium being reclaimed for reloading.

Inner and Outer Blanket Rod Inspection

Inspection of bonded inner and outer blanket rods was essentially the same as for the upper and lower rods. The only difference was that two encircling coils were used, one for detecting nonbonds, the other to detect sodium fill height. Attempts to obtain both measurements with a single coil resulted in a false value of the sodium fill height. This was due to the close turn spacing on the Inconel-X retention spring above the uranium and the tendency of the sodium to climb up the spring and adhere to it approximately $\frac{1}{4}$ in. above the general sodium level. A second coil with an experimentally chosen frequency of 2.54 kc produced deeper penetration of the induced current into the rod thus eliminating the "spring effect." A dual recorder was used to give a dual trace, one for bond defects, the other for sodium fill height.

Of the 15,433 rods inspected, 15,019 (97.4%) were accepted; 342 were rejected for low sodium fill, 56 for high sodium fill, and 16 as nonbonds.

Reclamation of Uranium Slugs

Uranium from damaged or otherwise unacceptable blanket rods was reclaimed either for reloading or for future programs. The salvaging

procedure for both size blanket rods was essentially the same. A stainless steel cylinder (5 in. diameter x 20 in. long), closed at one end, was filled with paraffin and heated by means of a tubular, electric resistance-heated furnace. The top ends of the blanket rods were cut off on a lathe and the rods were placed open end down in the molten paraffin bath. The bath temperature was maintained at 15 to 20°C above the melting point of sodium. After 10 to 15 min the tubes were raised and the uranium slugs slid out the open end into the paraffin. The uranium and any sodium adhering to it was thereby coated with paraffin and could be safely handled on exposure to air. Upon removal from the paraffin bath the uranium was placed in a tank containing a 50-50 mixture of kerosene and ethyl alcohol. The kerosene dissolved the paraffin while the sodium was dissolved by the alcohol. The slugs were then dried, washed in boiling water, alcohol rinsed, and coated with paraffin base oil to prevent oxidation.

Uranium from 2,415 rods has been reclaimed by this process. Included in this number were 461 rods containing reject uranium which had been assembled for development work.

6. Stainless Steel Hardware for EBR-II Core I (D. E. Walker and N. R. Grant*)

EBR-II Fuel Pin Jacket Components

During 1960, components for 22,879 fuel pin jackets were fabricated and assembled for use in the fabrication of EBR-II fuel pins. Each jacket (see Figure 9) consists of a 0.174 diameter x 0.009 in. wall, Type 304L stainless steel tube, 17.425 in. long, welded closed on one end to a precision-cast Type 304L stainless steel end plug (tip element), a 0.049 in. diameter, Type 304 stainless steel spacer wire spirally wrapped at a 6 in. pitch along the length and welded in place to the tip element on one end and to the tube wall at the other, and a restrainer plug welded to the top end of the tubular jacket after loading of the fuel pin.

The tip element to tube weld and the wire to the tip element weld were produced by means of the inert-gas shielded-tungsten-arc welding process. The spacer wire to the 0.009 in. tube wall was produced with a stored-energy condenser-discharge type spot welder. Both the wire to tube wall weld and the tip element to tube weld were inspected for leaks using a helium mass spectrometer leak detector.

A total of 23,191 fuel jackets were fabricated, assembled and inspected. Of this number 22,879 were acceptable for reactor use. Of the 312 jackets rejected, 51 were for leaky tip element to tube welds and 261 for physical damage incurred during processing.

*Reactor Engineering Division

EBR-II Blanket Rod Jacket Components

During 1960, a total of 12,560 upper and lower blanket rod jacket components were fabricated for use in the EBR-II core. The components which make up a jacket consist of a 0.022 in. wall x 0.0332 in. ID, Type 304 stainless steel tube, 20.375 in. long, welded closed on one end to a Type 304 stainless steel bottom plug, and a top plug welded to the tube after loading of the slugs. The bottom plug end closures were inspected for leaks using a helium mass spectrometer leak detector.

A total of 17,348 inner and outer blanket rod jacket components were fabricated during 1960 for use in the EBR-II core. Each jacket consists of an 0.018 in. wall x 0.457 in. ID, Type 304 stainless steel tube, 61.500 in. long, welded closed on one end to a Type 304 stainless steel bottom plug, and a top plug. The bottom end plug weld closures were inspected for leaks using a helium mass spectrometer leak detector.

In addition to the tubular stainless steel components required for fuel and blanket rods discussed above, a great number of stainless steel parts are required for the completion of fuel, control and blanket elements. A total of 32 different types of stainless steel parts are required, of which 27 types were completely fabricated in 1960. A listing of these stainless steel components supplied by commercial vendors is presented in Table V, along with amount ordered and completed.

Table V

EBR-II CORE HARDWARE COMPONENTS (VENDOR PRODUCED)

Part Name	Amount Ordered	% Completion December 1960
Top End Fixture	1,100 pcs.	100
Hexagonal Tube	7,000 ft	100
Upper Grid, Upper Blanket	200 pcs.	100
Lower Grid, Upper Blanket	200 pcs.	100
Grid Element	200 pcs.	100
Lower Grid, Lower Blanket	230 pcs.	100
Blanket Rod, Upper End	12,500 pcs.	100
Blanket Rod, Lower End	12,500 pcs.	100
Blanket Rod Spring	12,500 pcs.	100
Grid Spacing Rod	400 pcs.	100
Core, Lower Part	200 pcs.	71
Restrainer	26,000 pcs.	100
Tip Element	28,000 pcs.	100
Blanket Element Plug	16,000 pcs.	100
Blanket Element Tip	17,000 pcs.	100
Blanket Element Spring	16,000 pcs.	100
Blanket Grid	950 pcs.	100
Blanket Filler	10,000 ft	100
Inner Blanket Bottom Adaptor	175 pcs.	60
Outer Blanket Bottom Adaptor	700 pcs.	4
Top End Fixture, Subassembly	36 pcs.	100
Top End Fixture, Lower Part	36 pcs.	100
Hexagonal Tube, Inner Control Rod	50 pcs.	100
Guide and Spacer	36 pcs.	100
Shield Section	42 pcs.	100
Grids	36 pcs.	100
Shield Section, Lower	36 pcs.	100
Top Bushing	144 pcs.	100
Top Bushing Retainer	36 pcs.	100
Control Rod, Lower Part	36 pcs.	47
Control Rod Guide Tube	16 pcs.	12
Bottom Bushing	144 pcs.	100

Considerable difficulty has been encountered in obtaining from outside vendors some parts to the required dimensional tolerances. In some instances, it has been necessary either to terminate the contract and do the work in Central Shops at ANL or to provide specialized tooling to the vendor in order to obtain an acceptable product.

7. In-pile Performance of EBR-II Production Fuel Elements
(J. A. Horak)

Although many irradiation experiments have been made on the EBR-II reference fuel, none of the tests exactly duplicate EBR-II core conditions in terms of such items as burnup rate and temperature, and burnup distribution. The final answer on the performance of stainless steel-clad U-5 w/o Fs alloy as a fuel for EBR-II will therefore be supplied by EBR-II itself. In order to obtain the best data on the behavior in the reactor of production fuel pins, measurements which are much more precise than routine "go, no-go" inspections will be needed both before and after reactor exposure.

A sample of 105 production pins was selected for detailed measurements. The diameters of the bare pins were measured at close intervals. Lengths and immersion densities were also determined. After the pins were sealed into jackets, the measurements were repeated on the assembly. Each element is identified with a serial number. The elements will be loaded into known core locations where outlet coolant thermocouples are located so that as much information as possible will be available on the in-pile temperature history of the elements. The upper end closure was modified slightly in shape so that the measured elements can be recognized in the EBR-II reprocessing cell and returned to the Argonne site for detailed postirradiation examination.

Before any measurements were taken, each pin was given an extended anneal at 500°C to convert them fully to the alpha phase, so that the dimensions and density would not change significantly during subsequent sodium-bonding operations.

8. Development and Fabrication of EBR-II Steam Generators
(R. A. Noland, C. C. Stone, L. C. Hymes and D. E. Walker)

Fabrication of Evaporators

All of the eight evaporator units required for the EBR-II plant and one spare unit have been completed. Mechanically bonded tubes were used in four units; metallurgically bonded tubes were used in the remaining five. These units, designed at the laboratory, employ tube in shell construction. To protect against intermixture of the secondary sodium which supplies the heat, and the water phase being heated, duplex tubes (steam) and double tube sheets are used. Two metal membranes thus separate sodium from

the water phase when they are adjacent to one another. Only by complete violation of both plies of the duplex tube can the two materials intermix in a confined space. With the exception of a few parts not in contact with sodium or water, all components are made of a 2.25 w/o Cr, 1.0 w/o Mo, 0.15 w/o C (max) low alloy steel.

Several years ago the policy decision was made to assemble and weld these devices together at the laboratory. This decision was made to ensure maximum service reliability. In addition, commercial manufacturers had expressed their inability to make the steam tube to sodium tube sheet welds. The latter, because of the double tube sheet design, are essentially inaccessible for welding by existing commercial processes. To achieve reliable tube to tube sheet welds, the development of an appropriate welding method was required. A suitable technique employing a modification of the consumable electrode inert-gas shielded process has since been worked out at the laboratory.

All of the components for these units were purchased from commercial suppliers. With the exception of the tubes, these items were required to be in compliance with standard ASTM, ASME, and AISI specifications, where applicable. The steam tubes for the evaporators and for the superheaters were required to be in compliance with a laboratory specification. This specification, which includes ASTM A213 in its purview, stringently limits mechanical defects far beyond the limitations of commercial specifications. The tubing was made by the Babcock and Wilcox Company (seamless) from hot pierced (Mannesmann Process) 2.25 w/o Cr-1.0 w/o Mo steel billets of special cleanliness. Mill inspection of the finished tubing included: (1) hydrostatic testing, (2) dye-penetrant inspection of all external surfaces to a no detectable indication standard, and (3) shear wave ultrasonic examination.

Upon receipt at the laboratory all tubes were checked to determine compliance with specification. These checks included re-examination by shear wave ultrasound, eddy current, and helium mass spectrometer leak testing.

Duplex Tube Fabrication: In addition to development and control of the actual duplexing operations (drawing, expanding, bonding and annealing heat treatments), the fabrication of the 30-ft lengths of duplex tubing for the steam generators involved quality assurance and the development and control of processes for the (1) nickel electroplating the OD of the inner tube of the duplex, (2) electroless nickel plating the ID of the outer tube of the duplex, and (3) centerless brushing of the electroplated nickel coating to provide an active surface for bonding.

The fabrication of the duplex tubing for the evaporator units has been completed. Two types of bond were utilized in bonding these duplexes.

Approximately half (~ 400) of the tubes were mechanically bonded while the balance (~ 400) were metallurgically bonded using the nickel-electroless nickel process outlined in the 1959 annual report (ANL-6099).

The mechanical bond is attained by first drawing the unplated tubes together, over a mandrel and through a die. This operation is followed by an expanding operation in which a mandrel is pulled through the drawn duplex with no restraint on the outside diameter. This process results in a state of residual compressive radial stress which provides the mechanical bond. The mechanical bond has a typical shear strength of 2,000 psi at room temperature as well as at 900°F.

Room-temperature bond shear strengths on the order of 50,000 psi and 900°F bond shear strengths of 40,000 psi are typical for the metallurgically bonded tubes.

Evaporator Fabrication In manufacturing the evaporator units a certain number of problems were encountered. The problem most difficult to solve involved cracking in the craters of the tube to sodium tube sheet welds, despite the use of 1.25 w/o Cr-0.5 w/o Mo filler metal. The cracks were found to have been caused by oxidation of the weld deposit during deposition, occurring to the point where sufficient oxygen was taken up by the deposit to make it hot short. Elimination of oxygen contamination during welding by the use of a truly inert gas such as pure helium or argon was not possible because the consumable electrode welding method required the use of 1 to 5 v/o oxygen in the welding gas in order to achieve deposition by spray transfer of the electrode material to the work. Many gas mixtures were investigated, but none permitted sound welds to be made. The ultimate solution was to provide more of the high-temperature deoxidizers, carbon and silicon, in the welding wire. Some additional advantages are also gained by the fact that slags of lower melting points which free themselves readily from the deposit are obtained in wires having greater amounts of silicon. The resultant welding wire composition, largely because of the 0.12 to 0.18 w/o C requirement, is not available commercially but can now be purchased by special order.

All welding was done with the material preheated to 205°C minimum. As soon as possible after welding was completed, the welds were stress relieved at 676 - 760°C. Heating rates, cooling rates, and time at temperature were in compliance with Section VIII of the ASME Boiler Code. All welds were helium mass spectrometer tested for leaks at appropriate times in the manufacturing sequence. No leaks detectable at the maximum sensitivity of the instrument were permitted. Prior to shipment, the units were hydrostatically tested on the steam side, and were tested with high-pressure argon on the sodium side. Testing pressures and times were in accordance with those suggested by Section VIII of the

ASME Boiler Code. When completed, all of the units received the ASME code stamp indicating full compliance with the code in all matters including manufacture, material specification, and testing.

Fabrication Development for Superheaters: None of the superheater units has yet been completed because of a major problem encountered in the welding of the tubes to the sodium tube sheets. These units are essentially identical to the evaporators except that they are smaller in diameter than the latter and contain a larger number of smaller diameter and thinner walled steam tubes. All of the steam tubes are duplexes metallurgically bonded by the same method employed on the bonded evaporator tubes. Each duplex has an inner diameter of 0.404 in. (nominal) and an outer diameter of 0.591 in. A bond layer, approximately 0.006 in. thick, of Ni-1.0 w/o to 1.5 w/o P separates and metallurgically bonds the two tubes of essentially equal wall thickness (0.040 to 0.050 in.) which make up each duplex. The shear strength of the superheater bonds is typically 46,000 psi at room temperature and 34,000 psi at 900°F.

The problem first encountered in the welding of tubes to sodium tube sheet was that of over penetration of the steam tube by the weld wherein the fusion zone extended into or through the nickel-phosphorus bond layer. In many cases the weld penetrated through both tube walls. Penetration to and through the nickel-phosphorus bond layer is believed to be detrimental because of possible embrittlement of the tube material by phosphorus picked up from the bond. It is also desired to leave as much as possible of the tube in the wrought condition to provide maximum service reliability. Despite a considerable amount of development work, overpenetration has not been eliminated, although mitigated. The welding development has included a complete re-examination of all the welding parameters including welding current, wire speed, wire size, voltage, welding speed, bead size, preheat temperature, certain geometry changes, modified filler wire compositions, etc. Modifications have also been made to the welding equipment. Among these is a nozzle fitted to the welding gun, which enables a spray of water to be directed within the inner tube at a point directly beneath the weld to act as a chill. In addition, dip transfer has been substituted for spray transfer as the mode of metal deposition in an effort to lower the temperature reached by the work during welding. All of these changes have had the effect of reducing overpenetration, but have exaggerated localized nonwetting of the tube by the weld metal, particularly at and adjacent to the start of the weld. This condition is at least as dangerous as overpenetration. These faults extend from the root of the weld along the external diameter of the tube to a point only a few mils below the top of the fillet. The thin, remaining metal section could conceivably be torn open by service stresses. Sodium could then leak into the air space between the tube sheets and, under certain conditions involving oxidation, serious secondary consequences could result. Over

90% of the welds made by procedures designed to reduce overpenetration are found to contain nonwet areas of significance. In addition, all of the work to date has indicated that attempts to eliminate either condition (nonwetting or overpenetration) results in the exaggeration of the other. Nonwetting, in fact, can be eliminated only by the use of conditions which produce near or complete penetration of both tubes. At this time, welding development is continuing in an attempt to develop procedures which will eliminate these defects. The present prospects of achieving this, however, are not hopeful. In the event that all of the development effort is shown to have been fruitless, some consideration has been given to a suggestion that two evaporator units be used in the EBR-II plant in place of the four reference superheater units.

Inspection of Croloy Tube (R. H. Selner)

During the year, 2,989 Croloy tubes for the steam generators for EBR-II were examined by ultrasonic and eddy current techniques for wall integrity. An additional 414 duplexes were tested ultrasonically for bonding defects. Approximately 4%, namely, 130 single wall tubes and 3 duplexes, were rejected by the inspection system. The percentage of rejects is slightly deceiving in that many surface defects were detected in early shipments of evaporator tubing. The vendor improved the surface condition in subsequent shipments and consequently reduced the number of defects. All defective areas were scanned a second time at a reduced speed so that the behavior of the defect indications could be observed on the reflectoscope. Various types of defects, located and evaluated on the oscilloscope, were sectioned and processed in Metallography for correlation studies.

B. Development and Fabrication of EBR-I Core-IV Fuel Elements

1. Development of Methods for Fabrication of Fuel Rods (R. M. Mayfield, W. R. Burt, Jr., A. G. Hins)

The purpose of this program is to investigate methods of fabricating the Pu-1.0% Al reference alloy for EBR-I Core-IV jacketing and sodium bonding the fuel slugs in Zircaloy-2 jackets, closure welding, and testing the fuel rods.

Casting: Both centrifugal and injection precision castings were evaluated as methods for production of fuel slug castings. Centrifugal castings were produced by melting the metal in a bottom-pour crucible above a vertical-axis rotor table. A 16-runner graphite distributor was mounted at the center of the table, the runners of which terminated at the gates of sixteen 0.236-in.-diameter x 9-in.-long copper molds. The centrifugal mold axes lagged the radial lines drawn through the center of the rotor table by an angle of 40°.

Although a number of test castings were made, considerable difficulty was encountered in the use of this assembly. When MgO crucibles and stopper rods were used, a viscous slag formed, which prevented lifting the stopper rod. A tantalum tip was used on the stopper rod, which partly corrected this difficulty, but stopper rod sealing difficulties were encountered. A distributor temperature of 400°C was necessary to prevent freezing of the metal in the distributor, but burnout of heating elements and thermocouples was a regular occurrence. It was found extremely difficult to obtain a full 9-in.-long pin with a satisfactory surface. This condition was somewhat improved by reduction of the speed of rotor rotation, but the required speed of rotation was so slow that most of the advantages of centrifugal casting were lost. The centrifugal casting machine with its bulky parts was found to be difficult to maintain and operate in the hoods.

Because of the above difficulties, the injection-casting technique, developed for EBR-II Core-I fuel, was tested on the 0.235-in.-diameter pin. Full 18-in.-long castings have been made by this method. To date the surfaces of the plutonium alloy castings have not been quite as good as the EBR-II uranium-fissium castings and uranium-plutonium-fissium casting surfaces. Whether this is the result of the greater chemical activity of the high plutonium alloy or the result of the increased mass of metal per casting has not been determined. It is judged that the surfaces will be satisfactory for use, however. Yttria and graphite have been used as mold washes with fair success.

Previous EBR-I loadings employed spring centering clips between each fuel slug. This resulted in the reloading of many fuel rods when the slugs would slip from the clips in handling subsequent to loading. It was

suggested that centering fins be fabricated on the fuel slugs. These have been provided by upsetting the slugs in a die with four equally spaced 0.007-in.-deep grooves. The fins raised are approximately 0.006-in. high. A second method employs a star-shaped punch which, when driven against the end of the slug, stakes out four bumps, the height of which are controlled by a restraining ring. The former method appears more precise and satisfactory for the plutonium fuel, whereas the latter method may be more satisfactory for the uranium blanket material.

The nonavailability of full-scale Zircaloy fuel tubes has prevented as complete a rehearsal of loading, welding, sodium filling, bonding, and inspection as would be desirable. The following techniques are planned and have received a partial rehearsal.

Fuel tubes will be attached to the wall of the contaminated hood line by means of a vinyl pouch having a number of flexible plastic fittings. These fittings will contain an inverted inner lip to protect the edge of the fuel tube opening from contamination. A hose clamp will seal the fitting against the rigid tube and since the outside of the tube is outside of the contaminated hood, it will not become contaminated. After loading, the vinyl pouch is inverted over the ends of the tubes, dielectrically sealed, and transferred from the hood by standard pouch transfer techniques.

The loaded tubes are transferred to the welding line where, just before welding, the plastic fittings are removed and the Zircaloy coupler is inserted, and a heliarc girth weld is made.

NaK is metered into the fuel tube through a small opening left in the top of the coupler, which is later plugged and sealed by a capacitor discharge weld. Sufficient Zircaloy specimens have been available to develop and test the welding methods, but there have not been enough fuel tubes to develop and test the techniques for bonding, NaK level measurement, and bond testing.

2. Engineering and Physical Properties of the Plutonium-1 w/o Aluminum Fuel Alloy (F. L. Yaggee, R. J. Dunworth)

Selection of the Pu-1 w/o Al (8.2 a/o Al) composition as the probable reference alloy for the Mark-IV fuel loading of EBR-I has fostered an interest in certain engineering properties of this alloy as a guide to fuel rod design and as a basis for anticipating its probable behavior under reactor operating conditions. A more general interest in the delta-stabilized alloys of the plutonium-aluminum system covering the composition range from 0.35 to 1.24 w/o Al (3 to 10 a/o Al) is also implied. Toward this end, a program has been initiated to study the following properties of the as-cast reference alloy:

- a. thermal conductivity to 530°C;

- b. hot deformation or slumping tendency of the reference alloy under several static loads of the order anticipated in reactor operation in the temperature range 400-600°C;
- c. compatibility of the reference alloy with Zircaloy-2, the proposed jacketing material, at 400 and 500°C;
- d. thermal expansion of the reference alloy between 200 and 600°C; and
- e. thermal expansion of delta-stabilized Pu-Al alloys as a function of aluminum content for the composition range from 3 to 10 a/o Al.

The thermal conductivity of the Pu-1 w/o Al fuel alloy has been determined, with an accuracy between 5 and 10%, between 100 and 530°C a comparative type apparatus with Inconel and Armco iron standards, on a specimen 2 cm in diameter by 5 cm long. The values are listed in Table VI. The data fit a straight line with a precision of about 2%.

Table VI

THERMAL CONDUCTIVITY
OF Pu-1 w/o Al

Temp (°C)	Thermal Conductivity (cal/cm-sec-°C)
100	0.022
200	0.027
300	0.033
400	0.038
500	0.045
600	0.050(a)

(a) Extrapolated.

A series of slump tests have been completed on a centrifugally cast reference alloy having the reported composition Pu-1.11 w/o Al (9.2 a/o Al). Machined specimens measuring 0.205 in. in diameter by $1\frac{1}{2}$ in. long were made to carry static loads approximating the weight of the depleted uranium upper blanket slug plus $2\frac{1}{2}$ pounds of spring pressure applied in roughly $\frac{1}{2}$ -pound increments. While under load, each test specimen was held for 20 hours at each of three temperatures: 400, 500 and 600°C. The results are tabulated in Table VII.

In general, the first indications of specimen slumping were observed between 350 and 400°C, and, of the total measured deformation at the conclusion of these tests, roughly 3-10% occurred at 400°C,

23-30% occurred at 500°C, and 60-70% occurred at 600°C. The specimen in test #1 began to slump unexpectedly at 290°C. Although roughly 65% of the total measured deformation occurred at 600°C, approximately 25% occurred at 400°C and 9% occurred at 500°C. The difference in the contour of the specimens due to buckling during testing could account for such anomalies.

Table VII

SLUMP TEST RESULTS ON CAST
Pu-1.11 w/o Al

Test No.	Applied Load (psi)	Total Measured Slump (in.)
1	7.2	0.034
2	20.3	0.027
3	34.6	0.050
4	46.8	0.125
5	59.4	0.227

Note: Spring pressure of dial gage indicator included in calculated load.

The Rockwell "B" hardness of the centrifugally cast reference alloy specimens ranged between 90 and 95 in the as-cast condition. At the conclusion of each slump test in which the specimen had been heated for a total of 60 hours in the temperature range from 400 to 600°C, the hardness dropped to 85-90.

Five delta-stabilized plutonium-aluminum alloys ranging in composition from 0.26 to 3.06 w/o (2.25 to 21.63 a/o) were made by induction melting under vacuum and casting into thoria-coated graphite molds. The density of as-cast pins of these alloys measuring $\frac{1}{4}$ in. in diameter by $1\frac{1}{2}$ in. long are given in Table VIII.

Table VIII

DENSITY OF Pu-Al ALLOYS

Melt No.	Alloy Composition*		Density (g/cc)
	(w/o)	(a/o)	
209	0.26	2.25	16.05 $\pm$ 0.02
210	0.42	3.70	15.76 $\pm$ 0.02
207	0.78	7.30	15.38 $\pm$ 0.02
211	1.23	10.00	15.06 $\pm$ 0.02
208	1.22	9.80	15.16 $\pm$ 0.02
206	3.06	21.63	13.72 $\pm$ 0.02

*Note: Reported analyses.

3. Fabrication of Zircaloy Jacket Components, Uranium Blanket Slugs, and Stainless Steel Hardware, EBR-I Core-IV
(R. A. Beatty)

The Foundry and Fabrication Group is responsible for procurement, fabrication and inspection of all components other than plutonium fuel material for the EBR-I Core-IV fuel loading. These components, including Zircaloy-2, Zircaloy-3, Type 304 stainless steel, Inconel-X hardware and depleted uranium blanket slugs, will be delivered after machining and inspection to the ANL Fuel Fabrication Facility for glovebox assembly, NaK filling, and sealing of the fuel rods. The reference loading, which originally included 515 rods, was increased by the December 1, 1960, addition of 40 blanket assemblies and presently includes 420 plutonium fuel, 120 blanket, 10 fuel thermocouple, and 5 blanket thermocouple rods. In addition to the 555 rods ordered by the Idaho Division, components for 167 rods (30% excess) will be fabricated to provide development material and replacements for process rejects.

Unalloyed, beta-treated, depleted (0.20 ± 0.02 w/o U^{235}) uranium slugs will be used for the EBR-I Mark-IV fuel blanket. These slugs, procured for the EBR-II blanket loading, are free from internal defects as verified by an ultrasonic through-transmission inspection; however, they were unacceptable for EBR-II because of surface defects. The defects will be removed with the 0.035 in. to be ground off the slug surface in the reduction to EBR-I Mark-IV finished slug size. Drawings approved for construction of the uranium components will not be available until reference spacer upset equipment is fabricated and production proof tested.

An order was placed with Wolverine Tube Division of Calumet and Hecla in October of 1959 for 500 feet of 0.250-in.-OD and 1000 ft of 0.260-in.-OD Zircaloy-2 tubing to be converted from Mallory Sharon 15-in.-diameter, vacuum-melted ingots supplied by ANL. These were reference tube sizes to be used for development of the EBR-I Mark-IV loading. When jacket tubing specifications became known, the tubing order was changed and now includes 2200 ft of 0.257 ± 0.002 in.-ID x 0.021 in. $\pm 10\%$ wall. Delivery of the 2200 ft of tubing was promised for December 20, 1960. On December 20th, ANL was notified that the vendor did not have a process for making the 0.257-in.-ID tubing and all previously quoted delivery dates must be disregarded. Tubing samples rejected by the vendor's eddy current defect scanner were brought back to ANL and found to be acceptable when inspected with the ANL device. ANL metallographic investigation of the most positive defect indication from the vendor's device showed no defects of the type or size known to be readily resolved by the ANL device. The tubing vendor has now agreed to ship all jacket tubing that passes commercial size and straightness specifications and to accept the results of ANL eddy current inspection for crack-type wall defects. ANL expects receipt of a few hundred feet of this material during the second week in January, 1961.

An effort is being made to fabricate EBR-I Mark-IV fuel jacket tubing at ANL by alternately drawing and die sinking 0.375-in.-OD tubing presently on hand. This work is a backup effort in the event that commercial tubing does not meet specifications or is further delayed.

Zircaloy-2 rod stock, 0.299 in. in diameter, for rod tip, fuel connector, and filler plug components was fabricated at ANL from available $1\frac{5}{8}$ -in.-diameter forged bars. The 0.299-in. rod stock fabricated to date is sufficient for approximately 94% of the elements to be constructed. The Nondestructive Testing Group of the Metallurgy Division has completed the installation of the ultrasonic test equipment required for quality control of the material for rod tips, fuel connectors, and filler plugs.

Zircaloy-3 wire stock for spacer ribs to be welded along the outside wall of jacket tubes is being reduced to 0.060 in. in diameter from $1\frac{5}{8}$ -in.-diameter forged bar. Reduction of 4000 ft of wire by rolling, swaging and drawing is 88% complete. The 4000-ft yield expected from this effort is adequate for 90% of assemblies to be fabricated. Encircling coil-type eddy current equipment will be used to inspect rib wire stock for defects such as cracks, slivers, and voids. Metallographic investigations have shown that good correlation exists between eddy current indications and the location and size of actual defects.

Approximately 85 ft of NaK level spacer stock has been swage reduced to final size from 0.375-in.-OD Zircaloy-2 tubing. This is sufficient material for 94% of the assemblies to be fabricated.

The thermocouple assemblies for this reactor call for a total of 40 ft of 0.080-in.-OD Zircaloy-2 tubing. This small-diameter tubing was originally covered by an October, 1959, order with the jacket tubing vendor for 500 ft of nominal 0.080-in.-OD $\times$ 0.015-in.-wall tubing. Late in October ANL was notified that the vendor did not have a process for fabrication of 0.080-in.-OD tubing. Development work was immediately begun on processes for ANL fabrication of 0.080-in.-OD tubing. The vendor will make no effort to fabricate 0.080-in.-OD thermocouple tubing until the higher priority commitment for EBR-I Mark-IV jacket tubing has been fulfilled.

In the original design of all EBR-I Mark-IV assemblies, a 0.006-in. annulus was provided between jacket and uranium slug by Zircaloy-3 clips held on slug ends by spring tension. In an effort to eliminate the need for these spacer clips which are small and difficult to handle in glovebox assembly, a punch-and-die mechanism was fabricated to upset the slug ends forming 0.006-in.-high spacers located 90° apart around the circumference. The reference spacers were to be approximately $\frac{1}{32}$ in. wide and $\frac{1}{16}$ in. long in the direction of the slug axis. Both warm and cold upsetting processes were evaluated. One slug was upset at room temperature and one slug was heated in oil to 300°C and upset in a die heated to a minimum of 120°C. Slight deformation throughout the length of the slugs is characteristic of both the warm and cold processes and is measured as approximately 0.0005-in. increase in diameter at the midsection. From the standpoint of punch-and-die life, a warm process is considered desirable. Dies incorporating cartridge heaters and other modifications were designed to permit production upsetting of three slug sizes.

Apparatus for a 3-hr thermal cycle of slugs between 100 and 375°C has been set up. The material will be tested in a NaK environment. This test is designed to evaluate the behavior, under simulated EBR-I Mark-IV reactor conditions, of blanket uranium slugs that have been upset by the prototype punch-and-die equipment. After a 15-min. heating period, the uranium sample is held 15 min. at temperature and cooled to 100°C in $2\frac{1}{2}$ hr. Actual testing will begin when uranium samples are prepared.

Initial development efforts have been completed on an electrical discharge method for drilling holes in blanket uranium for sheathed thermocouples. Evaluation of 9-in.-long holes resulting from initial efforts to drill 0.086-in.-diameter holes showed prominent steps 3 in. from each end and a few $\frac{1}{4}$ -in.-long eroded areas along the slug axis. The steps resulted in ID variations of an estimated 0.020-in. within a length of less than $\frac{3}{16}$ in. The hole diameter was enlarged approximately 25% in eroded areas. Second-effort samples have been drilled without steps and look much better. A 9-in.-deep hole was drilled in 2 hr 35 min.

Development of rod-tip girth welds and rib-wire welds is complete. Girth welding was performed with inert-gas shielded-arc equipment mounted on a variable-speed glass lathe electronically synchronized to perform the welding cycle desired. Zircaloy-3 rib wires were attached to fuel tubes using condenser discharge type spot weld equipment developed for EBR-I Mark-III fuel. The wires were welded without distortion of the tube OD or ID.

Depleted uranium blanket slugs with machined spacers, 0.006 in. high, $\frac{1}{32}$ in. wide and $\frac{1}{16}$ in. long, three at each end, were evaluated by the Idaho Division. As a result of this evaluation, addition of a fourth spacer at each end was recommended. Uranium components for 12 blanket assemblies and 6 dummy fuel assemblies were machined to simulate upset slugs having 4 spacers at each end. The hardware components to complete these assemblies are being machined. The 18 assemblies will constitute trial-run material for setup of assembly and NaK-filling equipment in Building 350.

Adjustment of EBWR Core-IA eddy current inspection equipment for evaluation of EBR-I Mark-IV Zircaloy fuel jacket tubing was completed. Faulty electronic components were discovered and replaced. The equipment is presently being restandardized and evaluated to determine its sensitivity to very small defects in the 0.299-in.-OD tubing.

4. Ultrasonic System for the Inspection of EBR-I Core-IV Zircaloy-2 Rod Stock (R. H. Selner)

A technique for inspecting Zircaloy-2 rod stock for internal defects before final fabrication into EBR-I Core-IV fuel elements has been set up. The test facilities are similar to those used in evaluating the EBR-II blanket rods. These facilities include, (1) ANL-fabricated skewed roller assembly; (2) Bodine AC motor; (3) Atlas lathe and attachments; (4) Sperry reflectoscope and monitor used to generate, detect, display, and interpret the ultrasonic vibrations; (5) Branson Z-K transducers; and (6) brush amplifier and recorder.

Preliminary inspection of 50 rods fabricated in the foundry revealed several rods of questionable quality. Strip-chart recordings of suspect areas were compared to a standard recording obtained from a 15-in. length of rod with artificial defects ($2\frac{1}{32}$ -in.-diameter holes drilled $\frac{1}{4}$ in. and $\frac{1}{2}$ in. into the middle of the ends). Defects that produced a range of amplitudes on the recording paper were sectioned and examined in Metallography. Micros of the flaws revealed conical-shaped void areas situated at or near the center of the rods and close to the ends. The voids were 1 to $1\frac{1}{2}$ in. long, 5-10 mils wide, and 20-50 mils high. It appears, from the preliminary runs, that the system will be able to detect flaws

located perpendicular to a radius of the rod as well as those in the center. Further tests will be run to ascertain whether the system is sensitive to thin radial cracks that are not perpendicular to the beam of ultrasonic vibrations.

5. Irradiation of Plutonium-1 w/o Aluminum Alloy (J. H. Kittel and R. Carlander)

Little interest has been shown in the use of unalloyed plutonium as a reactor fuel, principally because of the large number of phase transformations in the metal, which would undoubtedly result in considerable dimensional instability. However, the isotropic face-centered cubic delta phase can be stabilized over a large temperature range by the addition of 1 w/o (10 a/o) aluminum. Because of this feature, the alloy has been selected as the fuel for the Core-IV of EBR-I.

In order to determine the effects of irradiation on the alloy, four fuel rods were made and inserted in EBR-I early in the summer of 1960. Each rod is made up of a 21-mil wall Zircaloy-2 tube containing a NaK-bonded 8.5-in.-long casting of Pu-1 w/o Al alloy, 0.200 in. in diameter. The thickness of the NaK annulus in the assemblies was varied from 0.004 to 0.019 in. Two of the rods contain axial holes in the fuel so that central temperatures can be measured during irradiation.

The two nonthermocoupled rods were recently returned for a detailed hot laboratory examination after they had achieved an estimated 0.1 a/o burnup at central temperatures near 350°C. No changes in jacket diameter or surface appearance resulted from irradiation. Preparations are being made to open the tubes and examine the fuel specimens directly.

C. Fabrication of EBWR Core 1-A Spike Fuel Elements

In modifying the Experimental Boiling Water Reactor to permit operation at 100 megawatts, (thermal), some of the original slightly enriched solid metal fuel elements were replaced with elements containing highly enriched fuel. The "spiked" core material is a solid solution ceramic composed of 82.21 w/o ZrO_2 , 9.13 w/o CaO , 8.16 w/o UO_2 and 0.5 w/o impurities. This ceramic is in the form of cylindrical pellets nominally 0.322-in.-diameter $\times \frac{1}{2}$ -in.-long. The fuel rods consist of these ceramic pellets jacketed in nominal 0.375 in. OD. $\times$ 0.325 in. ID $\times$ 49 in. long Zircaloy-2 tubes sealed at each end by 0.375 in. diameter $\times$ $1\frac{1}{2}$ in. long Zircaloy-2 end plugs. Element assemblies of 49 fuel rods each, held in 3.6 in. $\times$ 3.6 in. square bundles inserted in $3\frac{7}{8}$ in. $\times$ $3\frac{7}{8}$ in. square frames, complete the fuel elements.

The original reference fuel for Core 1-A of EBWR was enriched U_3O_8 dispersed in an aluminum matrix. This fuel was to be jacketed in close fitting Zircaloy-2 tubing. It was repeatedly found, however, that only a few thermal cycles between room temperature and $260^\circ C$ caused severe ratcheting between the aluminum base fuel and the Zircaloy-2 jacket. This caused the fuel to shorten in length and to increase in diameter, rupturing the jacket in some cases. Consequently, the aluminum-Zircaloy ratcheting forced the substitution of a ceramic for the aluminum dispersion fuel.

1. Fabrication of Zirconia-Calcia-Urania Fuel Pellets (J. H. Handwerk)

Investigations of the ternary system ZrO_2 -CaO- UO_2 revealed that extensive regions of cubic solid solution existed between lime-stabilized zirconia and urania. These solid solutions were also found to be formed by reacting mixtures of ZrO_2 , $CaCO_3$, and U_3O_8 .

Homogeneous, cubic solid solutions such as these are of interest for high-temperature fuel applications in which the reactor core requires high enrichment and high burnup. Therefore, based on the studies in the ZrO_2 -CaO- UO_2 system, a fuel having the composition of 81.83 w/o ZrO_2 , 9.24 w/o CaO and 8.93 w/o UO_2 was selected for the spike elements for the EBWR Core 1-A. The ceramic fabrication involved the production of approximately 150,000 pellets approximately 0.320 in. in diameter x approximately $\frac{1}{2}$ in. long.

The oxide ZrO_2 , $CaCO_3$, and U_3O_8 were mixed with 3 w/o polyvinyl alcohol in a pebble mill for 3 hr. This mixture was moistened with 28 to 30 w/o of a water solution containing 0.5 w/o Carbowax 4000 and 0.5 w/o Aerosol. The damp material was granulated by forcing it through a 16 mesh screen, and the granulars thus formed were dried for 4 hr at $90^\circ C$. The granulated mixture was charged to an automatic air press where it was compacted into right cylinders at 14,000 to 16,000 psi at the rate of 10 pellets per minute.

The pressed pellets were inspected and randomly loaded into stabilized zirconia crucibles. The cracked or chipped pellets were regranulated and returned to the press. The loaded crucibles were placed in an electric furnace and heated slowly to $600^\circ C$ to remove the organic binder. The crucibles were then transferred to a gas-fired kiln and sintered in air to $1675 \pm 25^\circ C$ in approximately 12 hr. The sintered pellets were visually inspected for chips and cracks. Defective pellets were crushed by means of a pebble mill, and this calcined material was added to the raw batches in order to control fired shrinkage, and to compensate for die wear in the press.

2. Procurement, Fabrication, and Inspection of Zircaloy-2 Hardware (W. C. Kramer, R. A. Beatty)

The Zircaloy-2 hardware required for the spike elements and frames consisted of 1666 jacket tubes, 3332 end plugs, 140 springs, 34 center spacers, 140 angles, 68 side plates, and 140 lift plates.

The jacket tubing was converted from a Mallory Sharon, 15-in.-diameter vacuum-melted ingot by the Wolverine Tube Division of Calumet and Hecla. End plug stock was hot rolled at ANL from $1\frac{5}{8}$ -in.-diameter bars forged by Anderson Schumaker and Company, Chicago, from an Alleghany Ludlum 12-in.-diameter atmosphere melted ingot. The spring stock was hot rolled and cold finished at ANL from existing $\frac{1}{8}$ -in.-thick plate. Center spacers were cut from $\frac{1}{4}$ -in. plate on hand at ANL. Angle, side plate, and lift plate stock was converted to sheet from two Mallory Sharon 15-in.-diameter ingots at the Blairsville Metals Plant of Westinghouse Electric Corporation.

To obtain the required 1666 jacket tubes, 0.375-in.-OD x 0.025-in.-wall for 34 Zircaloy jacketed elements, 16,000 ft of tubing was ordered in October, 1959, for delivery in February, 1960. Surface finish both inside and outside was to be smooth and free from such defects as laps, seams, and longitudinal striations. The tubing was also to be free of longitudinal cracks originating on the inside wall such as had been found in at least 30% of previous 0.385-in.-OD evaluation tubing. Visual inspection of 8-in.-long segments from approximately 100 of the first 152 lengths of tubing received indicated that 40% of the material received had undesirable ID or material defects such as scratches, gouges, pockmarks, galled spots, imbedded foreign particles, and spiral markings from roll straightening and mandrel removing operations. These defects could not be effectively removed even by extensive pickling. Cracks deeper than 0.004 in. (and all other equivalent defects) were detected in approximately 27% of all tubing tested with a dual-frequency probe-type eddy current testing unit.

The eddy current testing unit (see page 66) utilizes one frequency channel for spacing compensation and one for inspection information, thus reducing the effect of small changes in OD and other variables. The eddy current probe was mounted on a long-bed lathe in which tubes as long as 80 in. were rotated at 187 rpm. The probe moved with the lathe carriage at a feed of $\frac{1}{16}$ in. per revolution. This arrangement and the need for a permanent recording of inspection results on each tube permitted an inspection rate of 3.8 linear in. per sec. Approximately 2.8 min were required to inspect each tube length. Defect indications from the eddy current device showed good correlation with both the location and the depth of actual cracks. Because the inspection equipment, at the time this tubing had to be inspected, was not able to indicate unquestionably internal surface defects less than 0.004 in. deep at the required inspection rate, it was necessary to accept tubing which was sound only to this 4-mil limit.

The following procedures were followed in evaluation and inspection of the Zircaloy-2 tubing prior to machining to length. The tubes were cleaned by degreasing in hot trichloroethylene upon receipt, plug-gaged to assure that pellets could be inserted, and eddy current inspected for crack-type defects. Tubes were consecutively numbered after eddy current inspection and the following records were maintained:

- a. tube number;
- b. eddy current trace on acceptable tubes; and
- c. maximum plug-gage size which would pass through tube.

Final disposition of Zircaloy-2 tubing received for the EBWR spiked core loading is included in Table IX.

Table IX

INSPECTION OF ZIRCALOY-2 TUBING

Total Number of Tubes Received		3201
Inspected by eddy current	3060	
Rejected by visual and dimensional inspection upon receipt	33	
Used for process development and evaluation	<u>108</u>	
Total	3201	
Accepted by Eddy Current Inspection		2240
Loaded into fuel elements	1666	
Excess accepted tubes	446	
Used in loading development	95	
Rejected on dimensional inspection	<u>33</u>	
Total	2240	
Rejected by Eddy Current Inspection		820
Returned to vendor	575	
Resized at ANL prior to inspection and not returnable	<u>245</u>	
Total	820	

To provide sufficient material for angle components, side plate components, and lift plate components, an order was placed in November of 1959 for rolled, 0.062-in.-thick and 0.081-in.-thick strip stock. The material was delivered in 11-in. widths and 5- to 7-ft lengths. A yield from ingot to sheet of 68% was realized. After evaluation for conformation to specifications, all material was wet-abrasive blast cleaned to remove rolled-in dirt, and was followed by acid cleaning in a HNO_3 -HF solution.

To provide 3332 end plugs for weld closure of tubes, approximately 47 ft of $1\frac{5}{8}$ -in.-diameter forged bar stock was machine conditioned, dye-penetrant inspected, and hot rolled at 850°C to $\frac{3}{4}$ in. in diameter. Subsequent rolling to 0.402-in. diameter was done at a temperature of 600°C. Yield from forged bar to 0.402-in.-diameter rod was 78% minimum. After centerless grinding to finished diameter, the rod stock was ultrasonically tested for material defects. Of 600 ft tested, 4% was rejected due to suspected internal defects.

Stock for spring components was supplied by 850°C rolling of $\frac{1}{8}$ -in. plate to a thickness of 0.070 in., removing oxide contamination by wet-abrasive blasting and pickling, and 600°C rolling to 0.045-in. thickness. After a second wet-abrasive blast and acid bright dip the material was cold finished to 0.031 in. and again bright dipped in acid.

3. Eddy Current Equipment for the Inspection of Zircaloy-2 Tubing (C. J. Renken)

Early in 1960, samples of Zircaloy-2 tubing became available for tubing to be used in the 1-A core of the EBWR. Preliminary tests on these sample tubes showed that a nondestructive test was necessary on all the tubes which would go into the reactor. After evaluating the various test methods available, we decided to use a dual-frequency eddy current test system developed at Argonne.

The two frequencies used in this equipment were 1825 kc and 82 kc, and the tube was rotated while undergoing the inspection at a rate of 187 rpm with a test probe pitch of $\frac{1}{16}$ in. After a careful correlation of the recorded signal produced by the test system and actual crack depth as determined by metallography, it was decided to accept tubes having cracks less than 0.004 in. deep starting from the ID. Under this criterion, about 60% of the first 2500 tubes inspected were accepted. This inspection program showed that the dual-frequency test system should be improved in order to allow greater inspection speed. This has been undertaken, and although the project is not yet complete, inspection rates 100% higher are now practical with greater sensitivity than before.

4. Assembly of Fuel Rods (W. C. Kramer, F. D. McCuaig, J. H. Handwerk)

Zircaloy-2 end plug stock was finish machined after development of the arc-welding method had fixed the design of the end closures. A total of 3600 end plugs, representing approximately 80% of the stock supplied, were made. Acceptable Zircaloy-2 tubes which had been cut to final length of 49.000 in. $\pm$ 0.010 in. and plug-gaged to determine the exact ID size, were matched with end plugs which had been stamped with numbers corresponding to their respective identifying tube numbers. The matched

end plugs were inert gas-shielded arc-welded into one end of the corresponding tubes, and the resultant welds were checked with a mass spectrometer helium leak detector. The tubes were then manually loaded with a 48-in. column of ceramic pellet core material. The loaded fuel tubes were evacuated and back filled with a helium atmosphere, and the second end plug was welded into the open ends of the fuel rods. The helium atmosphere enabled the checking of the final end closure welds, and served as a more efficient medium for heat transfer across the 0.003- to 0.004-in. annulus between the ceramic fuel and the Zircaloy cladding. Of the number of welds required in fabricating 1568 fuel rods of this type, less than 0.1% were found to be incompletely sealed. After 0.070-in.-wide positioning slots were machined into both end plugs of each loaded and sealed rod, the rods were wet-abrasive blasted at 50-60 psi with 400 mesh Al_2O_3 grit, and pickled in a 35 v/o HNO_3 -5 v/o HF solution maintained at a temperature of 35-40°C to insure a corrosion-resistant surface finish.

During the fabrication of the fuel rods, the following records were maintained:

- a. maximum plug gage size which would pass through the jacket tube;
- b. rod number (identical in each case to the corresponding jacket tube number);
- c. weight of oxide fuel loaded into each tube; and
- d. outside diameter of rod after final cleaning.

5. Fabrication of Frame and Fuel Element Assembly Components (F. D. McCuaig, W. C. Kramer)

The 49 fuel rods which make up an EBWR spike element are supported in a square arrangement in Zircaloy-2 and stainless steel fittings, as shown in Figure 11. This fuel bundle is supported in a frame shown in Figure 12 for loading into the reactor. Zircaloy-2 was used in fabricating the $55\frac{1}{2}$ -in.-long x 0.064-in.-thick side plates, and the $\frac{1}{4}$ -in.-thick x 3.562-in.-square center spacer required for each element. Side plates were sheared to size and cold formed to final shape. Center spacers were drilled to accept 49 fuel rods and machined out to allow for coolant flow in reactor operation. Completed spacers were wet-abrasive blasted and pickled in warm 35 v/o HNO_3 -5 v/o HF solution. Side plates were similarly pickled.

End support holders were made by cold forming 0.081-in.-thick, Type 304 stainless steel sheet stock into channel-shaped half-boxes and inert gas-shielded arc-welding the two mated channel seams. Rod support combs were sheared from 0.062-in.-thick stainless steel stock and gang milled to final shape.

Figure 11. Fuel Element Components before and after Assembly.

Fig. 12. Frame Components in fore and aft Assembly.

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Seven rod supports welded in place on each support holder completed the end fittings. The end fittings were given an electrolytic polish as a final cleaning operation. Lifting lugs were sheared to size from $\frac{1}{8}$ -in.-thick stainless steel stock.

Except for the stainless steel end fitting, the frame assembly components shown in Figure 12 were fabricated from Zircaloy-2 strip stock. Angles were formed from 0.081-in.-thick strips on a press break, after resistance heating the strips to approximately 700°C. They were then wet-abrasive blasted, sheared to final length, milled and acid pickled for final assembly. Lifting plates were sheared and punched to specified dimensions from 0.081-in.-thick stock and were given the usual abrasive blast and pickle. A leaf spring, cold formed from $\frac{1}{32}$ -in.-thick Zircaloy-2 strip, was resistance spot welded under an inert gas shield to each lifting plate to aid in stabilizing the position of each element in the reactor. Stainless steel end fittings were sand cast at Watertown Arsenal. Formed crosspieces, $\frac{1}{8}$ in. thick, were heliarc welded onto the end fittings and the fittings were machined to final dimensions.

The 51-in.-long fuel rods are held in element assemblies by fitting the positioning slots in each end plug onto the rod supports at both ends. The rods are also supported at their centers by the center spacer. The fuel rod assemblies were completed by fastening the side plates to the end fittings with two $\frac{1}{4}$ -in.-diameter stainless steel rivets at each end of both side plates, and resistance spot welding the side strips to the center spacer. The lifting lugs were welded to the end fittings at each end to facilitate the loading of the rod bundles into the frame assemblies. During assembly of the rod bundles, records were maintained as to the element number into which each rod was loaded, and the location of each rod within the element. The length of a completely assembled fuel rod element, as shown in Figure 11, is $60\frac{3}{4}$ in.

Assembly of the frame components consisted of resistance spot welding the angles to the lifting plates at one end, and fastening the other end of each angle to the sand cast end fitting with two $\frac{1}{4}$ -in.-diameter flat-head screws. A completely assembled frame, as shown in Figure 12, is $3\frac{7}{8}$ in. square x $89\frac{1}{2}$ in. long. The frame assembly was designed in this particular manner so that an element, when inserted in it, can be easily positioned in, or removed from, the reactor core.

6. Fabrication and Testing of Special Elements (F. D. McCuaig, W. C. Kramer)

The spike fuel rods for EBWR were to have been rods of U_3O_8 dispersed in an aluminum matrix jacketed in tightly fitting Zircaloy-2 tubing closed at each end. Thermal cycling of this type of element induced dimensional changes in the core far beyond that which could be acceptable for

reactor use. These dimensional changes were first noted in a test element fabricated by drawing a Zircaloy-2 tube down upon an aluminum core. A $\frac{5}{16}$ -in. expansion gap for the core was left at one end of the jacket. This specimen rod was thermally cycled by heating it in oil at 300°C, followed by quenching in water. A radiograph made after ten such cycles revealed the expansion gap to have increased from the original $\frac{5}{16}$ in. to $1\frac{15}{16}$ in., a shortening of $1\frac{5}{8}$ in. in the original 48-in.-long aluminum core. The Zircaloy-2 jacket and the aluminum core increased 0.003 to 0.004 in. in diameter. The length of the Zircaloy-2 jacket remained the same.

This thermal ratcheting phenomenon was investigated further with an Al-U₃O₈ dispersion-type core in place of straight aluminum. Various methods of heating to 260°C (the approximate reactor operating temperature) and cooling were tried. These consisted of oil heating and water quenching, furnace heating and air cooling, furnace heating and water quenching, and electrical resistance-heating the core directly and air cooling. Samples were heated and cooled in the vertical as well as the horizontal position. Several additional specimen rods and rod sections were prepared with various modifications. Some were prepared with sealed end closures, others with open ends; zirconium alloy tubing was replaced with thinner wall stainless steel tubing; $\frac{1}{16}$ -in.-deep circumferential grooves were rolled into sections prepared with Zircaloy-2 tubing as well as with stainless steel tubing; and one rod was prepared using a core slug on which a spray coating of graphite had been applied. In every case, the same results were obtained - shortening of the core and increasing of the rod diameter. In two cases, cycling was carried far enough to cause a crack to appear in the jacket tube. The effect of one other variable was investigated; the annulus between core and jacket varied between essentially zero and 0.005 in. Ratcheting occurred on all specimens having an annulus less than 0.002 in. but was not observed in those specimens having an annulus greater than 0.002 in. between core and jacket.

One specimen was prepared for a core meltdown experiment. The specimen with Al-U₃O₈ core material in a Zircaloy-2 tube with end caps welded into each end was placed vertically in a muffle furnace which had been preset at 750°C. By means of a thermocouple attached to the outside of the tube, it was determined that the core melted at approximately 675°C. Examination of the specimen after cooling showed the core to have diffusion bonded to the tubing, leaving a large amount of void space running throughout the center length of the tube. At one point near the top of the vertical specimen, the core had diffused completely through the tube. Another specimen prepared by zone melting the core material inside Zircaloy-2 tubing to obtain a diffusion bond was cycled by slow heating to 300°C and then air cooled, and by subsequent heating to 300°C in oil and quenching in water. The diffusion bond achieved between the core and cladding prevented ratcheting or shortening of the core in both cases.

Another specimen rod was prepared using $\text{ZrO}_2\text{-CaO-UO}_2$ ceramic pellets as core material. The annulus between the pellets and the Zircaloy-2 tubing was from 0.003 to 0.004 in. Slow heating to 300°C and slow cooling, and heating to 300°C in oil followed by water quenching had no effect on the dimensions of the pellets or the tubing.

The conclusions reached from the limited amount of data collected were that the thermal ratcheting could be eliminated to some extent in at least four ways:

1. controlling the annulus between the dispersion-type cermet core and Zircaloy-2 jacket;
2. diffusion bonding the cermet core to the Zircaloy-2 cladding;
3. jacketing the cermet core in aluminum tubing to negate any effect caused by differences in thermal expansion; and
4. using a core material with a small coefficient of thermal expansion.

Since the fourth alternative was considered the most reliable and easiest to fabricate, 32 elements for use as spike elements in EBWR were made with ceramic oxide core material as previously described, and three experimental elements, one each based on the remaining alternatives, were fabricated.

The three special 49-rod elements fabricated consisting of the following:

Element No.	Fuel	Cladding Material	Annulus Between Fuel and Clad
33-A	$\text{Al-U}_3\text{O}_8$	Zr-2	(0.004-0.006-in.-diametral annulus)
35-A	$\text{Al-U}_3\text{O}_8$	Zr-2	(Metallurgically bonded)
34-A	$\text{Al-U}_3\text{O}_8$	A288 Al	(No annulus)

Fuel element No. 35-A was made by drawing the Zircaloy-2 cladding down on the $\text{Al-U}_3\text{O}_8$ fuel to ensure intimate contact between the two. The fuel rod, with one end plug welded in place, was then passed through an induction coil at the rate of 13 in./min in a helium atmosphere. Temperature of the Zircaloy clad as determined by an optical pyrometer was 700°C. The rate of travel and temperature were critical since the melted zone on the outer diameter $\text{Al-U}_3\text{O}_8$ fuel was to be held at the minimum required to obtain metallurgical bonding to the Zircaloy clad. Metallography of the Zircaloy $\text{Al-U}_3\text{O}_8$ bond indicated numerous compounds which, although hard, were sufficiently strong to overcome the ratcheting referred to previously.

7. Fabrication of Control Rods for EBWR Core 1-A (F. D. McCuaig)

Nine fueled control rods were fabricated for the EBWR Mark-IA core. Each rod, approximately 16 ft in length, consisted of two cruciform sections: (1) a 2% boron-stainless steel section, $87\frac{1}{2}$ in. in length, and (2) a stainless steel clad, stainless steel- UO_2 dispersion fueled section, $36\frac{1}{2}$ in. in length. The remainder was handle and end fittings.

Forty fueled control rod plates were purchased from the National Lead Company's Nuclear Metals Division of Albany, New York. Each plate was $\frac{1}{4} \times 5 \times 36\frac{1}{2}$ in. and contained 50 ± 0.5 gm of U^{235} . These plates were inspected dimensionally and ultrasonically, and were radiographed and corrosion tested by the Metallurgy Division.

The plates were first machined and then formed into 90° angle sections prior to assembly and welding to form cruciforms. A fixture was developed to hold four plates to be welded automatically by the T.I.G. method. Welds, $36\frac{1}{2}$ in. in length, were made at each of the four longitudinal edges on each control rod. The dimensions across each finished cruciform was 10×10 in. The nine completed control rods were loaded into the reactor February 19, 1960.

D. Fabrication of Borax-V Boiling and Superheater Fuel Elements

The Borax-V reactor has been designed and will be built to demonstrate nuclear superheat. The reactor will have within a single vessel a boiling core and a superheater core. The boiling core is to be made up of rod-type elements consisting of UO_2 pellets jacketed in stainless steel tubing, helium filled and welded closed. The UO_2 pellets are designed 0.343 in. in diameter $\times$ approximately $\frac{1}{2}$ in. long. A column 24 in. long will be jacketed in stainless steel tubing, 0.346 in. ID $\times$ 0.015 in. wall. The ends of the tube are closed with welded end plugs. Overall length of the rod is $33\frac{15}{16}$ in.

The superheater core is to be composed of plate-type fuel elements. The fuel is to be UO_2 dispersed in a stainless steel matrix clad with stainless steel. The overall dimensions of the plates are to be 0.030 in. thick $\times$ 3.665 in. wide by $25\frac{1}{4}$ in. long. The UO_2 -SS core, which is placed symmetrically within the plate, is to be 0.014 in. thick $\times$ 3.495 in. wide $\times$ 24 in. long. A fuel element will be composed of 20 of these plates brazed in stainless steel components.

1. Boiling Fuel Elements (J. H. Handwerk)

Twelve sample rods containing normal UO_2 pellets and 48 in. of depleted uranium dioxide pellets were received from Westinghouse (Blairsville). The pellets as received were measured and the densities

calculated. All pellets were found to be within the specified diametrical tolerance of 0.343 ± 0.0005 in. The densities as calculated from the measured dimensions ranged from 10.21 gm/cc to 10.52 gm/cc, with an average density of 10.38 gm/cc. These densities were above the specified minimum of 10.2 gm/cc.

The weight of contained UO_2 in the 12 sample rods according to the vendor's weights varied from 374.89 to 377.27 gm. This weight variation is above the total weight tolerance specified of 374 ± 2.5 gm. Prior to nondestructive inspection, the 12 rods were checked for straightness, and 9 of the 12 rods were found to exceed the straightness tolerance of 0.005-in. maximum deviation.

Five of the sample rods were exposed for one week in 600°F water in an autoclave. No evidence of corrosion or distortion of the rods was found. These rods were then immersed in 300°F oil; again no distortion of the rods was found, nor were any leaks detected from either bubbles appearing in the oil or swelling of the rods due to entrapped steam. Three of the remaining 7 rods were checked for leaks using a helium mass spectrograph. No leaks were detected, and the rods were sectioned for examination of the welds. This evaluation is not as yet complete, and the results are not available. The total weight of the UO_2 pellets contained in these 3 rods was found to agree with the vendor's shipping weights, and the individual pellets were found to vary in density from 10.28 to 10.42 gm/cc, with an average density of 10.38 gm/cc.

Ultrasonic Evaluation of Borax-V Boiling Core Fuel Elements (R. H. Selner)

The Borax-V fuel elements are to be ultrasonically inspected for tube integrity and wall thickness. Two separate systems are required for these tests. The tube integrity test utilizes shear wave techniques while the test for wall thickness uses resonance methods.

For evaluation studies, 12 stainless steel tubes loaded with normal uranium dioxide pellets were procured. An unloaded stainless steel tube, with a $\frac{1}{2}$ -in.-long and 3-mil-deep V-notch on the ID serves as the wall-integrity standard. Flat stainless steel pieces of varying thickness are used to calibrate the resonance system. Inspection of this preliminary shipment of fuel elements showed that the wall thickness varies a few ten-thousandths around 15 mils. No discernible defects in the wall were detected.

2. Superheater Fuel Elements (W. C. Kramer)

The contract for fabrication of superheat fuel plates for Borax-V was awarded to Atomics International Division of North American Aviation. These plates consist of a stainless steel-uranium oxide dispersion-type core

clad with stainless steel. There are four types of plates containing four different weights of UO_2 content based on plate location in the reactor core, as shown in Table X. A total of 840 plates containing highly enriched UO_2 will be supplied. In addition, 208 similar plates, 52 of each type, containing normal UO_2 will be fabricated before the enriched plates and will be used for evaluation and practice assemblies. Twenty-four of these will be evaluated by the supplier and 24 by ANL for adherence to ANL specifications.

Table X

WEIGHT OF UO_2 IN BORAX-V SUPERHEAT FUEL PLATES

Plate Type	Quantity	UO_2 Content, grams ($\pm 1\%$)
Central - half weight	190	18.3
Central - full weight	190	34.1
Peripheral - half weight	230	28.9
Peripheral - full weight	230	54.0

Nondestructive testing facilities have been designed and assembled at ANL to inspect all plates adequately for visual appearance; weight; thickness; length, width and squareness; flatness, surface finish; core position, length and width; total U^{235} content; distribution of U^{235} ; cladding thickness; bond integrity; radioactive surface contamination; and distortion due to heating. Equipment built by the Nondestructive Testing Group in Metallurgy was designed to utilize established eddy current, ultrasonic through-transmission, radiography, and alpha- and gamma-counting techniques.

Destructive analysis of the first 24 evaluation plates (containing normal UO_2) will be performed to evaluate the results of the nondestructive tests which measure internal, rather than external, plate characteristics. Destructive analysis will also be performed on production fuel plates when necessary to confirm the presence of suspected defects. Equipment has been readied at ANL to implement the following destructive tests: sensitization (Strauss test for carbon contamination), homogeneity of core, bond integrity, cladding thickness, and oxide fragmentation and stringering.

Plates which have been evaluated and found to be satisfactory are to be assembled into elements containing 4 plates each by personnel from Central Shops. The method of assembly of the plates has not been determined. Consideration has been given to the use of $\frac{1}{8}$ -in.-diameter x $\frac{1}{16}$ -in.-high stainless steel spacers on $1\frac{1}{2}$ x $1\frac{1}{4}$ -in. centers, or $\frac{1}{16}$ -in. square by 25-in.-long wire on $1\frac{1}{4}$ -in. centers, to maintain correct spacing between plates in an assembly.

Use of the $\frac{1}{8}$ -in.-diameter spacers presented the problem of how to bond the 2 rows of 17 spacers each in exact position on each plate surface. One method is to weld the spacers to one face of each plate and to furnace braze the stacked plates in a vacuum to complete the assembly. After due consideration was given to various other methods, attention was directed toward development of this type of assembly. Spacers were welded to the plates in specified locations, using, variably, condenser-discharge and resistance spot welds. GE81 commercial brazing alloy was applied to the top surface of each spacer, and the plates were then stacked in groups of four. Stainless steel side plates were placed in position along the two longitudinal sides of the element, and GE81 brazing alloy was added at the junction between each stainless steel plate and the side plate. For brazing, the elements were assembled in a thin-walled evacuation fixture made of stainless steel, and the evacuation fixture was enclosed in a much heavier casing of Hastelloy C. Since the fixture was evacuated to an internal pressure of less than one micron, the walls were caused to collapse inward and exert positive pressure on the plate assembly during brazing. The Hastelloy C casing served to support the evacuation fixture during heating to a temperature of 1175°C. This maximum temperature, which was dictated by the melting point of the brazing alloy used, was held for 6 to 8 min and the entire fixture was then furnace cooled.

The greatest difficulty associated with the condenser-discharge and resistance spot welding methods is that generally the weld area penetrates so deeply as to affect the core of the fuel plates. The most satisfactory bonding has been attained with a condenser-discharge-type weld; however, the experimental assemblies which have been made to date have contained only solid stainless steel plates, and there is no positive proof that the heat-affected zone will not penetrate beyond the cladding thickness of the fuel plates. Examination of side plate-to-plate and spacer-to-plate bonds has shown that effective brazing can be achieved if good contact is maintained at all the joints during the furnace brazing cycle.

Tensile tests were performed on four welded and brazed sections of an assembly. In each case, failure of the assembled sections occurred at brazed, rather than a welded, interface. The values obtained ranged between 47,600 and 51,760 psi. Four transverse sections were taken from the same assembly to test the strength of side plate-to-plate brazed joints. Two of the specimens failed within the stainless plates at approximately 80,700 psi. The other two failed at brazed joints at approximately 880 pounds/linear in. Because the side plates are grooved, failure occurring at a brazed junction must be attributed to a combination of shear and tensile stresses. For this reason, results are reported as pounds/linear in. Results of strength tests and metallographic examinations which have been performed indicate the need for more precise control of assembly operations to insure the achievement of satisfactorily brazed joints.

Most recent consideration is being given to the use of wire spacers between fuel plates. Initial efforts are being directed toward determination of an effective method of introducing the required brazing alloy along the entire length of the wire-plate interface.

E. Development of Ceramic Fuel Materials

1. Uranium and Plutonium Monocarbides

Uranium Carbide (G. D. White)

The use of UC as a reactor fuel requires the development of a procedure for producing UC which is economical and capable of being scaled-up for large production rates. The most successful method of production so far has been the arc-melting and casting procedure in which carbon and uranium are melted by an arc on a water-cooled hearth and the melted material is poured into graphite molds. This is expensive and is not adaptable to the production of small-diameter fuel pins. Another technique of some promise is the reaction of uranium hydride, or the metal powder resulting from the decomposition of the hydride, with a carbon-containing gas such as methane. This is a low-temperature procedure and would appear to be a feasible production method. The method, however, is very difficult to control and the carbide produced is highly pyrophoric. A third technique, which could be economical and controllable, is the direct reaction of UO_2 and carbon. Both of the reactants are readily available and the processing would involve conventional powder techniques. This is the approach now being pursued at ANL.

Uranium carbide of good quality has been produced by reacting UO_2 and C in a vacuum. The proper stoichiometric mixture was mixed with a binder and cold pressed into cylindrical pellets, which are fired in vacuum over a period of 48 hr to 1650°C . The production of gas during the reaction caused this to be a long and tedious firing. The resulting "clinker" was suitable for reprocessing into sintered pellets.

Efforts during the last three months have been directed toward reacting UO_2 and C in a flowing argon atmosphere. In addition to affording protection for the reaction, the argon provides a rapid sweep for disposal of the reaction gases.

Initial tests were made with four mixtures of UO_2 and C. Two different lots of UO_2 were each mixed with two different carbons. One of the lots of UO_2 was a -400M sieved fraction of a ball-milled product; the second lot was of high surface area with particle sizes averaging about 1 micron. The carbons were Thermax and an ultra-high-purity carbon which had been sieved to -325M.

The batch composition satisfied the stoichiometry of the reaction:

Each batch was mixed by ball milling in ethyl alcohol for 4 hr. Steel balls in a rubber-lined mill were used. The ball-milled material was air-dried, pulverized, and cold pressed into cylindrical pellets. The pellets were fired in a flowing argon atmosphere at 1650°C for 1 hr.

Examination of these products by X-ray diffraction and metallography revealed the presence in each of C, UC, UC₂, and UO₂, with the UO₂ predominant. The pellets were composed of a carbide matrix containing islands of UO₂ and carbon. Subsequent petrographic examination of some of the mixture before reaction showed the carbon to be present as agglomerates or chunks which were large with respect to the size of the UO₂ particles. The UO₂ apparently was breaking down into discrete particles rather than agglomerates.

The results of these firings indicate that the kinetics of the reaction between UO₂ and C requires large surface contact area between the reactants if complete reaction is to be achieved at moderate temperatures in a reasonable time. Small particle size and high surface area C and UO₂ which break down easily to discrete particles during mixing are necessary to achieve reaction. Since the UO₂ satisfied this condition, the problem resolved itself to finding satisfactory carbon. One obvious method of obtaining suitable carbon distribution is to add the carbon as a soluble carbonaceous material in the mixing operation so that each of the UO₂ particles is coated with the carbonaceous material after drying.

This method was tried by dissolving petroleum pitch in alcohol and mixing the solution with UO₂. The carburization value of the pitch was used as a basis for calculating the batch. The theoretical proportions for the reaction were again used as basis for the batch composition. This material, after mixing, was processed in the same manner as the previous batches. The pellets then were prefired in argon to 900°C to carburize the pitch. Carburized pellets were fired in a flowing argon atmosphere to 1700°C with a one-hr soak at 1400°C and one hr at 1700°C. Six firings were made with this procedure. In each instance the reacted product was found to be UC with not more than 10% UO₂. Calculated unit cell dimension on the UC from the X-ray diffraction pattern gave $a_0 = 4.950\text{--}4.956\text{\AA}$. Metallographic examination has shown the presence of UO₂ inclusions estimated to be about 10% of the volume. U₂C₃ was also found to be present where the pellet was in contact with the graphite setter plate.

A second firing procedure was tried on a batch of this material. Carburized pellets were fired in flowing argon to 1450°C and held at this temperature for 1 hr. The firing chamber was then evacuated to a pressure of approximately 10^{-4} mm and the temperature raised to 1700°C for 1 hr. No UO₂ was detectable in this material by X-ray diffraction. The unit cell dimension was calculated to be $a_0 = 4.956\text{ \AA}$.

Metallography of Uranium Carbide (J. P. Hugo)

In conjunction with the preparation studies involving uranium monocarbide, metallographic examinations were started to evaluate the carbide produced. The materials used were all in the form of grains, and at this time only a few grains of each sample have been examined. The results described, therefore, are perforce of a preliminary nature, and experience is still being gained in specimen-preparation techniques and the metallography of the uranium carbides.

In all cases the fragments of uranium carbide were mounted in cold-curing resin (Kold-Mount) using aluminum retaining rings.

Rough grinding was done on 120 and 240 grit SiC papers with kerosene as a lubricant. This stage of the preparation is slow if any appreciable depth of grinding is required. Consequently, the feasibility of surface grinding with a diamond-impregnated wheel was explored. Two samples were surface ground, one to a depth of about 0.05 in., using kerosene as coolant. Single cuts of 0.001 in. maximum proved possible. However, surface grinding is also fairly time consuming, and the expense involved will only justify its use in cases where fairly deep grinding is imperative.

After some exploratory tests the use of the following in polishing procedures has proved fairly successful:

1. 40-micron diamond paste on a wheel covered with a nylon cloth over a Teflon disc (the latter prevents impregnation of diamond into the bronze wheel, while the nylon prevents excessive "rolling" and loss of diamond);

2. 6-micron diamond paste on a wheel covered with Metcloth over a disc of Vellux paper; and

3. 1-micron diamond paste on a wheel covered with micro-cloth.

In all stages of polishing with diamond, Hyprez carrier/coolant fluid was employed. A completely scratch-free polish is not obtained, but the quality of the polish is sufficiently good for metallographic evaluation purposes.

An etchant consisting of equal volumes of nitric acid, glacial acetic acid, and water (subsequently referred to as NAW) was employed.

The results obtained from ANL-produced material are discussed below. The pellet from which one sample was taken had apparently been

heated for 1 hr at 1670-1700°C, portions of the pellet being in contact with a graphite crucible/susceptor. The cold-pressed pellet consisted of a mixture of UO_2 powder and carbon.

All the fragments examined were very porous, there being an "envelope" of greater than average porosity along those surfaces which presumably were the original pellet surfaces. Inclusions of UO_2 of varying size were present throughout the fragments, there being a tendency for the larger UO_2 inclusions to be associated with porosity. Volumetrically, it is estimated that UO_2 is present to about 5% and not more than 10%.

Along the original pellet surfaces there was a narrow layer of a nonetching but isotropic globular phase, which was judged to be the sesquicarbide U_2C_3 . This surface layer blended into a narrow zone of eutectoid $\text{U}_2\text{C}_3 + \text{UC}$, the latter occurring predominantly as lamellae, and this zone in turn blended into UC in the body of the fragments (see Figure 13). The body and vast majority of a fragment consisted of UC containing UO_2 inclusions and porosity. No UC_2 was detected.

Obtaining a clear photomicrograph of these surface zones is virtually impossible, due to the surface being rounded by polishing. It will be noted that the surface layer of U_2C_3 and other portions of the field shown in Figure 13 are out of focus.

Figure 13. Photomicrograph of ANL-prepared Uranium Monocarbide.

Black is voids; white material out of focus is U_2C_3 , which grades into zone of eutectoid mixture of U_2C_3 and UC, included UO_2 which appears as rounded grey material.

Micro 29566

Etchant: NAW

750X

The presence of the U_2C_3 surface layer and the eutectoid $U_2C_3 + UC$ subcutaneous zone is consistent with the carbon gradient, since the relevant surfaces had been in contact with the graphite crucible. It is known⁸ that U_2C_3 may exist as a stable compound below about $1800^\circ C$; if heated above $1800^\circ C$ it decomposes into UC and UC_2 . It is feasible, therefore, that U_2C_3 could be formed at the relevant reaction temperature ($1670-1700^\circ C$) at the site of a source of excess carbon.

Plutonium Carbide Bodies (R. C. Lied)

The current interest in fast reactors indicates a need for a fuel containing some form of plutonium along with normal uranium. The carbides seem suitable for this purpose because of the relatively high percentage of fissionable atoms, good thermal conductivity, and refractory characteristics they possess.

Accordingly, the preparation of PuC of suitable density, the fabrication of high-density bodies of various $UC-PuC$ ratios, and the evaluation of various physical properties of these bodies were investigated.

Work on uranium monocarbide indicated that a satisfactory material could be produced by reacting a pelletized mixture of uranium dioxide and carbon (see above). Similarities in structure indicated that the same general procedure might be followed in the production of plutonium monocarbide; and further, the UC and PuC should form a solid solution.

A single glovebox facility which contained the essentials for fabrication and sintering of plutonium carbide was put into operation.

Carbon and PuO_2 were mixed with a binder, compacted into right cylinders, and reacted, under vacuum, in a tantalum-resistor furnace. Reaction began about $1100^\circ C$ and proceeded rapidly above $1300^\circ C$. The product of this reaction, in a finely divided state, was unstable in the plutonium box atmosphere (nitrogen) when the moisture content reached approximately 500 ppm.

Properties of PuC (O. L. Kruger)

Uranium monocarbide has shown considerable promise as a high-temperature, high-burnup reactor fuel. By analogy, plutonium monocarbide appears promising as a potential fast reactor fuel. Therefore, the pertinent properties and methods of fabrication are being studied. The information gained as a result of this investigation will be useful in developing all types of fuel elements which contain the plutonium monocarbide phase.

⁸Mallet, M. W., Gerds, A. F., and Vaughan, D. A., Uranium Sesquicarbide, AECD-3060 (31 January 1950).

Arc-melting and casting techniques have been developed,⁹ and specimens near the monocarbide composition have been made and are under irradiation in EBR-I. The structure of alloys ranging in composition from 42 to 60 a/o C in the as-cast condition as well as the effect on the structure of thermal treatment are being studied by metallographic, X-ray, and dilatometric methods. Measurements of several properties of these alloys are in progress

Arc Melting: Pieces of spectrographically pure carbon and high-purity plutonium were arc melted in an interchangeable hearth arc furnace. A deep hearth was used when combining these materials, to prevent the loss of the lightweight carbon pieces. Buttons of about 30 gm, made with a graphite-tipped electrode, gained from 0.2 to about 0.5 w/o C with six melts of about 30-sec duration. These buttons are assumed to be heterogeneous, since the last melt probably added some carbon to the top of the button. The composition was held to within ± 0.1 w/o C when a tungsten tip was used. The tungsten contamination was kept to less than 50 ppm by changing the tip after the completion of melting on a single button. Homogeneous, arc-melted buttons had oxygen contents of about 100 ppm. Alloys which contain 45 to about 53 a/o C were difficult to cast into pins and had to be cooled very slowly to prevent cracking. Slow cooling was accomplished by using a graphite sleeve in the mold and by immediate evacuation of the arc furnace after melting. The alloys just above 50 a/o C were not as susceptible to cracking. Arc-melted buttons near the Pu_2C_3 composition must be cooled very slowly to prevent shattering

Metallography and X-ray Diffraction: Microstructures of the cast alloys containing 42.1 to 59.6 a/o C are shown in Figure 14 with their identified phases. A primary Pu_2C_3 phase is present in the PuC matrix of alloys containing 47.1 to 55.7 a/o C (see Figures 14-c, -d, and -e). The alloys of 42.1 to about 50 a/o C had a matrix of PuC which appeared homogeneous in the as-polished or lightly etched condition but which was actually a cored dendritic structure. This structure, which is shown in Figures 14-b and -c, was brought out by severe electrolytic etching and repolishing. Etching by exposure of the polished surfaces to the impure nitrogen atmosphere of the glovebox sometimes revealed a cored dendritic structure (see Figure 14-a). R. N. R. Mulford¹⁰ has shown that PuC is formed by a peritectic reaction of Pu_2C_3 with liquid at 1654°C . The cored dendritic matrix of the cast alloys below the stoichiometric composition of PuC does not seem to be due to the reaction of liquid with the Pu_2C_3 phase because there is no peritectic rimming seen around the Pu_2C_3 phase in Figure 14-c.

⁹ Foote, F. G., et al., Annual Report for 1959, Metallurgy Division, ANL-6099 (31 December 1959) p. 36.

¹⁰ Mulford, R. N. R., private communication.

Figure 14. Photomicrographs of Cast Alloys Containing 42 to 60 a/o C.

14-a.

Micro 29521 As Polished 200X
42.1 a/o C (3.52 w/o C) PuC den-
drites with interdendritic alpha Pu

14-b.

Micro 28258 Severely Etched 200X
44.4 a/o C (3.85 w/o C) PuC

14-c.

Micro 28244 Severely Etched 500X
47.1 a/o C (4.29 w/o C) primary
Pu₂C₃ dendrites (dark) in PuC
matrix

14-d.

Micro 28249 As Polished 100X
50.4 a/o C (4.85 w/o C) primary
Pu₂C₃ dendrites in PuC matrix

14-e.

Micro 29456 As Polished 200X
55.7 a/o C (5.95 w/o C) primary
Pu₂C₃ dendrites in PuC

14-f.

Micro 29523 As Polished 200X
59.6 a/o C (6.90 w/o C) Pu₂C₃

Density: The densities of alloys containing 4.5 to 5.5 w/o C have been determined by the displacement method in CCl_4 . All castings were sound and their densities were close to theoretical.

Microhardness: The average microhardnesses of the PuC dendrite, the PuC matrix, and the Pu_2C_3 phase are given in Table XI.

Table XI
AVERAGE MICROHARDNESSES (VPN) OF
SOME PLUTONIUM CARBIDE PHASES
(10-gm load)

Composition	PuC Dendrite	PuC Matrix	Pu_2C_3
44.4 a/o C	695	480	715
47.1 a/o C	750	700	
50.4 a/o C		770	

Heat Treating: Specimens heat treated near the melting point of PuC in a vacuum had large weight losses depending on the length of time and the temperature of the heat treatment. A somewhat porous specimen which was examined for melting after each 5-min heating in a vacuum to 1650, 1700, and 1900°C had a very large weight loss and an increase of carbon content from 4.85 to 6.74 w/o C. Further attempts to heat treat PuC in an argon atmosphere at atmospheric pressure resulted in a 600-ppm increase in oxygen content of the specimen.

A deposit on the inside of an evacuated sealed Vycor capsule used to heat treat several PuC specimens at 1000°C for 210 hr was further evidence in support of the high vapor pressure of plutonium monocarbide.

Heat treating at 1000°C for 210 hr did not produce any change in the cored PuC microstructure. Apparently much higher temperatures are needed to homogenize these alloys.

Thermal Expansion: Curves of the thermal expansions for successive cycles of arc cast 44.5, 46.9 and 50.4 a/o C alloys are shown in Figures 15, 16 and 17, respectively. The measurements were made on a dial gauge quartz push rod dilatometer. The specimen was held at each temperature for about 30 min on heating and on cooling to allow equilibrium conditions to be established before taking a reading.

During the first heating cycle the expansion of the 44.5-a/o-C specimen was erratic, probably due to the transformation of a retained high-temperature phase. Therefore, to avoid confusion, the specimen was heated to 700°C, held for several minutes, and then slowly cooled to room temperature. The dilation curves, Figures 15-a, -b, -c and -d, show that this alloy went through a phase transformation from about 400 to 560°C.

Figure 15. Thermal Expansion Curves for Successive Cycles of an Arc Cast 44.5 a/o C Alloy

Fig. 15-a

1st Cycle

Fig. 15-b

2nd Cycle

Fig. 15-c

3rd Cycle

Fig. 15-d

4th Cycle

This transformation and the existence of a new low-temperature phase was confirmed by metallographic examination. On cooling, the specimen was held overnight just below the transformation, but the specimen retained a permanent elongation of 2 to 7 mils on each cycle. Since there is a large expansion associated with this transformation, the phase boundary is of interest, and alloys from 42.5 to 50 a/o C are being investigated for the presence of the low-temperature phase. The cored structure of the 45 a/o C thermal expansion specimen was partially homogenized by repeated cycles through the low-temperature transformation.

Successive cycles of the 46.9-a/o-C specimen are shown in Figures 16-a, -b and -c. The abrupt change in expansion took place at higher temperatures and decreased in rate on subsequent cycles to 950°C.

Figure 16. Thermal Expansion Curves for Successive Cycles of an Arc Cast 46.9 a/o C Alloy

Figures 17-a and -b are curves of the first and second cycles of a 50.4-a/o-C specimen. The calculated linear thermal expansion coefficient from the curve of Figure 17-b is 10.6×10^{-6} units/°C for the temperature range from 20 to 900°C. Working of this specimen by breaking one end in a vise caused an abrupt change in expansion, similar to that present on the first heating cycle of the 46.9 a/o C specimen. This abrupt change in expansion annealed out on subsequent heating cycles, as shown in Figures 17-c through -g. Furnace cooling during the sixth cycle did not produce any significant change in the curve of the seventh cycle. Metallography revealed the presence of a network through the grains, which was extremely brittle and reactive, and which was usually almost completely removed from the specimen on polishing. X-ray diffraction studies did not reveal a second phase.

Figure 17. Thermal Expansion Curves for Successive Cycles of an Arc Cast 50.4 a/o C Alloy

Fig. 17-a 1st Cycle

Fig. 17-c 3rd Cycle

Fig. 17-b 2nd Cycle

Fig. 17-d 4th Cycle

Fig. 17-e 5th Cycle

Fig. 17-f 6th Cycle

Fig. 17-g 7th Cycle

Compatibility: Compatibility tests of tantalum and stainless steel with PuC are in progress. Since PuC is very brittle, a thin-walled tantalum capsule is used to contain the specimen. This allows the capsule to yield slightly as the stainless steel expands. Carefully prepared specimen surfaces could not be satisfactorily bonded in a vacuum at 800°C. Penetrations of 8.54 mils in stainless steel and of 1.67 mils in tantalum were accomplished with a 44.4-a/o-C specimen by heat treating in vacuum at 1000°C for 3 days. The stainless steel penetration includes a large void band.

High-temperature Furnaces for PuC Studies (O. L. Kruger, C. M. Walter)

Several high-temperature furnaces are being developed to further the study of properties and thermal treatments of plutonium carbide as well as other high-melting, plutonium-containing materials.

A vertical high-temperature, interchangeable tantalum and tungsten tube resistance furnace for use in a glovebox has been designed and constructed. It is capable of heat treating 2-in.-long specimens to temperatures near 2500°C. The furnace is designed for quenching and operation in a vacuum or an inert atmosphere under pressure.

A tungsten-iridium thermocouple with a recrystallized Al_2O_3 sheath was used to check out the furnace to 1900°C. The tungsten wire was brittle after use at this temperature. However, the iridium wire annealed and was ductile. The tantalum tube has been used to attain temperatures of about 2200°C, which is the limit of our testing power supply. At the present time we are trying several new methods of controlling this type of furnace with the ultimate goal of obtaining a fluctuation of less than $\pm 10^\circ$ at 2000°C. A tungsten-iridium thermocouple with BeO insulation in a tantalum sheath has been ordered for checking the furnace at high temperatures.

Development of Methods for Melting and Casting Plutonium Monocarbide and Plutonium-Uranium Monocarbide Fuel Shapes (R. M. Mayfield, W. G. Tope)

The purpose of the program was to develop equipment and methods for casting PuC and (U-Pu)C production scale fuel shapes.

A high-temperature, graphite-resistance furnace has been designed, constructed, and pretested. The furnace, installed in Hood line PF-14, is operable and progress is being made in closing up the hood in preparation for plutonium work. The furnace will attain temperatures of 2000 to 2100°C; higher temperatures can be reached, but arcing, which should be avoided, sometimes occurs. It appears that the furnace is best suited for operations in the range between 1600 and 2000°C. It should prove quite useful for PuC development work and possibly for a limited range of PuC-UC compositions.

Initial melting operations will be conducted using a 75-kva welding transformer which will be replaced by a more easily controlled and instrumented power supply at a later date.

Proposed direct melting studies on plutonium carbide will prove or disprove the feasibility of this approach to the carbide development program. Steps are being taken to procure limited supplies of both PuC and UC from commercial sources to facilitate the production of the test samples at the earliest possible date.

Irradiation of PuC and UC-20 w/o PuC (J. H. Kittel, R. Carlander)

Irradiation experiments in progress at other sites have shown that uranium monocarbide is of considerable promise for a fuel for high-temperature, sodium-cooled reactors. For fast reactor fuels, plutonium is preferred to uranium-235, so that the irradiation behavior of PuC is of interest. For fast breeder reactors the PuC would be diluted with as much fertile uranium carbide as possible to enhance the rate of internal breeding.

Preliminary irradiation experiments are in progress in EBR-I to explore the behavior under irradiation of PuC and UC-20 w/o PuC. The irradiations are being made in a fast reactor because of the "blackness" of PuC in a thermal flux. Three special fuel rods were made of 20-mil wall stainless steel tubes containing 0.30-in.-dia carbide specimens. The annulus between the specimens and the jacket is filled with NaK. Two of the fuel rods contain alternating 1-in.-long specimens of arc cast PuC and UC-20 w/o PuC. The third rod contains pressed and sintered pellets of UC-20 w/o PuC. The specimens in the third rod contain an axial hole so that central temperatures can be measured during irradiation. The uranium in all UC-PuC specimens is highly enriched to accelerate the burnup rate. The rods were inserted in EBR-I early in the summer of 1960 and have been irradiated to approximately 0.1 metal atom percent burnup at central temperatures ranging up to 430°C.

One of the rods containing cast specimens has been returned for a detailed hot laboratory examination. External measurements on the jacket show no dimensional changes. Preparations are being made to open the tube and measure the specimens themselves.

2. Urania-Thoria Bodies (E. D. Lynch)

The feasibility of a urania-thoria solid solution nuclear fuel was first demonstrated by the operation of the Argonne Borax-IV reactor. Since this time there has been an increased interest in the urania-thoria solid solutions, especially in the lower urania portion of the system.

In general, solid solution fuel materials in which uranium oxide is one component can be prepared either by air or hydrogen-atmosphere sintering techniques. Due to the oxidation characteristics of the materials, U_3O_8 must be used as the source of urania for air-sintering techniques, whereas either U_3O_8 or UO_2 may be used when sintering in a reducing atmosphere. The systems air-sintered $\text{U}_3\text{O}_8\text{-ThO}_2$ and hydrogen-sintered $\text{UO}_2\text{-ThO}_2$ or $\text{U}_3\text{O}_8\text{-ThO}_2$ differ in that a continuous, stoichiometric solid solution series is formed for the hydrogen-sintered materials while a stability limited, nonstoichiometric solid solution series is formed for the air-sintered materials. The upper limit for a stable solid solution formed by air sintering $\text{U}_3\text{O}_8\text{-ThO}_2$ is approximately 70 mole percent UO_2 equivalent. The stoichiometric solid solutions may be oxidized to varying degrees by heating in air. The nonstoichiometric solid solutions show a loss of oxygen during heating in air, and, in general, this is a reversible process during equilibrium thermal cycling. The nonstoichiometric solid solutions may be reduced to stoichiometry by heat treatment in hydrogen.

Although the nonstoichiometric solid solution fuel has been used successfully, there has been some concern as to the degree of nonstoichiometry of the air-sintered materials and whether or not this deviation from stoichiometry is desirable from a fabrication and use standpoint.

A study was made to determine and compare the densification behavior of a wide compositional range of urania-thoria solid solutions during both air and hydrogen sintering. The stoichiometry of the air-sintered solid solutions was also determined. In order to have a basis for comparison of densification, all samples were dry pressed to as nearly the same green density as possible, and measurements were made of the percentage change in density as a result of the sintering treatment.

The densification behavior of air-sintered $\text{U}_3\text{O}_8\text{-ThO}_2$ compositions was greatly influenced by the composition of the mixture. Compositions in the range from $2\frac{1}{2}$ m/o UO_2 to 10 m/o UO_2 were the most readily densified and reached the highest bulk densities of the compositions investigated. Bulk-density increases during sintering of 30 m/o UO_2 to 50 m/o UO_2 compositions were considerably less than other compositions in the series. At low sintering temperatures ($<1500^\circ\text{C}$) these compositions resulted in samples having a sintered density less than the original pressed density. The air-sintered 50 m/o UO_2 composition was densified only at a sintering temperature of 1650°C . Densification of 70 m/o UO_2 compositions was very temperature dependent and showed a significant change only after sintering at 1650°C . Solid solutions formed with 90 m/o UO_2 were not stable on cooling.

The density changes of hydrogen-sintered $\text{U}_3\text{O}_8\text{-ThO}_2$ and $\text{UO}_2\text{-ThO}_2$ were not as sensitive to compositional change as were the air-sintered materials. On the basis of density change, it appeared that the air-sintered materials begin the solid solution reaction at lower temperatures

than the hydrogen-sintered materials, but hydrogen sintering yielded the highest sintered densities and the greatest density changes.

Weight loss measurements have been made for air-sintered compositions during sintering and also upon hydrogen reduction following sintering to establish the stoichiometry of the solid solutions formed. The weight losses during air sintering of U_3O_8 - ThO_2 compositions show that at high temperatures there is a loss not accountable for as oxygen loss for all compositions, and this is also apparent for low urania compositions at lower temperatures. The calculation of weight loss per gram of U_3O_8 for the air-sintered compositions is shown in Table XII. For all compositions sintered at 1650°C , volatilization is indicated, for the loss is greater than can be accounted for by oxygen release. At all temperatures there was an indication of volatilization from low urania compositions.

Table XII

WEIGHT LOSS FOR AIR-SINTERED
 U_3O_8 - ThO_2 COMPOSITIONS

m/o UO_2	Wt Loss in Grams/Gram of U_3O_8 in Composition			
	1200°C	1350°C	1500°C	1650°C
2.5	0.080*	0.100*	0.138*	0.191*
5.0	0.040*	0.050*	0.047*	0.061*
10.0	0.022	0.023	0.021	0.048*
30.0	0.012	0.010	0.011	0.056*
50.0	0.013	0.012	0.013	0.054*
70.0	0.008	0.011	0.027	0.057*
90.0	0.003	0.006	0.034*	-

*Values greater than 0.038 indicate volatilization of uranium.

The stoichiometry of the air-sintered solid solutions is shown in Table XIII. Calculations were made on the basis of weight loss during subsequent reduction in hydrogen. The content of uranium was calculated on the basis that there was no loss of ThO_2 and that the reduction yielded stoichiometry. Solid solutions containing low percentages of UO_2 approach stoichiometry, and the general tendency was for a greater departure from stoichiometry with increasing UO_2 content.

Table XIII

RATIOS OF OXYGEN TO TOTAL METAL FOR
AIR-SINTERED U_3O_8 - ThO_2 COMPOSITIONS

m/o UO_2	Oxygen-Metal Ratios			
	1200°C	1350°C	1500°C	1650°C
2.5	2.05	2.06	2.06	2.02
5.0	2.02	2.03	2.03	2.03
10.0	2.06	2.06	2.06	2.05
30.0	2.17	2.18	-	2.17
50.0	2.30	2.25	2.25	2.25
70.0	2.40	2.38	2.32	2.32
90.0	2.60	2.58	2.52	-

3. Lanthana-Urania Bodies (D. C. Hill)

The success of UO_2 - and ThO_2 - UO_2 -fueled reactors has stimulated interest in other oxide systems for nuclear power applications. Oxidation and subsequent volatilization of UO_2 at elevated temperatures, however, may restrict the use of these fuels. This program is concerned with the development and testing of fuels containing urania in solid solution with various oxide additives with the objective of improving high-temperature stability. Phase relationships, stability, and testing of fluorite-structured compositions is of prime interest.

Investigation of the lanthana-urania system was initiated during 1960. In this investigation the stoichiometry variance and volatilization behavior at elevated temperatures and in various environments of this system will be evaluated by X-ray, metallographic, petrographic, and thermogravimetric means.

Mixtures of lanthana-urania were made by milling dried powders of La_2O_3 and U_3O_8 in rubber-lined mills for 3 hr. The milled mixtures were placed in platinum crucibles and calcined in air at 1650°C for 2 hr. Sinterable powders were produced from the calcined material by dry milling in rubber-lined mills for 16 hr. Samples of these powders were analyzed chemically to determine U^{+4} , and total U and La percentages. X-ray diffraction patterns of powdered compositions were taken to determine solid solution formation.

Solid solutions produced by this procedure appeared to be quite stable when exposed to air for extended periods of time. No weight or structural changes were noted for cubic solid solutions. Compositions in which free La_2O_3 existed, however, were found to pick up moisture and form $\text{La}(\text{OH})_3$.

Lanthana-urania compositions containing from 10 to 97 w/o urania were made and are being evaluated. Compacts from the powdered solid solutions were pressed isostatically at 50,000 psi and sintered in air at 1675°C for 4 hr, and in hydrogen at 1750°C for 21 hr. Samples of the powdered solid solutions were also placed in Vycor capillaries in the presence of uranium metal chips and vacuum sealed. The sealed capillaries were annealed at 900°C for 200 hr. X-ray diffraction examination of annealed compositions was used to determine solubility limits for these heat treatments.

Experimental results showed a variation in solubility limits and lattice parameters for compositions subjected to these three experimental environments. Solubility limits of 30 to 80, 35 to 100, and 45 to 100 w/o urania were noted for the air, hydrogen, and vacuum heat treatments, respectively. Lattice parameter measurements were found to vary with molar composition as shown in Figure 18. The wide variation of lattice

parameters for solid solutions of identical lanthanum content suggests stoichiometry differences arising from the different heat treatment. Chemical analyses of hydrogen- and air-treated solid solutions appear to confirm this possibility as shown by the results and calculated compositions in Table XIV.

Figure 18. Observed Lattice Parameters for Lanthana-Urania Solid Solutions

reduction of oxygen-to-uranium ratio when compared with the oxidized composition.

It would appear that oxygen-to-uranium ratios for the air-oxidized solid solutions approached 3.0 for compositions containing less than 50 w/o urania. Higher urania concentrations resulted in a decrease in O/U ratio to a minimum value of 2.5 at about 85 w/o urania. Chemical analyses of hydrogen-treated solid solutions showed a significant

TABLE XIV

CHEMICAL ANALYSIS AND CALCULATED COMPOSITION OF
AIR- AND HYDROGEN-TREATED LANTHANUM-URANIUM FLUORIDES

	Sample No.	Chemical Analysis (wt %)			Calculated Composition			Molecular Composition $(U_xL_{1-x})O_f$		
		Total U	U ⁴⁺	La	O:U Ratio	w/o UO ₂	w/o La ₂ O ₃	α	β	γ
Air	6U-2	10.25	0.18	74.8	2.98	12	87.7	0.674	0.926	1.61
	15U-2	17.42	0.17	67.4	2.99	20.9	79.1	0.611	0.889	1.70
	20U-2	25.86	0.06	58.7	3.00	31.1	68.9	0.504	0.796	1.81
	25U-2	31.81	1.57	52.8	2.95	38.1	61.9	0.260	0.740	1.88
	50U-2	35.90	0.05	48.8	3.00	50.1	49.9	0.502	0.698	1.95
	55U-2	41.05	0.07	43.4	2.95	43.1	56.9	0.556	0.644	2.01
	60U-2	45.35	8.62	4.5	2.81	53.9	46.1	0.402	0.598	2.05
	45U-2	50.15	15.14	4.4	2.74	54.7	45.3	0.461	0.539	2.07
	50U-2	55.62	12.58	0.7	2.67	64.0	36.0	0.566	0.434	2.14
	55U-2	57.92	17.60	26.9	2.70	68.4	31.6	0.557	0.443	2.17
	60U-2	61.00	21.44	24.0	2.65	71.9	28.1	0.537	0.463	2.19
	65U-2	64.75	26.51	20.4	2.60	76.0	24.0	0.649	0.351	2.22
Hydrogen	70U-2	67.67	1.42	17.7	2.54	79.0	21.0	0.691	0.309	2.25
	80U-2	74.50	18.31	11.1	2.48	87.0	13.0	0.746	0.254	2.29
	25U-1	5.14	16.00	54.0	2.47	0.0	100.0	0.251	0.749	1.74
	50U-1	6.20	6.8	49.1	2.53	42.3	57.7	0.500	0.500	1.81
	35U-1	34.04	16.56	45.7	2.588	0.8	99.2	0.559	0.441	1.87
	45U-1	50.87	26.71	5.0	2.47	0.0	100.0	0.458	0.542	1.95
	50U-1	54.01	32.11	31.8	2.406	62.7	37.3	0.448	0.552	1.99
	55U-1	57.62	37.35	28.1	2.38	67.1	32.9	0.506	0.494	1.97
	65U-1	68.84	49.65	20.0	2.255	75.8	24.2	0.651	0.349	1.99
	70U-1	69.52	51.8	17.2	2.20	79.8	20.2	0.702	0.298	1.99
	80U-1	76.55	66.92	11.5	2.12	86.0	14.0	0.804	0.196	2.00
	95U-1	81.75	80.0	0.0	2.000	95.0	5.0	0.900	0.100	2.00

1. Lanthanum concentration

A convenient and meaningful way of expressing oxygen contents of cubic fluorite solid solutions is to consider their oxygen-to-metal atom ratios. Deviations from stoichiometric $MO_{2.00}$ were noted for hydrogen- and air-treated compositions, and the variation of oxygen-to-metal atom ratio with metal atom composition is shown in Figure 19. Air-oxidized compositions were found to be oxygen deficient or oxygen excessive depending on lanthanum atom concentration. Hydrogen-reduced compositions containing more than 70 w/o UO_{2+x} , however, were close to the stoichiometric $MO_{2.0}$ composition.

Lattice parameter measurements of the vacuum-annealed powders suggested the uranium valence of these solid solutions had been significantly reduced. No attempt was made to analyze these materials chemically, but in all likelihood their oxygen-to-uranium ratios approached the minimum value of 2.0.

Figure 19. Calculated Oxygen-to-metal Ratios for Lanthana-Urania Compositions

Present experimentation with the lanthana-urania system is being directed toward high-temperature stability of solid solutions. Sintered compacts are undergoing extended heat treatments in air at 1000, 1450 and 1700°C. Phase stability, weight loss due to volatility, and microstructural changes will be examined. A high-temperature thermobalance has been constructed and will be used to determine stoichiometry of solid solutions at elevated temperatures. Standardization of the equipment is now in progress.

4. Fueled Glasses

Development and Testing of Compositions (E. D. Lynch, J. H. Handwerk)

Glasses and glassy materials have some characteristics which make them of interest as possible nuclear fuel materials or additives. Glasses are inorganic liquids whose viscosity is temperature dependent and at low temperatures where the viscosity is extremely high they are, for all practical purposes, solid. As the temperature of a glass is increased, there is no sharp melting point, but a gradual decrease in viscosity until they reach a fluid condition. Glasses may be made to flow under pressure at low temperatures, and the stresses resulting from this treatment or thermal stresses may be annealed out by low-temperature heat treatment.

Of immediate interest in the application of glasses in nuclear fuels are two primary areas of study: (1) the use of glass as a single-phase fuel, and (2) the use of glass, in admixture with crystalline materials, as a fuel-dispersion medium and sintering agent.

For possible use as a single-phase fuel material, a glass was desired which would dissolve a large amount of uranium oxide and maintain its integrity as a solution at temperatures approximating the use temperature. Three types of glasses were selected for initial studies, and in each case a base glass composition was melted, quenched, and ground to a fine powder. Urania additions were made to the ground glass and the mixtures remelted to determine the extent of solubility of uranium oxide in the glass. Those glasses which showed complete solution of the uranium oxide on remelting were held in a temperature gradient of approximately 350 to 1000°C to evaluate their resistance to devitrification. Glasses which could be maintained in this gradient for one week without crystal development were considered suitable for further study. The results of preliminary tests on the three base glasses are discussed below.

Na₂O-CaO-SiO₂ Glasses: A base glass composition of 16.5 w/o Na₂O, 11.0 w/o CaO, and 72.5 w/o SiO₂ was prepared. Additions of 10, 20, 30, 40, 50, 60, 70, 80 w/o U₃O₈ were made in the base glass, and melting was carried out at 1400°C. Complete solution of the U₃O₈ in the glass was obtained through the 40 w/o addition; additions of 50 w/o to 70 w/o resulted in a mixture of glassy and crystalline phases, and above 70-w/o addition the material sintered to a hard mass. All compositions which were essentially glassy were held in a temperature gradient of 400 to 950°C for one week. All compositions showed crystal precipitation under these conditions, and the approximate temperatures of crystal formation are shown below:

Composition	Approximate Temperature of Crystal Formation (Liquidus), °C
Base Glass	720
10 w/o U ₃ O ₈ addition	740
20 w/o U ₃ O ₈ addition	725
30 w/o U ₃ O ₈ addition	725
40 w/o U ₃ O ₈ addition } 50 w/o U ₃ O ₈ addition }	Crystallization over entire temperature range
60 w/o U ₃ O ₈ addition } 70 w/o U ₃ O ₈ addition }	
	Well-developed crystals as w/o U ₃ O ₈ increased

Na₂O-PbO-SiO₂ Glasses: Two lead-type glasses representative of low liquidus temperature were used. Compositions were as follows:

35 w/o PbO		45 w/o PbO
15 w/o Na ₂ O	and	10 w/o Na ₂ O
50 w/o SiO ₂		45 w/o SiO ₂

Liquidus Temp = 650°C

Liquidus Temp = 625°C

Additions of U₃O₈, U₃O₈ + PbO, and U₃O₈ + Na₂O were made to the base glass and devitrification tests were made with the following results:

- a. Base glass: No crystallization in 6 days.
 - b. 10 w/o U₃O₈ addition
 - c. 20 w/o U₃O₈ addition
 - d. 30 w/o U₃O₈ addition
- } Crystallization in the range from 500 to 700°C began in 5 hr. Crystals were very small. Some skin formation occurred on top of glass.
- e. 10 w/o U₃O₈ + PbO in ratio PbO-UO₂ (minute crystals in range from 500 to 700°C; pronounced skin effect.)
 - f. 10 w/o U₃O₈ + Na₂O-UO₃ (minute crystals in range from 500 to 700°C; pronounced skin effect.)

The addition of urania to the lead glasses promoted devitrification. The crystals formed were very small, indicative of rapid crystallization. The skin effect noted is related to volatilization and indicates a possible problem of vapor pressure with lead glasses.

Na₂O-K₂O-SiO₂ Base Glasses: The base glass for this evaluation was composed of 70 w/o SiO₂, 10 w/o Na₂O, and 20 w/o K₂O. This glass had a liquidus temperature of 600°C and was very viscous at 1600°C. Additions of uranium were made to this base glass in the form of K₂UO₄ and Na₂UO₄. The maximum solubility of UO₂ in the base glass was approximately 50 w/o when the glasses were cooled rapidly after complete solution had taken place.

There was a wide range of glass compositions in this field that were very resistant to devitrification. Compositions containing up to 25 w/o UO₂ did not show any crystalline development in 2 weeks in the temperature gradient. A composition containing 15 w/o UO₂, added as K₂UO₄, has been held in a temperature gradient of 350 to 950°C for 3 months without devitrification occurring.

A preliminary study has been made of the use of urania-bearing glasses in the formation of dispersion-type fuel with crystalline MgO and SiC. Samples were prepared of MgO-glass mixtures by means of standard powder fabrication and sintering techniques to evaluate the usefulness of the glass as a sintering agent as well as the fuel carrier. For this purpose

a glass containing 11 w/o Na_2O , 7.3 w/o CaO , 33.2 w/o UO_2 , and 48.5 w/o SiO_2 was used, with the results shown in Table XV. Metallographic examination of the sintered samples showed the glassy phase to be well dispersed throughout the MgO with partial solution of MgO grains evident.

Table XV

BULK DENSITY OF SOME SINTERED MgO -GLASS MIXTURES

Composition	Sintering Temperature (°C)	Bulk Density	
		% Theoretical (Mixture) ¹	% Theoretical (MgO Content) ²
MgO	1500	69	69
MgO	1650	76	76
MgO	1725	76	76
MgO + 5% Glass	1500	80	74
MgO + 5% Glass	1650	90	83
MgO + 5% Glass	1725	92	86
MgO + 10% Glass	1500	91	80
MgO + 10% Glass	1650	80	70
MgO + 10% Glass	1725	93	81
MgO + 15% Glass	1500	83	68
MgO + 15% Glass	1650	92	76
MgO + 15% Glass	1725	89	73

1 Calculated on the basis of the theoretical density of the MgO or the MgO -Glass mixture.

2 Calculated on the basis of the MgO content in the specimen (weight MgO /volume of specimen $\times$ T.D. MgO).

Samples were prepared from mixtures of SiC and glass utilizing the viscous property of the glass to provide lubrication during fabrication. Samples were formed by pressing the mixture in a steel mold at temperatures near the softening point of the glass (400 to 600°C). It was possible to form high-density samples of the same dimensions as the mold without further sintering. This technique and others are being evaluated for the forming of samples of maximum density for irradiation tests.

Cladding Materials for Fueled Glasses (L. C. Hymes)

Investigation of reactions at elevated temperatures between fueled glasses and possible cladding materials has been initiated. Information with respect to the occurrence and extent of any such reactions will help determine compatible cladding materials and the possibility of obtaining a bond between the fueled glass and the cladding.

Initial experiments have involved isothermal heat treatment of a 30% UO_2 -soda-lime-silica glass in a Type 304-L stainless steel capsule at 800°C for a period of 650 hr. A slight reaction approaching a bond was in evidence.

Experiments in progress include samples of a 20% UO_2 -soda-potassia-silica glass contained in graphite and in Type 304 stainless steel capsules. These samples are being held at 900°C where the glass has a low viscosity, i.e., it is "liquid."

Investigation of the compatibility of additional cladding materials and methods of fabrication of clad glass fuel elements, such as hot rolling, extrusion, zone melting and injection casting, is contemplated.

5. Poisoned Glasses (J. H. Handwerk and E. D. Lynch)

The preliminary investigations in the area of fueled glasses indicated that glasses would be a suitable carrier for high-cross-section oxides. In this application, the glass or liquid phase would act as a solvent and permit an infinite dilution of such rare earth oxides as Eu_2O_3 , Dy_2O_3 , and Gd_2O_3 . Using various unfueled glasses, which were found to resist devitrification, amounts of Eu_2O_3 , Dy_2O_3 and Gd_2O_3 up to 15 w/o were found to be readily soluble. These compositions are now being evaluated, and methods for fabricating specimen control rods are being studied.

In conjunction with the studies involving the warm (at 400 to 600°C) pressing of mixtures of SiC and glass, boron carbide was substituted for the silicon carbide. Boron carbide is a relatively inexpensive compound. This compound, due to the high melting point and chemical inertness to reactor coolants, is suitable for a control material for thermal reactors. The fabrication of boron carbide into pellets or plates, which are suitable for assembling into control rods, necessitates hot pressing, and this fabrication procedure is time consuming and expensive. However, as boron carbide has a high capture cross section for thermal neutrons, and high densities are not necessary for most control rod applications, many control rods utilize boron carbide grain compacted to densities of from 60 to 75% of theoretical (1.50 to 1.87 g/cc).

In some control rod applications, the movement of the rod during normal reactor operations causes the boron carbide grains to fracture and settle. This leaves a void in one end of the control rod, which may be troublesome to the reactor operator. In order to alleviate this settling, a study was investigated to develop an inexpensive method of fabricating boron carbide into shapes which would remain intact under mechanical shocks.

Pellets of 85 w/o boron carbide and 15 w/o glass could be readily formed by warm pressing in a steel mold at temperatures from 400 to 600°C. These pellets were found to have densities of 85 to 91% of

the theoretical density (2.13 to 2.27 g/cc) of boron carbide, and that the pellets would resist chipping when dropped from a height of 4 ft. This procedure produced an acceptable fabricated shape of boron carbide. Equipment for warm pressing a large quantity of pellets was not available; therefore an alternative method of forming a control rod was investigated.

In warm pressing, the temperature and pressure used was dependent on the softening point and viscosity of the glass. A low-temperature glass was made by smelting a mixture of SiO_2 , K_2CO_3 and Na_2CO_3 in a platinum crucible. The melted glass had a composition of 69.53 w/o SiO_2 , 19.84 w/o K_2O , and 10.63 w/o Na_2O . This glass was crushed to pass a 100 mesh screen (minus 149 microns) by grinding in alcohol in a pebble mill. The boron carbide as received would all pass a 60 mesh screen (minus 250 microns) and contained 76.5 w/o boron. A portion of this material was crushed to minus 325 mesh (44 microns), and a mixture of these fractions of boron carbide was made by blending 70 w/o of the 60 mesh fraction with 30 w/o of the 325 mesh fraction.

A slurry of the glass was made by mixing with alcohol. The boron carbide mixture was added to this mixture to form a mixture of 15 w/o glass and 85 w/o boron carbide. The slurry was dried, at 100°C , and the dry glass-boron carbide mixture was vibrated while hot into stainless steel tubes. Densities as calculated from the tube dimensions ranged from 65 to 75% of the theoretical density (1.63 to 1.87 g/cc) of boron carbide.

These loaded tubes were slowly lowered through a heating coil at a rate of $\frac{1}{2}$ in./min. The furnace temperature was controlled at 950°C , and the temperature, as measured, on the surface of the tube was found to be 850°C . The stainless steel tubes were stripped from the sintered glass-boron carbide, and the density of the sintered mixture was found to be within the range of 66 to 75% of the theoretical density of boron carbide. This would indicate that very little volume change had occurred during the sintering operation. The sintered mixture was found to have good mechanical strength and would resist chipping when dropped from a height of 4 ft.

Sintered mixtures of glass and boron carbide are now being evaluated. However, using essentially the same procedure, 32 stainless steel tubes were filled and sintered. These tubes will be used for the control rods in the High "C" critical experiment.

6. Uranium-Thorium Sulfide Bodies (P. D. Shalek)

Uranium monosulfide has potential as a reactor fuel, for it has a high uranium atom density, a high melting point, and semimetallic properties. This program is directed toward the preparation of pure, dense US bodies and includes the measurement of the properties of these bodies. US-ThS solid solution bodies are also under investigation.

Fabrication of US bodies has progressed to the point where meaningful property measurements can be made. Processing begins with the hydriding of uranium turnings. The UH_3 is decomposed to give fine uranium powder which is reacted with a measured amount of H_2S at 550°C . The resulting mixture of US_2 , $\alpha\text{-U}$, and UH_3 is homogenized to US at high temperatures, crushed, pelletized, and finally sintered at high temperatures.

A sintering study was made in which batches of US powder homogenized in vacuum at 1500, 1600, 1700, and 1800°C for one hour were isostatically pressed into pellets at 55,000 psi and sintered in vacuum at 1700, 1800, 1900, and 2000°C for one hour. It has been found that either 1800 or 1900°C is the best temperature for homogenization. Above this, weight loss would be considerable and the material would be very difficult to crush for powder processing. In all cases the fired density reached a maximum at either 1800 or 1900°C , dropping slightly at 2000°C . The material of highest density (85.8% theoretical) analyzed as 99% $\text{US}_{0.98}$ + 1% (U + UOS), which represents about 0.05% O_2 contamination. Weight loss increased considerably over 1800°C . Vapor deposition of US at 2000°C is being attempted as a method of preparing emitter targets for thermionic emission studies.

The effect of argon homogenization and sintering on the densification of US has been studied. Argon processing produced US with a density of 91.5% theoretical as compared with 84.6% for vacuum processing at 1800°C . Of this 7% density gain, 3% apparently can be attributed to the argon homogenization and 4% to the argon firing. Results from hydrogen firing are still inconclusive.

The latter parameter of stoichiometric US, which has the NaCl structure, is chosen as 5.4926 Å since, with few exceptions, US with a S/U ratio of less or greater than 1.00 had a lattice progressively contracted from this maximum value to a minimum of 5.4855 Å. Limited solid solution of UO_2 ($a = 5.4581$ Å) would account for only a fraction of this contraction, so for the present it must be attributed to sulfur- or uranium-deficient structures. A study now in progress of US with S/U ratios of 0.8 to 1.2 should help clarify this. The lower compositional limit of the US phase is believed close to $\text{US}_{0.965}$ since none of the many samples analyzed have shown lower sulfur contents in the US phase in the presence of excess uranium. The upper limit is undetermined.

ThS has been investigated to a much lesser extent. Material analyzing 96.5% ThS (remainder ThO_2) which was homogenized in a vacuum at 1700 or 1900°C was vacuum sintered to about 85% theoretical at 1900°C for one hour and to about 98% theoretical at 2000 and 2100°C .

Equipment has recently been set up to measure the electrical resistivity and modulus of rupture of pellets used in the sintering studies, and other property measurements are planned. US samples measured thus

far have had resistivities ranging from 160 to 400 $\mu\Omega$ -cm and indicate that this property might be used as a measure of some physical and chemical variations in the bodies. The only ThS measured showed a much lower resistivity of 16 $\mu\Omega$ -cm. For comparison, some published resistivity values are: Nichrome 100, Ta 15.5, Mo 5.7 and Cu 1.7 $\mu\Omega$ -cm. Modules of rupture values for US also fall in a wide range, going from a minimum of 2000 psi to a maximum of 24,000 psi. The ThS measured was considerably stronger, having moduli ranging from 16,000 to 31,000 psi. The relative effect of density, porosity, grain size, S/U ratio, and impurities on these properties has not been determined.

Microstructures are being used extensively in order to understand better sintering characteristics and property variations. A 3 to 4 v/o solution of H_2SO_4 in water is the best etchant found thus far for US polished sections. Immersion for 3 to 8 min produces a rapid gaseous reaction which must be stopped within a few seconds for best results. Average grain size for samples observed thus far has ranged from 30 to 140 μ . A secondary phase, believed to be UOS or a U-O-S eutectic, appears in varying degrees in all samples and exists mainly as occlusions in samples fired at 1700°C. This phase appears to migrate to the grain boundaries at 1800°C, and at 2000°C is found mainly on the crystal planes in a Widmanstätten-type structure.

F. Irradiation Evaluation of Various Experimental Fuel, Control and Structural Materials

1. Restrained and Vented Uranium-2 w/o Zirconium Alloy (J. A. Horak, J. H. Kittel)

In order to determine the effect of cladding and internal venting on the swelling characteristics of a metal fuel, several specimens of U-2 w/o Zr alloy with a 0.030-in.-dia axial hole were jacketed in 0.010-in.-thick stainless steel cladding for irradiation at high temperatures. The specimens consisted of an enriched core tightly fitted in an unenriched sleeve. The specimens were bonded to the cladding with a 0.010-in.-thick NaK-filled annulus. Zirconium foil was used as a diffusion barrier to prevent eutectic formation between the fuel and the cladding.

The specimens were irradiated in NaK capsules to volumetrically averaged burnups ranging from 1.4 to 2.1 a/o and at calculated central temperatures ranging from 620 to 1260°C. These temperatures are well above the normal swelling temperature of 500°C for cast U-2 w/o Zr alloy. The clad temperatures ranged from 330 to 620°C. The table below summarizes the irradiation conditions for each specimen and supersedes the preliminary data given in the previous annual report (ANL-6099).

Specimen Number	Burnup, a/o		Max Fuel Temp, °C	Clad Surface Temp, °C	%Δ Volume a/o Burnup
	Core	Assembly(a)			
DF-2	10.2	1.8	960	480	0
DF-3	10.2	1.8	960	480	0
DF-4	12.2	2.1	1260	620	(b)
DF-5	11.4	2.0	1140	570	(b)
DF-6	12.0	2.1	1200	590	0
DF-7	8.0	1.4	650	330	0
DF-8	11.4	2.0	1090	(Unclad)	(b)
DF-9	9.0	1.6	890	440	0
DF-11	8.0	1.4	620	(Unclad)	6.3
DF-13	9.2	1.6	830	420	0.2

(a) Volume average burnup of the enriched core and natural sleeve.

(b) Unable to remove specimen from capsule.

Metallographic examination revealed that at least some degree of melting had occurred in all of the specimens irradiated at temperatures above 960°C. In these specimens the fuel had also dissolved the zirconium diffusion barrier and had formed a molten eutectic with the stainless steel. All of the clad specimens had swollen to the volume of the cladding and

could not be removed from the cladding. All of the specimens contained considerable porosity, with the line of demarcation between the enriched core and natural sleeve no longer visible. The outer diameter of the stainless steel cladding was effective in restraining fuel swelling up to fuel temperatures of approximately 950°C. In eight of the specimens the central vent had swollen shut and in one specimen it was partially closed. In one specimen the vent had enlarged from $\frac{1}{32}$ to $\frac{3}{16}$ in., with a corresponding increase in clad diameter.

The results of these irradiation experiments indicate that the use of an axial hole to enhance the release of fission products, combined with mechanical restraint, extends the application of metallic fuels to temperatures several hundred degrees higher than the temperature limits of unrestrained and nonvented fuels. This approach is of greater interest for fast reactors, which can more readily tolerate the amounts of cladding necessary to provide restraint, and in which high burnups, high fuel surface temperatures, and high uranium densities are required. The successful results obtained from these experiments have lent encouragement to the approach being taken for restraining swelling in the uranium-plutonium-fissium alloy fuel scheduled for the second core of EBR-II.

2. Irradiation Behavior of Thorium-Plutonium Alloys (J. A. Horak)

Thorium-uranium alloys containing additions of uranium up to approximately 20 w/o have shown excellent behavior under irradiation. Presumably, thorium-plutonium alloys in the same composition range should also show excellent stability, since according to the plutonium-thorium equilibrium diagram, the face-centered-cubic, alpha thorium phase will contain up to 50 a/o Pu. Preliminary irradiations have been made on two alloys. A cast specimen of Th-5 w/o Pu alloy and another of Th-10 w/o Pu alloy were examined after 1.4 and 2.3 a/o burnup, respectively, at 450°C. Dimensional and surface stability were excellent and were equal to comparable thorium-uranium alloys irradiated at this temperature. Further irradiations are planned at higher temperatures.

3. Irradiation of X8001 Aluminum Alloy-clad, Lead-bonded ThO₂-UO₂ Pellets (L. A. Neimark, R. Carlander)

Two assemblies of ThO₂ pellets containing 25.6 w/o UO₂, lead bonded to Al-1 w/o Ni alloy, were examined metallographically after longitudinal cladding failures occurred during irradiation in the MTR-ETR process water. Burnups are estimated at 27,000 MWD/T with maximum internal temperatures of the order of 2400°C and with heat fluxes on the order of 700,000 BTU/hr-ft².

The cladding failures occurred near the bottom of each assembly in regions of highest temperature and in regions where the cladding thickness was appreciably less than specifications. Figure 20 shows a cross section of a failed area. The missing fuel entered the MTR coolant water through the defect. The ceramic fuel exhibited the characteristic central void, and radial and circumferential cracking. Other voids were present in the ceramic and ranged from large equi-axed voids near the center region, to long radially oriented voids farther from the center, and to small, randomly oriented voids at the periphery. Also evident in the hotter of the two specimens were the large, radially oriented, almost void-free grains associated with high-temperature irradiation, and a center region of void-free, two-phase material with a distinct dendritic pattern. Figures 21 and 22 show the two-phase region in the center of the pellet.

The fission gas release from these two specimens was about 90% of the theoretical yield.

Figure 20. Metallographic Section through Failed X8001 Aluminum Alloy-clad, Lead-bonded ThO_2 -25.6 w/o UO_2 Pellet Irradiated to Approximately 20,000 MWD/T Burnup at a Central Temperature above 2000°C.

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Figure 21. Metallographic Section through X8001 Aluminum Alloy-clad, Lead-bonded ThO_2 -25.6 w/o UO_2 Pellet Irradiated to Approximately 20,000 MWD/T Burnup at a Central Temperature above 2000°C, Showing a Two-phase Area in Center of Pellet.

Figure 22. Boundary of Two-phase Area in Center of Pellet Shown in Figure 21. Showing the Dendritic Structure of the Second Phase.

4. Irradiation Behavior of Metal-Fibered ThO₂-UO₂ Pellets
(L. A. Neimark)

Fission gas release measurements are in progress on irradiated pellets of ThO₂ containing 10, 30, and 50-w/o UO₂ and 10-w/o Mo or Nb fibers. A direct comparison of gas-release rates between fibered and unfibered pellets at the same irradiation temperature is not possible because the unfibered pellets disintegrated into fragments during irradiation, probably when they were first heated.

Fibered pellets which were irradiated to an estimated burnup of 20,000 MWD/T at internal temperatures (>2600°C) sufficiently high to melt molybdenum fibers, released a maximum of 28% of the theoretical fission gas yield. Preliminary data indicate that the ratio of xenon to krypton in the released gas increased with increasing UO₂ content in the ThO₂.

As noted in the previous annual report (ANL-6099), the metal fiber additions permitted higher heat fluxes to be taken from the pellets before central void formation occurred.

5. Irradiation Behavior of Cast Thorium-Uranium Alloys
(J. A. Horak)

Forty-four specimens of irradiated cast thorium-uranium alloys have been examined in the hot cells. The range in composition includes Th with 10, 15, 20, 25, and 28 w/o U. The enrichments were varied so that each specimen contained 10% U²³⁵, except for the 28-w/o U alloy, which contained 26% U²³⁵.

All of the alloys containing up to and including 20 w/o U appear to have very good irradiation stability at the burnups and temperatures investigated to date. As in the previous group of specimens, it was found that irradiation stability decreased significantly near the monotectic composition. The 25-w/o U specimens showed moderate surface roughening and warping, and the 28-w/o U alloy showed similar but much more extensive damage.

Table XVI shows, for each alloy composition, the effects of irradiation on typical specimens irradiated at the highest temperatures and burnups. These values are estimated from flux monitors and are subject to change when isotopic analyses are completed.

Table XVI

IRRADIATION EFFECTS ON Th-U ALLOYS

Alloy	Estimated Burnup, a/o	Estimated Irradiation Temp, °C	% Vol. Change a/o Burnup	Appearance
Th-10 w/o U	2.8	680	2.8	Excellent
Th-15 w/o U	2.9	680	4.0	Excellent
Th-20 w/o U	2.9	680	4.7	Excellent
Th-25 w/o U	2.8	670	6.8	Slightly warped and roughened
Th-28 w/o U	4.5	820	19.3	Severely distorted and roughened

6. Development of Control Materials (C. F. Reinke)

An ideal control material would combine the following properties: large thermal macroscopic absorption cross section, significant epithermal and resonance properties, plus a chain of neutron-absorbing isotopes, ease of fabrication, room- and elevated-temperature strength and ductility, irradiation stability, corrosion resistance, lightweight for rapid movement with minimum inertia effects, good heat transfer properties, and availability at low cost.

At present, materials used extensively as the absorber material in reactor control rods include boron, hafnium, and cadmium, none of which is ideal. The main disadvantage of boron is the $B^{10}(n,\alpha)Li^7$ reaction which introduces two new atoms into the lattice. Each atom is larger and possesses different properties than the parent boron atom. For high-flux, long-life cores, radiation damage in boron-containing control materials can be expected to be significant, and thus the suitability of boron materials for such applications is questionable. The use of hafnium produces a rod possessing desirable nuclear and mechanical properties and long life. However, hafnium is not readily available and is expensive. Cadmium and its alloys have low mechanical strengths and do not have adequate absorption properties in the epithermal region.

The lanthanides (rare earths) appear to offer greatest promise as a basis for development of a class of control materials that will not be subject to the disadvantages of present materials. Work is in progress to incorporate dispersions of these elements into various matrix materials. After determinations of physical and mechanical properties, the more promising combinations will be evaluated by long-term irradiations at elevated temperatures.

At present, both 25 w/o and 38 w/o Dy_2O_3 have been dispersed in plates of X8001 aluminum alloy. Two tensile specimens will be machined from each plate.

A composite plate has been fabricated with 30 w/o Sm_2O_3 in the outer layers and an inner core containing a 20 w/o Gd-Sm-Eu oxide mixture plus 10 w/o Er_2O_3 . The matrix material in both the inner and outer layers is cobalt.

Specimens containing the lanthanide oxides in a $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ glass matrix are being fabricated. Two compositions are under development: 80 w/o Dy_2O_3 , and an 80 w/o Gd-Sm-Eu oxide mixture. The fabrication technique is being varied in order to provide both single-phase and two-phase structures. Also, specimens containing 15, 50 and 90 w/o B_4C in $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ glass will be produced.

7. Monitoring of Irradiation Effects in the Borax-V Pressure Vessel (W. F. Murphy)

An experimental program has been initiated in order to monitor continuously the rate of irradiation damage to the Borax-V pressure vessel. The vessel is made from SA-212-B steel clad on the inside with Type 304 stainless steel. The nominal wall thickness of the vessel is $2\frac{1}{16}$ in., of which $\frac{3}{16}$ in. is stainless steel. The operating temperature and pressure of the reactor will be 255°C and 600 psig, respectively.

Although it is well known that steels of the SA-212-B type are subject to deleterious changes resulting from fast neutrons, present knowledge does not permit an accurate prediction of the magnitude of the changes for a given reactor exposure. Therefore, in common with the approach being used at several other installations, monitor specimens will be used to determine the changes occurring in the vessel itself. The specimens will be cut from the plates used to fabricate the vessel. They will include parent metal, weld metal, and metal from heat-affected zones.

Four $11 \times 12 \times 2\frac{1}{16}$ -in. pieces of plate have been received from the vessel fabricator and are presently being machined into test specimens.

Under the present program, 112 impact specimens, 45 tensile specimens, and 36 bend-test specimens are being made from the coupons of SA-212-B steel provided. These specimens will be divided into four sets. One set will be unirradiated controls. Three sets will be loaded into three capsules for irradiation in the Borax-V reactor in a location adjacent to the inside of the pressure vessel wall. Each of the capsules will be provided with a thermocouple for measurement of the internal temperature.

A capsule of typical specimens was irradiated in CP-5 in order to determine the temperature rise in the specimens to be expected in Borax-V as a result of gamma heating under the most extreme conditions (40 Mw). The temperature rise was 80°C. Efforts are in progress to use more efficient packing to decrease the temperature rise.

8. Development of Controlled High-temperature Irradiation Facilities (W. N. Beck, C. C. Crothers)

A continuing effort has been in progress on the development of instrumented capsules for use in the Laboratory's CP-5 reactor. Six of the fuel thimbles in the reactor were modified to bypass heavy water into the thimbles so that adequate cooling would be available for experimental fuel irradiations. The instrumented capsules that have been developed for these thimbles are 1.5 in. in diameter and approximately 1 ft long. Each capsule contains up to six fuel specimens with a thermocouple adjacent to or inserted in the center of each specimen. Temperature control is provided by up to 2000 watts of auxiliary electrical heat in each capsule. The capsules are constructed with a double wall of Zircaloy-2. They are attached to special shield plugs in such a manner that the capsules can be withdrawn from the reactor and replaced with new experiments within a period of a few minutes.

At the present time, six instrumented capsules are in the CP-5 reactor for periods ranging up to nine months. All are operating successfully. Measured central fuel temperatures range up to 785°C. Temperature control during normal reactor operation is within 2°C of the desired temperature.

A controlled-temperature capsule capable of accommodating full-length (14.22 in.) EBR-II fuel elements has been developed for installation in the MTR. The capsule is largely based on a design successfully operated by the Reactor Engineering Division in the CP-5 reactor. The assembly consists of an EBR-II fuel pin mounted inside an externally finned stainless steel tube. The fuel pin is bonded with NaK to the inside of the finned tube. The finned tube is thermocoupled along its length and is in turn located inside a tightly fitting, second stainless steel tube. The space between the fins is filled with an inert gas. The second tube is concentrically located within a third stainless steel tube. The space between the second and third tubes is filled with stagnant water and is pressurized with helium gas.

Temperature control is largely self-stabilizing and is obtained by first adjusting the pressure over the water annulus, so that, at the desired fuel element temperature, nucleate boiling is occurring on the outer wall of the second tube. If the heat output of the pin should increase, the amount of nucleate boiling increases with a corresponding increase in the heat transfer coefficient.

The capsule contains probes for liquid-level indication. Make-up water can be injected into the facility during operation to compensate for losses due to radiolytic dissociation.

G. Examination of Full-scale Reactor Fuel Elements

1. Metallurgical Evaluation of Failed Borax-IV Reactor Fuel Elements (C. F. Reinke, L. A. Neimark, R. Carlander and J. H. Kittel)

The fuel elements for the Borax-IV boiling water reactor consisted of ThO_2 -6.36 w/o UO_2 pellets in X8001 aluminum alloy tube plates with silicon-bonded end closures. When the reactor was brought to power on February 19, 1958, after having been operated for approximately one year, over one-third of the fuel elements were found to have developed leaks, as evidenced by significant fission gas release into the process water. Since no fission breaks had been detected during the last previous operation of the reactor on December 5, 1957, it appeared that the leaks had developed during the $2\frac{1}{2}$ -month shutdown. A detailed metallurgical examination was completed during 1960 of two elements containing several failed tubes to determine the causes of failure and the amount of fission gas released from oxide pellets in unfailed tubes. It was found that the upper portion of each tube, where a void space had been intentionally left above the pellets, had collapsed under the reactor operating pressure. The reverse bending which occurred in the tube walls caused local cracking. The most probable cause for the leaks which developed during shutdown is considered to be corrosion in cracks and crevices of the collapsed tubing. The performance of the silicon-bonded end closures appeared to be quite adequate for at least normal reactor operation. Measurements and analyses of gas samples taken from unfailed tubes showed that the pellets released an average of 3.4% of the total fission gas yield, although they had operated at relatively low temperatures. The release is attributed to open porosity which existed in the pellets.

2. Performance of EBWR Core 1A Fuel Elements at 100-Mw Reactor Operation (C. F. Reinke and W. N. Beck)

The condition of the fuel elements in the EBWR after operation to approximately 0.4 a/o burnup is reported in ANL-6091. As part of the program to determine the condition of the fuel elements, annealing studies

were conducted on sections of irradiated EBWR fuel plate. The data from these studies indicate that at the 0.4 a/o burnup level, significant volume increases resulted within 45 hr at 600°C.

Information on the nature and extent of surface deposits of scale on surfaces of fuel plates is given in the above reference and in ANL-6136. The thermal conductivity of the scale has been measured as 0.45 ± 0.1 BTU/hr-ft-°F.

Calculations of the maximum fuel plate temperatures during 100-Mw operation vary. Some calculations indicate 600°C or above, depending on the thickness and condition of the boehmite scale deposits. Thus, the quantity of scale on the fuel plate surface and the effect of its characteristics upon the temperature of the fuel plates when considered in conjunction with the swelling data indicate an area of possible difficulty during 100-Mw operation. The difficulty, if it should occur, would manifest itself by decreasing the water channel between plates.

Because of this uncertainty, a device was developed which is able to measure the water channel gaps on the EBWR fuel elements. An eddy current technique is applied in measuring the channel gap. A commercial unit, normally used for detecting flaws in materials, was modified for the present application. A special, single-wound coil probe was made and potted in a waterproof holder. Twenty feet of flexible cable was connected to the holder. This probe was mounted in a spring-loaded positioner, which positioned the probe within a channel holding a constant probe-to-plate spacing on one face. The probe measured the variation of magnetic inductance as a function of the distance from the opposite plate face. The readings of the channel gap are recorded continuously.

The unit has been assembled and tested in a mock-up using an unirradiated fuel element submerged in water. The unit has been shown to give excellent duplication of readings within a channel. At present, work is under way to calibrate the probe so that the thickness of the channel gaps can be read directly from the strip chart. Also, tests are under way to determine the response of the probe to changes in bulk water temperature. After completing the calibration runs, water channel measurements will be made on fuel elements in the EBWR which are representative of the maximum burnup and temperature conditions in the core.

The fuel elements will be checked periodically throughout the remainder of the life of the core as additional burnup and elevated temperature operation is obtained. This procedure will determine if and to what extent swelling is occurring and the water channel dimensions are decreasing.

H. Development of Corrosion-resistant Fuel, Jacketing and Structural Materials

1. Uranium Alloys (S. Greenberg)

This program has been temporarily suspended. However, additional exposure of the alloys discussed in the 1959 Annual Report (ANL-6099) did not result in increased corrosion rate. The pertinent data are in Table XVII.

Table XVII

CORROSION OF URANIUM-TITANIUM ALLOYS IN WATER

Alloy and Heat Treatment	Time Days ^(a)	Avg Rate of Wt Loss, mcd, ^(b) at 290°C
(1) U-3 w/o Ti-0.25 w/o Ru, Gamma Quenched	147	8-9
(2) U-3 w/o Ti-0.5 w/o Nb-0.1 w/o Ru, Gamma Quenched and Aged: 400°C for 2 hr	233	3-4
(3) U-3 w/o Ti-0.5 w/o Nb-0.25 w/o Ru, Gamma Quenched and Aged: 400°C for 2 hr	234	3

(a) The total time includes 82 days for alloy (1) and 80 days for alloys (2) and (3) at 260°C.

(b) mg/cm²/day

When this program is reactivated, the effect of ruthenium on alloys of lower cross section, e.g., niobium alloys containing no titanium, will be investigated. In addition, a larger casting of alloy (2) is available for a more detailed study of the relationships between corrosion rate, structure, and heat treatment.

2. Thorium Alloys (J. Y. N. Wang)

Thorium is more plentiful than uranium and is a potential valuable source of secondary nuclear fuel (U^{233}) for power-producing reactors. Its dimensional stability is good. However, its corrosion resistance is poor. The objective of this project is to develop alloys with good resistance to corrosion by water at elevated temperatures.

In a preliminary evaluation of the corrosion of unalloyed thorium-iodide metal exhibited uniform corrosion in distilled water at 125°C, while calcium-reduced thorium showed early catastrophic corrosion failure. At 150°C, both materials were disintegrated within 96 hours. Since the calcium-reduced thorium contains impurities of oxygen, iron, nickel, calcium and carbon as high as 1200 ppm, and all are less than 50 ppm in iodide metal, the influence of these impurities on corrosion resistance in high-temperature water was apparent. As a result of these initial tests, iodide thorium was chosen for base stock in the preparation of thorium alloys.

Thorium-Carbon Alloys: Carbon is one of the main impurities found in thorium. The extent of contamination varies with the method of preparation. Thorium and carbon form two compounds: ThC and ThC₂. The solid-solubility limit of carbon in thorium is temperature dependent, with a maximum solubility at 1215°C of 0.91%. The effect of carbon content on the corrosion behavior of thorium in high-temperature water is uncertain. Short-term corrosion tests have indicated that the presence of carbon in a small amount seems desirable. Longer periods of observation, up to 12 days, in high-temperature water (150 to 200°C) revealed that thorium-carbon alloys often suffered intergranular penetration attack. At 260°C, all the thorium-carbon binary alloys up to 1 w/o C suffered catastrophic corrosion failure within six days.

In an effort to remove the carbon from the thorium phase (by precipitating a stable carbide), a series of thorium-carbon ternary alloys with Nb, Ti, and Fe were arc melted and tested in distilled water at 260°C (500°F). Alloy Th-0.5 w/o C-0.2 w/o Ti showed the lowest corrosion rate. However, this alloy suffered intergranular attack after 12 days of exposure. Alloy Th-1 w/o C-1 w/o Ti exhibited no apparent intergranular penetration through six days of exposure, but after 12 days was split into two pieces containing microscopic cracks. No favorable result was found from the addition of niobium and iron.

Thorium-Uranium Alloys: The solid solubility of uranium in thorium at room temperature is limited, and no intermetallic compound has been reported in this system. It is not anticipated that the addition of uranium to thorium would result in any significant improvement of the corrosion resistance of thorium. However, because of the importance of thorium-uranium alloys as possible reactor fuels, the investigation of the corrosion behavior of these alloys was initiated. The purpose of this work is to examine the corrosion behavior of thorium-rich uranium alloys in high-temperature water and to investigate the possibility of developing corrosion-resistant fuel alloys.

A series of thorium-uranium alloys were arc melted in increments of 5 w/o U in thorium up to the maximum of 40 w/o U. These alloys were exposed in distilled water at 150°C at different time intervals. Test results are recorded in Table XVIII.

Table XVIII

CORROSION OF THORIUM-URANIUM ALLOYS
EXPOSED IN 150°C WATER

Alloy Composition w/o (Nominal)	Average Rate of Change for Total Period, mg/cm ² /day			
	2 days	4 days	7 days	12 days
Unalloyed Th-1	-113.0	-	-	-
Unalloyed Th-2	-111.0	-	-	-
Th-5 U	-25.8	-77.6	-	-
Th-10 U	-18.2	-63.5	-	-
Th-15 U	-47.1	-64.0	-67.8	-74.6
Th-20 U	-	-98.3	-	-
Th-25 U	-118.0	-123.0	-	-
Th-30 U	-115.0	-	-	-
Th-35 U	-434.0	-234.0	-	-
Th-40 U	-312.0	-218.0	-	-

The thorium-uranium alloys exposed to 150°C water were characterized by an uneven and laminar attack. Corrosion products underneath the flakes could not be removed effectively. In most cases, corrosion rates could not be determined because of disintegration. However, after seven days of exposure, Th-15 w/o U alloy was the only survivor among the tested alloys.

On the basis of these test results, ternary additions of zirconium to the Th-15 w/o U alloy were investigated. Zirconium was chosen as the additive because of its good performance as a binary alloying element and because of its solubility in both thorium and uranium. Arc-melted alloys were prepared with the addition of 1-, 2-, and 4-w/o Zr. All were annealed at 1000°C in an inert atmosphere for 24 hr and then quenched in Wood's metal.

The two alloys with lowest Zr contents showed catastrophic corrosion failure within 24 hr in water at 200°C. It appeared that the addition of 4 w/o Zr to Th-15 w/o U had a beneficial effect. The sample was free from localized attack, with corrosion rates in the range from 23 to 45 mg/cm²/day. These rates are high for such a temperature, but the trend indicates that the ternary addition with zirconium may be worth further study.

Miscellaneous Alloys: A number of binary additives have been investigated. None of the alloys had really satisfactory corrosion resistance. On the basis of the testing which has been done (see Table XIX), those alloying constituents which have proved beneficial include aluminum, yttrium, and zirconium. As time permits, further work based on these materials will be done.

Table XIX

AQUEOUS CORROSION OF THORIUM ALLOYS

Alloy Composition, Nominal w/o	Time on Test, Days	Test Temp, °C	Avg Rate of Change during Total Exposure, mg/cm ² day	Remarks
Th-1 Al	1	200	-7.16	Grey coating.
Th-3 Al	2	150	-0.02	Adherent multicolor tarnish.
	1	200	+0.17	Adherent dark blue-grey tarnish.
	3	200	-313.00	Partially disintegrated.
Th-5 Al	3	200	+0.036	Grey tarnish.
	1	260	+1.99	Adherent grey translucent film.
	3	260	-	Disintegrated.
Th-7 Al	1	200	-1.13	Grey tarnish.
	6	200	-	Split into two pieces.
Th-5 Y	24	150	-0.25	Adherent smooth grey-black coating.
	24	200	-36.4	Same type of coating as above, except slightly rough surface.
	144	200	-	Disintegrated.
Th-10 U	24	200	-0.26	Light brown-blue tarnish.
	24	260	-0.23	Slightly pitted.
Th-1 Pd	48	150	-	Disintegrated.
Th-3 Pt	48	150	-	Disintegrated.
Th-9 U-2 Zr	48	150	-3.93	Thin slightly grey powder over adherent black coating, surface smooth.
Th-5 Fe	48	150	-1.09	Loose rust colored powder covered adherent dark grey coating. Surface smooth.
	24	200	-89.7	Adherent slightly grey-green coating, uniform.
Th-9 U-2 Zr	1	200	-582.0	Cracked and spalled.
Th-5 Sn	1	200	-	Disintegrated.
Th-3 Mo	1	200	-449.0	Black loose powder surface slightly rough.
Th-3 Pb	1	200	-1.3	Adherent grey coating.
Th-5 Pb	3	200	-0.41	Small pits.
	7	200	-66.20	Cracked.
Th-1 Ru	1	200	-	Disintegrated.
5 Ti	6	200	-	Disintegrated.
10 Ti	1	200	-26.20	Cracked and pitted.
	6	200	-	Disintegrated.
5 Zr	6	200	-25.40	Unevenly attacked.
10 Zr	1	200	-0.49	Grey tarnish.
	6	200	-0.05	Adherent smooth grey-black coating.
10 Ce	1	200	-	Disintegrated.
10 Cr	1	200	-	Disintegrated.
5 Nb	1	200	-	Disintegrated.
5 Ni	1	200	-	Disintegrated.
5 U	1	200	-	Disintegrated.
2 V	1	200	-	Disintegrated.
2 W	1	200	-	Disintegrated.

3. Aluminum Alloys (W. E. Ruther, J. Y. N. Wang and S. Greenberg)

Alloy Development: Adequate corrosion resistance and mechanical strength are required of an aluminum alloy to make it acceptable for fuel cladding in a power reactor. In the past year a long test of a low silicon alloy A288 (1 w/o Ni-0.5 w/o Fe-0.1 w/o Ti-0.001 w/o Si) has been completed, with the results shown in Figure 23. Data from tests of X8001 aluminum (and Zircaloy-2), included for reference, show A288 to be a substantially improved aluminum alloy under these conditions. The corrosion test was performed in a refreshed autoclave system at 350°C.

Figure 23. Corrosion of X8001 and A288 Aluminum Alloy and Zircaloy-2 in Distilled Water.

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Unfortunately, as briefly described last year, no way has been found to maintain the relative corrosion improvement at 290°C and lower temperatures. At temperatures of 315°, 337°, and 360°C, a series of tests with five alloys of the A288 basic composition has indicated the effect of silicon in the range 10 to 150 ppm. The corrosion rate was observed to decrease as the temperature increased. At each of the three temperatures, the corrosion rate increased with increasing silicon content. It appeared that all of this series of alloys were approaching a low limiting rate at some high temperature and that the alloy containing the least silicon was dropping towards this value at the lowest temperature. The importance of quite low silicon seems greater at moderate temperatures (such as 315°C) than at the higher temperatures.

It has been suggested that alloys containing more iron than nickel might offer the opportunity to reduce the deleterious effect of

silicon by combining the silicon with the excess iron to form a compound. In a test at 305°C, A288 had a lower corrosion rate than an alloy containing 1.5 w/o Fe-0.5 w/o Ni-0.1 w/o Ti (~10 ppm Si). In tests at higher temperatures, the A288 composition has consistently had corrosion rates as low as any of the other compositions tested.

The improvement is not limited to static corrosion. A288 alloy has been exposed to flowing water at 18 ft/sec, 315°C for 224 days with the results presented in Figure 24. Points are for four individual specimens. A comparison line for X8001 is also shown. The "surface to volume" factor for this particular corrosion apparatus is quite unfavorable. In spite of this, the alloy shows a very distinct improvement in corrosion characteristics.

Figure 24. Dynamic Corrosion Test
Data for Aluminum Alloys
A288 and X8001.

A commercial 2000-lb melt of A288 was purchased. Samples of this large melt have been corrosion tested, statically and dynamically, giving results equal to those from the small Argonne casting.

To check the possibility of stress corrosion, samples of A288 alloy were exposed to degassed, distilled water at 260 and 360°C for periods up to six months and at stresses up to 1000 psi. Control samples were exposed unstressed in water and air. The samples were pulled on a tensile machine after exposure. There was no reduction in tensile properties, indicating no intergranular attack. This was confirmed by metallographic examination.

Some efforts have also been made to develop different alloys. As shown in Tables XX and XXI, cobalt and rhodium provided the most corrosion-resistant binary alloys of all the group eight elements. Metallographic examination of the best alloys showed the compound to be largely at grain boundaries.

Table XX

CORROSION DATA FOR BINARY ALUMINUM ALLOYS
EXPOSED IN DISTILLED WATER AT 360°C

Alloy Composition, w/o, Nominal	Time, hr	Avg Rate of Wt Change during Total Period, mg/cm ² /day	Remarks
0.5 Ru	137	-	Completely disintegrated.
0.5 Os	24	-	Completely disintegrated.
0.5 Ir	24	-166.00	Heavy grey oxides covered ruptured sample.
0.5 Pd	137	-	Completely disintegrated.
9 Pt	24	-18.55	White scale over adherent black coating.
9 Pt	137	-3.74	White scale over adherent black coating.
0.1 Rh	24	-	Completely disintegrated.
0.3 Rh	24	-0.125	Black oxide film covered with randomly scattered white oxide.
0.3 Rh	144	+0.039	Black oxide film covered with randomly scattered white oxide.
0.5 Rh	168	+0.29	Smooth adherent black scale.
0.5 Rh	672	+0.05	Smooth adherent black scale.
0.5 Co	24	+0.83	Light grey scale over black surface.
0.5 Co	144	+0.06	Light grey scale over black surface.
0.5 Co	672	+0.03	Light grey scale over black surface.

Table XXI

BINARY ALUMINUM ALLOYS EXPOSED IN SUPERSTEAM
AT 540°C AND 600 psig

Alloy Composition, w/o, Nominal	Time, hr	Avg rate of Wt Change, mg/cm ² /day	Remarks
0.3 Rh	95	-0.197	Black oxide film covered with randomly scattered white oxide.
0.5 Rh	1256	-0.027	Smooth black adherent film.
0.5 Co	1256	-0.022	Blue grey adherent film.

X-ray identification of such phases in the Al-0.5 w/o Rh and Al-0.5 w/o Co alloys revealed the compound formulas to be Rh_2Al_9 and Co_2Al_9 , respectively. These are isomorphous with the ternary intermetallic compound $(\text{Fe} + \text{Ni})_2\text{Al}_9$; the similarity in good alloys may not be accidental.

It should be noted that while this work was being done, similar results were also obtained by Alcoa Research Laboratories.

New ternary alloys which show good corrosion resistance in water at 360°C have been made by the addition of 1.5 w/o Ti + 0.5 w/o Fe, and of 1 w/o Zr + 1 w/o Fe. The former has shown occasional blistering subsequent to about 40 days of corrosion exposure; the latter loses its corrosion resistance with working. Both of these problems are being attacked by the development of modified alloys.

The zirconium-iron alloy is attractive because of cross section and because of its high-temperature strength (9000 psi U.T.S. at 315°C). Perhaps it will be possible to use powder metallurgy to avoid the brittleness which might be the cause of the poor corrosion behavior after working.

Mechanical Properties: The A288 type alloys and wrought alloys in general have poor mechanical properties, particularly creep resistance, at elevated temperatures. For certain reactor applications they are too weak. Several possibilities for strengthening aluminum are being investigated. The first is by conventional alloying. The addition of 0.3 w/o Cr and 0.2 w/o Zr to the basic A288 formula increased the ultimate tensile strength from 3000 psi (315°C) for A288 to about 9000 psi (315°C) for the stronger alloy A341. The corrosion resistance of A341 appears to be comparable to that of A288 in continuing tests. Unfortunately, the creep resistance of alloys strengthened by minor additions remains rather poor.

A second method of increasing strength is through the use of powder metallurgy techniques. Two different approaches are being used. In the first, the strength is achieved by ball milling the atomized A288 powder to increase the oxide content as in the conventional SAP (sintered aluminum powder) approach. Impact extruded tubing made by Alcoa from powder so treated was not corrosion resistant, although an experimental rod extruded by Armour Research Foundation did appear to have adequate corrosion resistance.

A second approach to the problem utilizes powder produced from a stronger alloy (such as A341). The powder is recompact and extruded without ball milling. The advantage to this method is that corrosion resistance has been demonstrated for tubing fabricated by Alcoa from "as atomized" A288 powder. Currently, creep and corrosion tests are being performed on an extruded powder rod of A341 composition.

Corrosion Phosphoric Acid: Elevated-temperature corrosion tests are described in detail in ANL-6206, Corrosion of Some Reactor Materials in Dilute Phosphoric Acid.

In a 307-day dynamic test at 18 ft/sec and 315°C, X8001 aluminum corroded at a rate of $\frac{1}{2}$ mdd for the first 240 days of test. In subsequent exposures the corrosion rate increased and the attack became uneven, but total average penetration at 307 days was only 0.0005 in. At 200 days, the total corrosion in this test was $\frac{1}{50}$ that in distilled water. Static tests at 225°C gave corrosion rates too low to measure (<0.2 mdd).

Corrosion in Superheated Steam: The details of the investigation are described in ANL-6207, Corrosion of Aluminum and Its Alloys in Superheated Steam.

The corrosion behavior of pure aluminum and some of its alloys in superheated steam was found to depend markedly on the method of starting the corrosion test. Pure aluminum samples survived only in tests that were brought to temperature and pressure very rapidly. Resistant Al-Ni-Fe alloys performed well only if a relatively slow starting procedure was used, suffering extensive blistering or complete disintegration in a test started rapidly.

Over the range of temperature and pressure investigated (from 400 to 540°C; from 150 to 600 psig) with optimum starting conditions, either pure aluminum or resistant Al-Ni-Fe alloy samples quickly formed a very protective oxide film. Interference colors were noted after exposures of several weeks. Samples surviving a 260-day test (540°C, 600 psig) had a weight gain less than 1-mg/cm².

Nonresistant alloys disintegrated in short corrosion exposures. A penetrating attack, initiated in only a few spots, rapidly destroyed the samples.

The effects of composition, dispersion of second-phase compounds, hydrogen porosity, and pretreatments were investigated for a resistant alloy (5.6 w/o Ni-0.3 w/o Fe-0.1 w/o Ti) in 540°C, 600-psig steam. It was concluded that porosity produced by corrosion product hydrogen was a major factor in the survival of samples. A mechanism for the rapid penetrating attack has been proposed, based on observations made during the study of hydrogen porosity.

Pretreatment of resistant alloy samples in dry air (540°C) or in high-temperature water (350°C) greatly reduced the amount of porosity produced by corrosion in superheated steam.

4. Zirconium Alloys for Use in Superheated Steam (S. Greenberg)

Work to develop alloys suitable for use as fuel cladding has continued. To date, all alloys have been tested at 540°C and 600 psi in the as-cast condition. However, larger ingots of the more promising alloys have been ordered, and the effects of heat treatment and working on these alloys will be studied. Some of the best alloys and their corrosion behavior are listed in Table XXII.

Table XXII

CORROSION OF SOME ZIRCONIUM ALLOYS IN STEAM AT 540°C and 600 psi

Composition, w/o	Test Time, days	Avg Rate of Wt Gain, mdd
3 Ni-0.5 Fe	210	1-2
2 Ni-0.5 Fe	129	3
0.5 Fe-0.5 Cu	104	2
2 Fe	129	4

Average rates of weight gain refer to the relatively constant period which develops after the first few days of exposure. They are determined by periodic weighings of the samples as removed from test. Close inspection reveals slight spalling of oxide at sharp edges, resulting in errors in the calculated rates. Efforts are under way to develop non-destructive absolute methods of determining rates. Weight gain rate (mdd) can be converted to mils per year average penetration rate by multiplying by 0.64.

Embrittlement due to absorption of corrosion product (or radiolytic) hydrogen represents a potential barrier to the use of zirconium alloys as cladding. For this reason, it is desirable to study the distribution of corrosion product hydrogen and its effects on properties of interest. Initial studies in this area have begun and are discussed below.

Appreciable quantities of hydrogen are absorbed, e.g., a Zr-2.8 w/o Ni binary alloy contained 723 ppm hydrogen after 235 days in superheated steam at 540°C and 600 psi. Allowing for the initial hydrogen content of 99 ppm, this content was 66% of the calculated corrosion product hydrogen. However, there is evidence that the rate of absorption decreases with exposure time. For example, the Zr-3 w/o Ni-0.5 w/o Fe alloy absorbed 93% of the corrosion product hydrogen during the first 35 days of exposure. During the next 62 days, the amount absorbed fell to 36%.

There has been no hardening of any of the samples, including the one with 723 ppm hydrogen. In fact, some of the samples are actually softer after exposure to steam. It has been demonstrated (by heating in vacuum) that annealing takes place at corrosion test temperature.

5. Corrosion of Ferrous Materials in Water (W. E. Ruther)

As a structural (or cladding) material, carbon steel or a low alloy steel would be preferable to stainless steel because of lower cost and somewhat lower cross section. Mild steels have generally been felt to corrode too rapidly to be used in water where there is risk of the presence of dissolved oxygen. However, there have been indications that it is only a low concentration of oxygen which is harmful; that greater amounts might provide inhibition.

The effects of temperature and oxygen content of the water on the corrosion behavior of electrolytic iron have been investigated over a range of values. The results may be summarized as follows:

When sufficient oxygen is present at temperatures from 100 to 260°C, a smooth tightly adherent corrosion film is formed and no pitting or accelerated attack is noted. The color of the thin temper film changes only slightly from 3 to 30 days of exposure. Defilmed samples give metal losses that indicate a very low corrosion rate.

If slightly less than adequate oxygen is present in the water, the temper film forms, but pitting and undercutting of the film take place at numerous sites. The average metal loss rates are still low but pit sites are deep.

As the oxygen concentration is decreased further, depending on the temperature, the attack becomes general and, by comparison, quite rapid.

Finally, as the oxygen content is reduced to about 0.1 ppm, the attack is uniform and the corrosion rate is low. However, the rate under these conditions is faster than for the adequate oxygen case and the corrosion product is only loosely attached to the specimens.

The regions of temper film formation are shown in Table XXIII.

In addition, several steels were tested in 260°C, 35-ppm-oxygen water. All had microscopic pitting and a slight amount of light brown corrosion product after 3 days of exposure. The test was continued for an additional 160 days.

Table XXIII

CORROSION BEHAVIOR* OF IRON
IN WATER CONTAINING OXYGEN

Temp, °C	Oxygen Content, ppm			
	~35	~50	~290	~540
50	P	P	P	P
100	P	P	P	T
150	P	T	T	T
200	P	-	-	T
260	P	P	T	T
315	P	-	-	-

* T = temper film in 3-day test.

P = pitting noted in 3-day test.

The metal losses were of the order of $\frac{1}{2}$ mg/cm² for this period, and the pitting did not continue. Since this was a region of pitting performance (Table XXIII) for iron, it suggests that the steels (212B; T-1; A285; Croloy 5) form a protective film with less oxygen than the pure iron. Currently, experiments with arc-melted alloys of iron are being performed to determine those elements most beneficial in this respect.

The benefit from operating in the temper film region is twofold for reactor applications. First, the corrosion rate is lower than for the typical low-oxygen conditions. Second, and more important, the nature of the corrosion product is such that much less of it would be expected to be released to the water stream. This would decrease the "crud" problem in an operating system.

6. Corrosion of Structural and Cladding Materials in Superheated Steam (540°C, 600 psi) (S. Greenberg)

Three groups of ferrous alloys have been under test for periods up to about one year. Results are summarized in Table XXIV and the comments that follow. Although all materials may be serviceable, it is clear that the 18-8 stainless steels are superior to the others tested.

The stainless steel samples are covered with a dulling tarnish film, with isolated areas of grey film and rust colored spots. Metallographic examination after 117 days indicated carbide precipitation but no intergranular corrosion. Future metallographic examination will also check for formation of sigma phase.

Table XXIV

CORROSION OF STEELS IN SUPERHEATED
STEAM AT 540°C AND 600 psi

Material	Test Time, days	Wt Gain, mg/cm ²
304 S.S.	374	0.2
347 S.S.	374	0.1
Martin Alloy 258: 7 Al; 5 Cr; 0.5 Ti; 1 Nb; Bal. Fe	286	80.5
Martin Alloy 259: same as 258	286	80.4
Martin Alloy 261: 7.5 Al; 5 Cr; 3 Nb; 0.5 Zr; Bal. Fe	286	30.8
Croloy 2 $\frac{1}{4}$ (Sample #1)	120	5.1
(Sample #2)	120	5.6
Croloy 5 (Sample #1)	120	4.6
(Sample #2)	120	3.9

The Martin iron-aluminum alloys are covered with a relatively heavy grey scale. A few, small, rust-colored pits are visible at 15X magnification. The Croloy samples were covered with a flaking dark grey film. Weight change data are therefore of little value. The tests on the Croloys have been terminated. The other materials remain in test.

7. Corrosion of Structural Materials in Dilute Phosphoric Acid Solution (S. Greenberg)

18-8 stainless steels tested for six months (see ANL-6099) at 315°C in degassed phosphoric acid (pH 3.5 at room temperature) were examined metallographically. Only the sensitized 316 showed intergranular corrosion. Corrosion rates were low. Weight losses ranged from about 1 to 1.5 mg/cm² for most samples. However, one annealed 304 sample lost only 0.1 mg/cm². One sensitized 316 sample lost 2.2 mg/cm².

Low carbon steel is protected by a sprayed and diffusion heat-treated coating of aluminum alloy X8001 in the same phosphoric acid environment at 315°C. Adequately heat treated samples (732°C for 2 hr in vacuum) showed no failure of the bond after 100 days with the aluminum-steel interface exposed to the solution.

This work is described in detail in ANL-6206 (to be published): Corrosion of Some Reactor Materials in Dilute Phosphoric Acid, J. E. Draley, S. Greenberg, and W. E. Ruther.

8. Light Alloys Suitable for Use with Mercury at Elevated Temperatures (J. Y. N. Wang and S. Greenberg)

The proposed Lunar Reactor requires the use of a lightweight tubing material that will resist liquid mercury at elevated temperatures. Information regarding the compatibility of lightweight metals and alloys with mercury at the temperatures of interest are not available. This project consists of two main phases. The purpose of the initial phase is to evaluate the corrosion resistance of commercially available titanium alloys. If the results of this first phase are not favorable, the second phase will deal with new alloy development and inhibitor evaluation.

Preliminary work began in September, 1960. Static corrosion tests were conducted in a constant-temperature-and-pressure system at 370°C (700°F) and 100 psia for time periods of 7 and 30 days. Commercially pure titanium, titanium alloy Al10-T (Ti-5 Al-2.5 Sn), and Type 304 stainless steel were included in these tests. The latter material was added for the purpose of comparison. The results of these tests are shown in Table XXV.

Table XXV

MERCURY CORROSION TESTS AT 370°C AND 100 psia
STATIC TEST SYSTEM

Sample	Length of Test, days	Weight Change,* mg/cm ²	Remarks
Commercially pure Ti	7	1.796	Pin-point pitting attack all over.
	30	1.118	Pitting attack to depth of 2 mils.
Ti Alloy Al10-T	7	0.870	Slightly attacked. Some discolorations.
	30	**	Adherent black coating on polished surfaces.
S.S. #304	7	nil	No visible attack.
	30	nil	No visible attack.

*Average of two samples.

**Weight change was not calculated due to difficulty in removing the corrosion product.

In the 7-day test period, commercially pure titanium suffered a pin-point pitting attack. This attack was accelerated during a 30-day exposure. Titanium alloy Al10-T was slightly corroded in the first test. It was partially attacked on the polished surfaces, showing adherent black powdery coatings. These coatings were not dissolved in nitric acid or decomposable at high temperatures (450 to 500°C) in an evacuated system. There was no significant weight or surface changes of the stainless steel specimens in both exposure periods.

Metallographic examination revealed that titanium alloy Al10-T was almost uniformly attacked in the 30-day test (Figure 25); no intergranular penetration was observed. X-ray diffraction indicated the presence of HgTi_3 in the corrosion product (black coating).

Figure 25. Titanium Alloy Al10-T Following Exposure to Mercury.

Micro 29520

250X

Test condition: Static, 370°C (700°F) and 100 psia, 30 days.

A small amount of titanium in the mercury after exposure has also been identified (by spectroanalysis). The lack of corrosion resistance of titanium and titanium alloy Al10-T is apparently attributable to the solubility of titanium materials in mercury under test conditions.

Oxygen and nitrogen are two main impurities found in titanium. The extent of contamination varies with method of preparation. A short-term test has shown that gaseous oxygen has no effect on the corrosion resistance of titanium and titanium alloy Al10-T in mercury at 370°C. However, mercury reacted with oxygen at an accelerated rate at test temperature, forming an orange compound that floated above the unreacted mercury. The effect of nitrogen on the corrosive properties of mercury and of titanium and its alloys will be also studied.

I. Nondestructive Testing Developments

1. Ultrasonic Techniques

Ultrasonic techniques are useful for measuring material properties and for the nondestructive evaluation of nuclear materials. The ultrasonic techniques program at ANL includes the measurement of elastic constants of single crystals, Lamb wave propagation, ultrasonic inspection of tubing, ultrasonic inspection of uranium and Zircaloy rod, and ultrasonic attenuation in engineering materials.

Lamb Waves (R. A. di Novi)

During the past year a theoretical and experimental study of Lamb waves has been made. Lamb waves are waves that are transmitted in a medium when the thickness of the medium and the wavelength of the ultrasonic radiation are of the same order of magnitude.

In addition to verifying the theoretical frequency-thickness curves experimentally, a number of possible applications of Lamb waves have been investigated. Lamb waves have been investigated for detecting unbonded areas. An area of nonbond will appear as a thin plate and a Lamb wave mode will be generated over this region when the proper frequency-thickness condition is satisfied. Over a region of good bond, a frequency-thickness relationship will no longer be satisfied and the Lamb wave will no longer be generated. Thus the appearance of a Lamb wave mode would indicate nonbonded area. It has been found that Lamb waves can be generated in thick plates, although their amplitude is small relative to thin plates. This great decrease in amplitude is to be expected as the available energy must be shared over the larger number of modes that occur at large frequency-thickness products.

Experiments have been carried out to determine the effect of stress and fatigue in aluminum plates on Lamb wave propagation. As yet no correlation has been found between velocity and stress in aluminum specimens. Lamb waves have also been investigated for the inspection of welds in thin materials. No significant results were obtained from these experiments.

Ultrasonic Attenuation (R. G. Peterson)

An investigation is underway to determine the ultrasonic attenuation as a function of temperature in engineering materials. In order to carry out this investigation it has been necessary to make a number of experiments concerned with portions of the overall problem. A rather critical examination of couplants for use in this application has been required. Since attenuation measurements are to be made, it is absolutely essential to know the effect of the couplant on the attenuation. It has been necessary to devise electronic circuitry which will adequately display the echo pattern without generating additional signals.

Investigation in some detail of the effect of surface roughness of the specimen has been necessary. The effect of surface roughness may affect the amount of energy that is transmitted into the specimen. The surface roughness on the sides of cylindrical specimens may affect mode conversion and cause "extraneous" reflections. The echo pattern received from such specimens is rather complex, and a detailed analysis has been made to determine the origin of all echoes. Finally, it has been necessary to construct the vacuum equipment and necessary furnace to carry out the measurements.

2. Eddy Current Techniques

An Electromagnetic Reflection System Using Pulsed Inductive Fields (C. J. Renken)

In 1959, a method of producing inductive fields of small cross-sectional areas was developed. This technique was first used in a through-transmission system which measured the amount of delay of the current field as it diffused into the metal. This technique had the disadvantage of requiring circuit elements on both sides of the metal; for instance, when inspecting tubing, the field source was outside of a tube, and the pickup inside. For long tubes or pipes and in many other situations this was inconvenient or even impractical. This year a technique for using the small area inductive fields with field source and pickup on one side of the metal was devised. Instead of a measurement of pulse delay, reflections of the field from internal discontinuities are detected. Circuitry has recently been devised which allows electronic separation of the surface reflections

and reflections from the possible internal discontinuities. This method is capable of providing a high-resolution inspection of tubing with wall thicknesses too thick for previous methods. It has also shown promise as a sensitive method for inspecting certain types of welds.

Eddy Current Inspection Techniques (K. R. Bell)

A probe type eddy current equipment is being used to evaluate redrawn Zircaloy-2 tubing.

A technique for inspecting 0.055-in.-diameter Zircaloy-3 wire has been completed. A sample of good and cracked wire were examined with an eddy current instrument. Good correlation was obtained between the defective wire and the eddy current results.

Eddy current thickness measurements have been made on prototype Borax-V fuel elements. The system will measure cladding thickness provided there is sufficient uranium in the core alloy.

3. Neutron Techniques (H. Berger)

The photographic detection of neutron images is being investigated, with at least one long-range objective being to apply neutron radiography as a useful inspection method for nondestructive testing. Because neutrons have little influence on normal photographic emulsions, it is necessary to use intermediate materials next to the film. These materials emit photographically detectable radiation when bombarded with neutrons. The intermediate materials used thus far include a B^{10} -loaded zinc sulfide phosphor, cadmium, rhodium, indium, silver and gold. These materials have been rated as to neutron photographic speed, and as to image resolution qualities and relative response to neutron and gamma radiation. In regard to the speed comparison all the materials have been rated against a silver screen which has arbitrarily been assigned the rating of one. On this basis, the scintillator speed rating is 6.61, rhodium 1.93, indium 1.46, cadmium 1.32, and gold 0.37. Work is still in progress concerning resolution qualities for these intensifier materials. At this time it appears that rhodium, indium, silver, and gold will yield useful image resolution. Cadmium and the scintillator material are both very poor as far as resolution is concerned. In the case of cadmium, the hard gamma radiation from the end gamma reaction probably contributes appreciable image unsharpness.

The responses of these intensifier materials in film to gamma radiation have also been investigated to choose the best material for use in a mixed radiation beam. Neutron radiography is potentially useful because the relative neutron absorptions of materials is different from those for gamma radiation. Since gamma radiation is almost always associated with a neutron beam, it is desirable to apply a combination of material and film

having a low response to gamma radiation in order that the desired neutron image not be masked by gamma rays. Using this criterion, rhodium appears very good for use in such mixed-radiation beams. Silver, cadmium, and indium are good, with gold and the scintillator being the least desirable.

Another method of eliminating completely the effect of gamma radiation is to use a radioactive foil transfer imaging technique. In this technique, the film itself is not exposed to the neutron-gamma radiation field. Only the foil material which becomes radioactive is exposed to this radiation. The radioactive image carrying foil is then transferred to a sheet of film in order to produce a visible image of only the neutron image. Several materials have been investigated for use with this imaging method. In the neutron flux from CP-5, rhodium and silver do not appear to be useful for this technique. A large portion of the activity associated with these materials which is contributed by very short-lived active isotopes means that a large part of the photographic effect produced by these materials occurs during the neutron exposure or very shortly afterwards. Transfer techniques with these materials are therefore very inefficient and are generally not useful at all except in a suitably higher neutron flux. Indium and gold appear to be useful in this neutron flux and require exposures in the order of hours.

A Van de Graaff accelerator has also been investigated as a source of neutrons. Advantage of using this neutron source is the yield of uniform neutron flux over a larger inspection area and the opportunity to investigate the effects of a fast neutron beam and the effects of white thermal neutron beam. In the preliminary experiments using the Van de Graaff, difficulties were encountered in the problem of low effective neutron flux, the effect of gamma radiation in the beam, and poor image sharpness.

4. Radiography of Fuel Elements and Reactor Components (N. S. Beyer*)

Work on the assay for U^{235} content by gamma-ray spectroscopy is continuing. During the past year this technique has been applied to Juggernaut fuel elements and to the Fast Flux Reactor fuel plates.

An experiment has been set up to evaluate the Borax-V fuel elements for U^{235} content when they are delivered. Equipment has been installed and calibrated for use in alpha particle detection on the Borax-V superheater plates. Calculations indicate that approximately $6 \pm 0.12 \mu\text{gm}$ or more of enriched uranium, alpha contaminated, can be detected per plate side.

*Special Materials and Services Division.

During the year, gamma-ray spectrographic assay techniques have been improved. Precision total area scanning now eliminates the necessity of measuring the dimensions of the core area and the standard foil area.

The development of a gamma-ray counting technique to determine total uranium is also in progress. Encouraging results have been obtained for the case of an aluminum-uranium alloy core.

The Picker Polaroid X-ray film has been evaluated. This film appears to be satisfactory for determining the width of side and end clad in fuel elements, and it is a much faster process than ordinary film radiography. The sensitivity, resolution, and reproducibility compared with ordinary X-ray film is being evaluated for various applications.

In usual applications of radiography, scattering of the X-ray energy cannot be prevented. It is an undesirable situation and tends to fog the film. A technique is being developed in which use is being made of the scattered radiation to form radiograph images. The scatter-type image is not as sharp as ordinary radiographic images but has been found to be useful in certain specialized cases.

J. Metallurgical Assistance to the Fast Reactor Safety Program

1. Thermocouple Fuel Elements for TREAT (F. D. McCuaig)

The problem of joining dissimilar metals metallurgically for use in fuel elements and irradiation capsules has been investigated, and the results are given below.

Four stainless steel-to-tantalum seal samples were made for the Reactor Engineering Division. The samples simulated a tantalum-sheathed thermocouple, 0.040 in. in diameter, passing into a stainless steel-clad fuel element. Leak testing and metallography proved the joints to be satisfactory.

Six instrumented EBR-II simulated fuel pins having tantalum-sheathed, tantalum-molybdenum thermocouples embedded in each pin by zone melting were received from a vendor. The natural uranium has failed to bond to the tantalum sheath. These pins were salvaged by induction brazing in a helium atmosphere using ANL #11* brazing alloy, which was developed by the Metallurgy Division last year.

End closures were also made on four completed EBR-II-type fuel rods. These rods were filled with sodium and had a 40-mil tantalum-sheathed thermocouple passing through the end cap. The seals between

*84 w/o Zr, 8 w/o Ni, 8 w/o Cr.

the tantalum sheathed thermocouple, the 304 stainless end plug, and the 304 stainless steel fuel tube were made simultaneously by induction brazing in helium, using GE #81 braze alloy.

In addition to this closure, an end plug located 3 in. above the fuel tube on the thermocouple was also brazed as above to permit welding the end plug to a containing vessel.

2. Samples for TREAT Metal-Water Meltdown Experiments (F. D. McCuaig)

At different times in the past year the Metallurgy Division has delivered to Chemical Engineering a total of 44 meltdown specimens to be used in the TREAT reactor. These specimens varied in material, shape, and composition, as summarized in Table XXVI.

Table XXVI

TREAT MELTDOWN SPECIMENS

Fuel Material	No. Required	Cladding Material	Density (g/cc)	Enrichment (%)
Specimen: Right Cylinders 0.320 in. OD x 0.500 in. Long				
81.52 w/o ZrO ₂ -	{ 6	A288 Aluminum	4.92	93
9.06 w/o CaO-		Zircaloy-2	4.92	93
8.68 w/o UO ₂ -		304-L SS	4.92	93
0.74 w/o Al ₂ O ₃	{ 4	304-L SS	6.11	93
10 w/o UO ₂ -		None	6.11	93
304-L Stainless		None	5.99	normal
Steel Dispersion		None	4.97	93
10 w/o U ₃ O ₈ -	4	None	5.88	normal
304-L Stainless				
Steel Dispersion				
Specimen: Plate 0.100 in. x 0.500 in. x 1 in.				
10 w/o UO ₂ -	6	None	5.55	93
304-L Stainless				
Steel Dispersion				

3. TREAT Experimental Dummy Fuel Rods (F. D. McCuaig)

Four of these elements were made to hold irradiation samples at the time the regular TREAT fuel loading was made. Four additional elements of this type were later requested to accommodate the additional numbers of samples to be irradiated. The original elements were clad in a Zircaloy-3 tube, 8 ft long. A considerable cost saving was made by joining two acceptable 4 ft sections, removed from tubes rejected from the regular fuel loading because of welding defects.

4. TREAT Slot Liner and Capsule Assembly (F. D. McCuaig)

One of these assemblies, which is approximately 50 x 20 x 3 in., was made of Zircaloy-3. The assembly consisted of a Zircaloy-3 capsule assembly, which contains the irradiation sample, and a Zircaloy-2 liner assembly in which the capsule is inserted. The complete assembly is inserted into the center of the reactor through the access hole fuel elements.

The widest Zircaloy-3 sheet stock available was 9 in. wide x 0.025 in. thick. Considerable TIG welding was required to complete the assembly, as well as resistance welding to attach stiffeners to support the 0.025-in.-thick Zircaloy-3 sheet. The complete assembly was leak tight.

5. Ceramic Engineering Assistance to the Fast Reactor Safety Program (J. H. Handwerk, D. C. Hill)

The ceramic engineering rendered assistance to other divisions of the Laboratory by developing and fabricating fuel samples. A summary of this work is as follows:

ZrO₂-CaO-UO₂: Seventeen fuel specimens were fabricated for the metal-water experiments performed in the TREAT reactor. These specimens were composed of 81.52 w/o ZrO₂, 9.06 w/o CaO, 8.68 w/o UO₂ (93%), and 0.74 w/o Al₂O₃. They were fabricated by cold compacting a mixture of ZrO₂, U₃O₈, and CaCO₃, and then sintering this mixture in air to 1700°C. The specimens were approximately 0.320 in. in diameter and 0.500 in. in length, and had an average density of 4.93 g/cc.

UO₂-304 ELC Stainless Steel: A total of 28 fuel specimens were made for the TREAT water-metal experiments. Six plates measuring 0.90 x 0.46 x 0.10 in., and 8 cylinders measuring approximately 0.30 in. in diameter x 50 in. in length were made with fully enriched UO₂. These specimens were made by cold compacting a mixture of 10 w/o UO₂ and 90 w/o stainless steel, and sintering these compacts in vacuum at 1200°C for 1 hr. The average density of these specimens was 5.56 g/cc.

Six cylinders containing 10 w/o normal UO_2 were made in a similar manner, and sintered. Four cylinders containing 10 w/o UO_2 and 4 cylinders containing 10 w/o U_3O_8 were pressed but not sintered.

K. Miscellaneous Developments

1. Operation of the ANL-2 High-pressure Water Loop in MTR (C. C. Crothers)

The ANL-2 high-pressure water loop has been in operation in MTR for over six years. During this period, a steadily increasing amount of suspended solids has been observed in the coolant water. These solids proved troublesome in that they plated out on heat transfer surfaces and caused fuel specimens to reach undesirably high temperatures during irradiation.

Early in 1960, the loop was decontaminated and cleaned by a chemical procedure in order to remove the particulate material that had accumulated but which was not successfully filtered out. The procedure used and the results obtained are described in ANL-6151, Chemical Decontamination of the ANL-2 High-Pressure Water Loop. The treatment used approximately 70% of the corrosion film on the internal loop surfaces and lowered the total solids content in the coolant to <0.5 ppm.

2. Procurement and Inspection of Fuel Tubes for CP-5 (L. C. Hymes)

Specifications are completed, and approximately 30% of the tubes for the three fuel tube subassemblies required for operation up to 10 Mw have been received.

Initial difficulties in controlling the fuel core configuration at the core ends appear to have been overcome by the vendor.

A blister anneal test on each tube between extrusion and cold drawing has been initiated in an attempt to insure that only tubes with acceptable bond integrity are used for operation at the higher power levels.

Attempts to use an eddy current apparatus to measure cladding thickness have proved unsuccessful to date. Autoradiography has been used with some success in interrogation of pits in the cladding on the outside diameter. Densitometer measurements of radiographs of the fuel core ends have been used satisfactorily in determining relative core thickness at this position.

PART II
BASIC METALLURGY

A. Preparation of High-purity Materials.

1. Preparation of High-purity Uranium (G. B. O'Keeffe and L. T. Lloyd)

Preparation of high-purity uranium was discontinued temporarily during 1960 in order to divert available manpower to the preparation of high-purity plutonium (see below). An adequate inventory of the material is available for immediate programmatic research needs. A total of 29 melts were made to the time of casting the last ingot in July, and 28 ingots, with a total weight of 76 kilograms, were obtained. Disbursements were made in various quantities to the following organizations during 1960:

Chemistry Division - ANL
Comision Nacional de Energia Atomic (Argentina)
Nuclear Metals, Inc.

Metallurgy Division research programs consumed 13 kg during 1960.

2. Preparation of High-purity Plutonium (M. B. Brodsky)

Experimental work in connection with the electrefining of plutonium has continued during the past year. The studies on Cell IV which were begun toward the end of 1959 have been completed. The cell was described briefly in the 1959 Annual Report (ANL-6099). It was made of Vycor, and it was operated with PuF_4 dissolved in specially dried KCl-LiCl eutectic as the electrolyte, with impure plutonium anodes and with irradiated tantalum cathodes.

Thirty-three runs were made intermittently over three and one-half months, with a total production of 406 gm of plutonium at an overall recovery of 65%. The metal recovery in the last 30 runs was 88%. When it was necessary to discontinue operation for repairs to the water-cooling system, a total of 215gm of plutonium was in the cell. An additional 400 gm of electrodeposited plutonium probably could have been prepared before the 300-gm permissible buildup limit was reached.

Analytical Results: Analyses of buttons M31 and M34, which were obtained near the end of the cell operation, are given in Table XXVII. Also listed in the table, for comparison, are data from earlier runs taken from the last Annual Report. The data for silicon, uranium, and tantalum were obtained during the past year.

Uranium analyses in the earlier runs were generally lower than those obtained in previous cells (see ANL-6099). The tantalum results are generally low except for M23, M31, and M34. Since the tantalum analyses for M31 and M34 were performed after most of the neutron-induced radiation had decayed, these data might have greater error than the earlier results.

Table XXVII
ANALYSES OF HIGH-PURITY PLUTONIUM

Sample Identification	M19	M20	M21	M22	M23	M27	M31	M34	LM5 (M30, M31)		
Deposited in Run No.	6	7	8	9	11	15	23,24	31,32,33	Top	Center	Bottom
Element	Composition in Parts Per Million by Weight										
H	5	7	6	6	16	5	10	12	8	7	8
C	25	62	44	33	43	20	44	43	63	54	44
N	<5	<5	17	6	7	6	N.D.	N.D.	33	11	19
O	14	4	5	4	13	8	N.D.	N.D.	9	13	12
Si	5	27	14	26	17	13	N.D.	N.D.	N.D.	N.D.	N.D.
U	9	16	8	31	7	10	39	24	47	51	41
Am ²⁴¹ (a)	4	4	3	0	5	2	0	137	158(d)	122(d)	147(d)
Al	<2	<2	<5	5	<2	<2	10	3	20	20	20
Ca	<2	<2	<2	<2	<2	<2	<2	<2	<3	<3	<3
Cr	1	10	2	8	4	1	15	<1	25	20	15
Cu	N.D.(c)	N.D.	N.D.	N.D.	N.D.	N.D.	10	2	10	10	8
Fe	<4	<4	<4	17	<4	<4	15	<5	15	15	15
Ga	<0.2	1	3	15	2	<0.2	5	1	6	8	6
K	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	7	<5	<5	<5	<5
Li	0.4	0.5	3	3	0.4	0.2	1	0.4	0.05	0.03	0.01
Mg	<1	<1	<1	<1	<1	<1	<2	15	<2	<2	<2
Mn	0.1	0.5	0.5	2	0.5	0.05	1	0.1	1	1	1
Mo	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	3	<1	2	4	4
Na	<2	<2	9	<3	<2	<2	7	<3	<3	<3	<3
Ni	<1	5	3	30	10	<1	20	2	25	25	20
Pb	1	3	2	3	2	<1	3	<1	5	5	5
Pu ^(b)	6	2	1	1	27	1	11	9	29	9	2
Zr	<1	<1	<1	<1	<1	<1	<1	<1	<2	<2	<2

(a) Am²⁴¹ grows in with time. Data are corrected to date of electrolysis, except for LM5.

(b) Pu was determined by irradiation of cathodes.

(c) Not determined for this sample.

(d) Not corrected to date of electrolysis.

In general, the purity of M34 was comparable to the purity of the earlier cell IV runs, except for the ultra-pure M19 and M27. The total impurity content of M31 is higher by about a factor of two. High values for potassium and sodium content imply that some of the impurities in M31 may be due to trapped salt. The source of the high americium in M34 is not understood.

Liquation: Table XXVII also lists the data from the top, center, and bottom slices of reasonably high-purity metal, LM5, which was directionally solidified under vacuum. The metal was from buttons M30 and M31, and it was melted in a high-purity MgO crucible at 700°C for 30 min. In general, the impurity contents of M31 and LM5 agree within experimental errors; also, there is no definite pattern of liquational segregation of impurities.

The present apparatus appears to be adequate for consolidation of high-purity buttons without causing further contamination, but liquation does not seem to improve the metal purity. Further work on liquation and consolidation will not be undertaken until sufficiently large quantities of electrolytic plutonium become available to permit better analytical statistics.

Density: Densities of cast plutonium samples were determined by measuring the loss in weight by immersion in CCl_4 ; the results are given in Table XXVIII. The data indicate that metal containing less than 200 ppm by weight of impurities is needed to obtain as-cast densities of 19.60 gm/cm^3 ; the density-impurity relationship would, of course, depend on the specific impurities present.

Table XXVIII

AS-CAST DENSITY OF PLUTONIUM.^(a)

Sample	Approximate Total Impurity Content ^(b) (ppm by weight)	Density at 25°C (g/cm^3)
LM3	800	19.32-19.34
LM5	200-300	19.52-19.56
LM5 (Top)	200-300	19.56
LM5 (Center)	200-300	19.50
LM5 (Bottom)	200-300	19.57
M18	65 ^(c)	19.65
M25	100 ^(c)	19.62
M27	66	19.61

(a) Theoretical density = 19.84 g/cm^3

(b) Not including Am content

(c) Approximate

Use of Cs_2PuCl_6 Electrolyte for Electrowinning Plutonium*;

The double chloride of cesium and plutonium may be prepared by aqueous methods¹¹ to yield a water-free solid salt. The usefulness of this salt in plutonium electrolysis is being studied. A number of mockup runs were made with Cs_2UCl_6 , as a stand-in for the plutonium compound, in an attempt to electrowin the metal. In these runs, graphite anodes were used with molten lead cathodes at 700°C . Electrical contact was made to the cathode

*Including work by G. Carleson, on leave from AB. Atomenerg;,
Lövholmsv. 7, Stockholm, Sweden

¹¹ J. Kooi, E. Weisskopf and D. M. Gruen, Solubilities of Cs_2UCl_6 , $\text{Cs}_2\text{UO}_2\text{Cl}_4$ and Cs_2PuCl_6 in Hydrochloric Acid, J. Inorg. Nucl. Chem. **13** 310 (1960).

with a submerged molybdenum wire which was insulated from the bath by a quartz tube. Uranium yields up to 73% were obtained.

Similar attempts to obtain plutonium from solutions of Cs_2PuCl_6 in CsCl at 700°C were unsuccessful; the cells made use of graphite anodes and cathodes of molten plutonium in MgO . Examination of these cells indicated that the tantalum lead wires might have been exposed to the salt, and, although the cell potential (2.8 v) was lower than the expected potential for cesium deposition, a dark reaction product was found on the wall of the quartz cell. This deposit was very similar to reaction products found in cells wherein cesium was deposited from CsCl .

A further attempt to obtain plutonium was made in a Vycor cell with a graphite anode and a tantalum cathode at 700°C . Ten weight percent Cs_2PuCl_6 was dissolved in CsCl to form the electrolyte, and the electrolysis was carried out at a potential of 3.2 v and a current of 0.45 amp for 8.75 hr. Examination of the cooled cell showed the presence of a small amount of plutonium beads on the cathode, but the salt still had the yellow color of Pu IV. When the cathode deposit was melted in NaCl-KCl , the salt turned to the blue color of Pu III. The total yield of metal was only 0.42 gm, corresponding to an efficiency of 4.7%.

The low yield and the presence of Pu IV in the electrolyzed salt implies a high residence time for Cl_2 in the salt mixture, so that the Cl_2 formed at the anode is able to reoxidize the Pu III in solution and also any metal formed at the cathode.

Use of Cs_2PuCl_6 Electrolyte for Electrorefining Plutonium:

A 14-w/o solution of Cs_2PuCl_6 in KCl-LiCl eutectic has been electrolyzed at 550°C , using impure plutonium anodes and tantalum cathodes. Although an initial back emf was observed, which is believed to be associated with residual water in the salts, it all but disappeared after 1.5 amp-hr of break-in operation. Only 0.15 gm of metal were recovered in this run. In the following run, 3.83 gm of metal were recovered at 0.6 v and 1.5 amp, with a material efficiency of 70%. The work with this cell is being continued.

Production of High-purity Plutonium: The past studies have shown that high-purity plutonium can be deposited from fused salt electrolytes containing PuF_4 and KCl-LiCl eutectic. Equipment making use of this electrolyte is currently being set up in the temporary Bldg. 40 facilities to produce sufficient quantities of the metal to satisfy immediate research needs. Two small gloveboxes are being assembled: one box contains a resistance furnace for operating a cell of the same design as Cell IV; the other box contains a furnace for anode preparation and deposit consolidation. The furnaces have been installed in the boxes, and the cooling water system is nearly completed. It is planned to use dry nitrogen as a box atmosphere, together with a cell cover gas of either argon or helium. These small boxes will be incorporated into the permanent high-purity plutonium refining setup in the plutonium facilities of the new metallurgy building.

B. Texture Studies

1. Recrystallization of Room-temperature-rolled Uranium Sheet (L. T. Lloyd and M. H. Mueller)

The early work of this study was reported by Yario and Lloyd.¹² The large grain size in the specimens caused heterogeneous deformation in the final rolling and made it impossible to obtain quantitative measurements of preferred orientation by X-ray diffraction techniques. To overcome this difficulty and to permit correlation of microstructural observations, thermal expansion behavior, and X-ray preferred orientation measurements, the study has been continued with high-purity material prepared in a manner such that the starting grains were uniform and small in size. The last annual report (ANL-6099) gave some of the early observations of this investigation. The experimental work now has been completed, and the results are summarized in the following.

In general, the metallographic and thermal expansion results are similar to those of the previous work with the heterogeneous material. The early stages of recrystallization at low and moderate temperatures were accompanied by the formation of very fine grains which were then absorbed by discontinuous growth of larger grains. Mean thermal expansion coefficients in a direction transverse to the rolling direction and lying in the rolling plane, for samples annealed to complete recrystallization at temperatures up to 400°C, were not significantly different from those of as-rolled specimens; samples annealed at higher temperatures had appreciably different coefficients. The expansion coefficients for a direction parallel to the rolling direction following complete recrystallization at 360°C showed a decrease from those for the as-rolled material, and as the annealing temperature was increased the decrease in expansion coefficient became greater.

At the time of the last annual report, X-ray data had been obtained for the first three of the following sets of samples. Discussions of the preferred orientations at that time were not possible because the data for annealing at the higher temperature were not available. During the past year the X-ray data have been completed for the following five different conditions:

1. As rolled
2. Annealed 300 hr at 380°C
3. Annealed 15 hr at 400°C
4. Annealed 15 hr at 450°C
5. Annealed 300 hr at 380°C plus 15 hr at 450°C.

The 400°C anneal produced a condition close to that resulting from the 380°C anneal; the discussion will therefore be limited to sets 1, 2, 4, and 5 only.

¹² W. R. Yario and L. T. Lloyd, Recrystallization of Heavily Cold-rolled Uranium Sheet, ANL-5966 (May 1959).

Figure 26 shows the (020), (110), (002) and (200) pole figures for the four conditions indicated above. Since the material was fabricated to give symmetry around the rolling and transverse directions, only one quadrant is needed for each pole figure. Each composite pole figure therefore has one quadrant for each of the conditions.

The (020) pole figures for the as-rolled and annealed conditions are very similar, with maxima in the rolling direction; however, recrystallization results in a significant increase in intensity at the maximum.

The (110) pole figures show more striking differences. The as-rolled figure has a high intensity band located approximately 15° from the rolling direction toward the normal direction and spread out toward the transverse direction. The three pole figures for the recrystallized conditions show a spread of high intensity between the rolling direction and the transverse direction, but the significant feature is the buildup of intensity at a point about 30° from the normal direction toward the rolling direction. This buildup for the sheet annealed 300 hr at 380°C gives conclusive proof of orientation changes occurring upon recrystallization at low temperatures.

The (002) as-rolled pole figure has two regions of high intensity: the highest is approximately 20° from the normal direction toward the rolling direction, and the other is at approximately 30° from the normal direction toward the transverse direction. The two maxima are retained in approximately the same intensity for the low-temperature annealed and duplex-treated material; annealing at 450°C , however, wipes out the maximum between the normal direction and the rolling direction.

The (200) pole figure of the as-rolled material shows an intensity spread from near the rolling direction toward the transverse direction. Recrystallization results in the appearance of a maximum in the normal direction with a spread out toward the transverse direction. Here, too, the pole figure for the 380°C annealed material indicates a distinct preferred orientation change from that of the as-rolled material.

The work with the homogeneously deformed material has shown that high-purity uranium sheet reduced approximately 80% in thickness at room temperature and recrystallized at low temperatures has a different preferred orientation than the as-rolled material, contrary to the observations reported by Cabane and Petit.¹³ Annealing at higher temperatures is accompanied by further changes in the recrystallized preferred orientations. These changes with annealing temperature may be related to the metallographic observations of initial recrystallization to extremely fine grains followed by discontinuous growth to larger grains.

¹³ G. Cabane and J. Petit, Study of the Annealing of Rolled Uranium, *Revue de Metallurgie* 51 603-613 (1954).

2. Recrystallization Textures in Deformed Single Crystals of Alpha Zirconium (L. T. Lloyd)

In a study of orientation relationships between deformed single crystals of alpha uranium and grains grown in them by annealing, it was found that a singular relationship could be developed if the recrystallized grains were considered to originate from deformation twins as well as from the parent crystal.¹⁴ Similar studies have been carried out with single crystals of cubic materials, but mechanical twins are not important in the deformation of these crystal structures. A study has been undertaken to determine if the relationship between twins and recrystallized grains applies to hexagonal metals where twinning is a significant deformation. Because of the large number of twin systems found in alpha zirconium ($\{10\cdot2\}$, $\{11\cdot1\}$, $\{11\cdot2\}$ and $\{11\cdot3\}$ twinning planes),¹⁵ it was chosen for this work.

The single crystals were oriented and formed into suitable geometrical shapes by techniques similar to those employed by Lloyd and Chiswik.¹⁶ Compressive deformation was performed at room temperature in an Instron tensile machine fitted with a fixture designed to minimize end restraints imposed on the samples. The operative mechanisms for each crystal were determined by metallographic measurements, X-ray orientation data, and stereographic analysis. The crystals were then annealed and observed for evidence of recrystallization. The orientations of the recrystallized areas were determined by Laue back-reflection techniques.

Table XXIX gives the compression directions and summarizes the deformation for the eleven crystals of this investigation. The results are consistent with the deformation systems reported by Rapperport, except for the relatively unimportant $(00\cdot1)$ plane slip found in crystal F; this occurred as cross slip in connection with $\{10\cdot0\}$ slip planes. Also, twinning on $\{11\cdot3\}$ planes has not been found in the present work, possibly because the deformations were small; Rapperport found this type of twinning in samples subjected to large strains.

With the exception of crystals I and K, all samples were annealed for one hour, crystal A at 750°C and the others at 800°C. Crystals A, B, D, E, F, and J showed appreciable recrystallization; the other annealed samples remained essentially unrecrystallized. The latter were the crystals which deformed primarily by slip on $\{10\cdot0\}$ planes and, apparently, the residual internal strains, because of the special fixture design, were insufficient to bring about recrystallization. For this reason crystals I and K were not given annealing treatments.

¹⁴ L. T. Lloyd, Recrystallization of Deformed Alpha Uranium Single Crystals, J. Nucl. Mat. 2 141-146 (June 1960)

¹⁵ E. J. Rapperport, Room Temperature Deformation Processes in Zirconium, Acta Met. 7 254-260 (1959)

¹⁶ L. T. Lloyd and H. H. Chiswik, Deformation Mechanisms of Alpha-Uranium Single Crystals, ANL-5367 (December 1954)

Table XXIX

DEFORMATION MECHANISMS FOR ALPHA-ZIRCONIUM SINGLE
CRYSTALS COMPRESSED AT ROOM TEMPERATURE

Crystal	Angle between Compression Direction and Plane Pole (degrees)			Deformation Mechanisms	
	(00·1)	{10·0}	{11·0}	Type of Slip Planes	Type of Twin Planes
A	71.0	25.0	23.5	{10·0}	{11·1} , {10·2}
B	53.0	46.0	37.0	{10·0}	{11·1}
C	41.5	51.5	49.0	{10·0}	-
D	41.5	48.5	54.0	{10·0}	{11·1} , {10·2}
E	59.5	30.5	42.0	{10·0}	{11·1} , {10·2}
F	30.5	60.5	61.0	{10·0} , (00·1)*	{11·2}
G	89.0	13.0	17.0	{10·0}	-
H	89.5	14.0	16.0	{10·0}	{11·1} *
I	89.0	1.0	30.0	{10·0}	{10·2} *
J	0.5	89.5	89.0	{10·0} *	{11·2}
K	89.0	30.0	1.0	{10·0}	{10·2} *

* Only minor deformations were noted for these planes.

The gathering of the orientation data for the recrystallized grains is nearly completed, but the stereographic analyses and statistical treatment of the data have just begun, and the observations below are necessarily of a preliminary nature. The orientations of the recrystallized grains are definitely grouped with respect to those of the original crystals. The data appear to show a correlation of the recrystallized grain orientations with the deformation twin orientations. Very few grains seem to be related to the deformed parent crystal orientation; this is probably due to the minimizing of end restraints in the compression fixture. In general, the (00·1) poles of recrystallized grains appear to be grouped near the (00·1) poles of the deformation twin orientations, as was found in the uranium study.

C. Uranium and Plutonium Alloys: Constitution and Properties

1. Phase Diagrams of Uranium with Fissium Elements (A. E. Dwight)

Publication:

1. A. E. Dwight, The Uranium-Molybdenum Equilibrium Diagram below 900°C, J. of Nuc. Materials 2(1) 81-87 (March 1960)

Investigation of the uranium end of the uranium-molybdenum diagram was completed and is described in the above paper. The equilibrium diagram is essentially the same as was described in the 1958 and 1959 Annual Reports.

The work on the uranium-ruthenium equilibrium diagram is essentially complete and closely resembles the version shown in the 1958 Annual Report. The temperature of formation of U_2Ru_3 is now placed near 1000°C, which is somewhat lower than was earlier believed. The diagram is described in detail in a forthcoming publication.

Work on the ternary system U-Mo-Ru is continuing.

2. The Crystal Structure of U_2Ru (A. F. Berndt)

An investigation of the structure of the compound U_2Ru by single-crystal X-ray methods has been completed. Equi-inclination Weissenberg pictures were taken and the observed intensities were analyzed with the aid of Harker sections calculated on the IBM 650 computer.

Lattice parameters for the monoclinic unit cell calculated from Debye-Scherrer photographs are:

$$\begin{array}{ll} a_0 = 13.110 \text{ \AA} & \sigma = 0.004 \text{ \AA} \\ b_0 = 3.345 \text{ \AA} & \sigma = 0.002 \text{ \AA} \\ c_0 = 5.206 \text{ \AA} & \sigma = 0.002 \text{ \AA} \\ \beta = 96^\circ 9.24' & \sigma = 0.2' \end{array}$$

The structure, as determined by a qualitative comparison of observed and calculated intensities (a quantitative comparison could not be made due to uncertainties in the observed intensities caused by the high absorption of the crystal), is shown in Figure 27, and can be referred either to the space group $P2/m$ (axes $\underline{a}$ $\underline{b}$ $\underline{c}$) or to the space group $P2_1/m$ (axes $\underline{a'}$ $\underline{b'}$ $\underline{c'}$).

Figure 27. Structure of U_2Ru

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The structure may be considered to consist of layers of bonded atoms parallel to (001). The Ru atoms are confined to alternate layers, with the intermediate layers consisting entirely of U. The interatomic distances are: Ru-Ru, 2.63 Å; U-Ru, 2.81 Å; U-U (between layers), 3.09 Å. These compare with the sum of Pauling's metallic radii,¹⁷ 2.67 Å, 2.85 Å, 3.03 Å, respectively. The smallest U-U distance is 2.75 Å, which compares favorably with the smallest distance in α -U, namely 2.76 Å.¹⁸

3. Properties of Uranium Fissium Alloys (S. T. Zegler and M. V. Nevitt)

This program, dealing with the structures and properties of synthetic uranium-fissium alloys has now been completed. A detailed report of the program will appear in ANL-6111, now in preparation.

Measurements of thermal conductivity as a function of temperature were made during the year for as-cast U-5 w/o Fs and U-5 w/o Fs-2.25 w/o Zr alloys. The conductivities of these alloys and also those of the uranium and 3, 8 and 10 w/o fissium alloys reported last year are presented in Figure 28. The addition of 2.25 w/o zirconium to the U-5 w/o Fs alloy is seen to increase conductivity at temperatures below $\sim 500^\circ\text{C}$ but to decrease it at higher temperatures.

4. Phase Diagrams of Plutonium with Fissium Elements (D. B. Jugle and M. V. Nevitt)

Uranium-Plutonium-Ruthenium Ternary System: This phase of the program has been inactive for most of 1960. The deferral of this work was occasioned by the departure of the staff member who had undertaken the problem, and by the observation, made in conjunction with the Applied Physical Metallurgy Group, that certain problems in phase identification in U-Pu-Fs alloys might be attacked more effectively by a supporting study of equilibrium structures in the Pu-Mo-Ru system.

¹⁷ L. Pauling, J. Am. Chem. Soc. 69 542 (1947).

¹⁸ C. W. Jacob, B. E. Warren, J. Am. Chem. Soc. 59 2588 (1947)

Figure 28. Thermal Conductivity Vs. Temperature for Uranium and Uranium-Fissium Alloys.

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Plutonium-Molybdenum-Ruthenium Ternary System: The investigation of this ternary system was begun during 1960. Progress thus far has been confined to the preparation of the six intermetallic compounds occurring in the pertinent binary systems, and to the preparation of the initial series of ternary alloys. The alloys, having compositions which place them at the intersections of lines defining potential pseudobinary systems, will provide the first appraisal of the general features of the diagram. The alloys are now ready for annealing.

5. Ternary Phase Diagrams of the Thoride Metals with Carbon
(S. Rosen and M. V. Nevitt)

A program has been initiated in 1960 to study the ternary phase equilibria between carbon and the thoride metals thorium, uranium, and plutonium. The investigation will be limited to the thoride-rich portion of the diagrams, probably above 50 a/o thoride, with emphasis on the U-Pu-C system. The essential features of isothermal sections below, and to a limited extent above, the solidus will be determined.

The work has thus far been limited to a metallographic and X-ray study of the 400°C, 570°C and 620°C isothermal sections of the ternary U-Pu-C system below 50 a/o carbon. The results to date indicate that the eutectic valleys originating at the U-C and Pu-C binary sides of the ternary phase diagram run very close to and parallel to the U-Pu binary side of the diagram. Except for the Pu-rich portion of the 400°C isotherm, where the occurrence of the binary Pu_3C_2 carbide phase introduces some complexities, the U-Pu binary phases all appear to come into equilibrium with the (U, Pu)C phase. The appearance of the Pu-rich portion of the diagram is still speculative. Work is under way to establish whether the Pu_3C_2 phase forms peritectoidally from epsilon Pu and PuC at about 575°C, as the published version of the Los Alamos Pu-C diagram indicates, or by some other mechanism.

6. Substitutional Solid Solutions in Alpha Uranium (A. F. Berndt and L. T. Lloyd)

Present theories of substitutional solid solution alloy formation are based primarily on data from metals with cubic or hexagonal symmetry. A program to study substitutional solid solutions in metals of lower symmetry has been initiated. Orthorhombic alpha uranium is a desirable solvent because many of its structure-sensitive parameters have been investigated, thus forming a good basis for a study of the variation of these parameters with solute addition. As the first phase of the present program, a reinvestigation is under way of the variation of the lattice parameters of alpha uranium as a function of concentration of dissolved plutonium. The initial step was the development of a technique by which reliable lattice parameters for the alpha-uranium phase could be obtained by the Debye-Scherrer method. In view of the greater ease of preparation, smaller surface exposed to oxidation, and the lesser hazard of handling needles, it was decided to concentrate on this method of sample preparation rather than using the normal powder specimens.

Needles were prepared from arc-melted buttons of high-purity uranium by first cutting sections about 1 mm x 1 mm x 10 mm in size with a cutoff wheel. These sections were reduced to needles by mounting in a room-temperature polymerizing plastic, grinding on two sides, remounting and finally grinding on the other two sides to an approximately square cross section about 200 microns on a side.

The needles were water quenched from a temperature above the $\alpha \rightleftharpoons \beta$ transition. Some of these were then annealed overnight at a lower temperature in the alpha phase and furnace cooled. Several specimens were also subjected to heat treatments before grinding. All needles were electro-polished to remove the oxide layer, and Debye-Scherrer photograms were made. The needles were then mounted for metallographic examination. No metallographic evidence of recrystallization upon annealing was observed.

The Debye-Scherrer photograms were examined for graininess and for sharpness of the lines in the back-reflection region. Patterns which gave fairly sharp lines were measured and lattice parameters were calculated by least squares on GEORGE computer. A plot of $\sin^2\theta_{\text{calc}} - \sin^2\theta_{\text{obs}}$ vs. θ was used to estimate the amount of random and systematic errors in the measurements, for each of several correction terms used. For each specimen, the proper correction term to be used was chosen as the one which minimized the systematic errors as shown by the above plot and gave a low value of the probable error calculated by the least-squares program.

From the above considerations the following conclusions are drawn:

1. A high quenching temperature is advisable.
2. A heat treatment after grinding is necessary.
3. An anneal after quenching is advisable.
4. The needle cross section should be small and symmetric.

Table XXX gives the results obtained to date. The deviations of these values from the single-crystal data probably result from strains introduced in cooling. This factor would not be eliminated in powder specimens unless each particle were actually a single crystal. In view of the fact that the deviations from the true values are significantly smaller than the changes in lattice parameters reported for the alpha-uranium-plutonium solutions, it was decided that this method would be of sufficient accuracy for a study of the uranium-plutonium system. Preparation of these alloys is in progress.

Table XXX

LATTICE PARAMETERS OF ALPHA URANIUM (Angstrom)

Lattice Parameter	Single Crystal by Diffractometer at 27°C ¹⁹	Best Needle*	Range, for All Specimens Measured
a_0	2.8538	2.8538	2.8538-2.8542
b_0	5.8699	5.8676	5.8665-5.8679
c_0	4.9558	4.9549	4.9549-4.9564

* This sample was prepared by grinding, quenching from 1000°C, and annealing at 400°C for 17 hr. The photogram was taken at room temperature (25 ± 2) °C.

¹⁹ W. Bond, Private communication, (1960).

D. Alloying Properties

1. Occurrence and Magnetic Properties of C8 and Sigma Phases (M. V. Nevitt)

Publications:

1. M. V. Nevitt, Magnetization of the Compound TiFe, J. appl. Phys. 31 155-157 (1960).
2. M. V. Nevitt, Magnetization of the Alpha and Sigma Phases in Several Fe-V Alloys, J. Metals 12, 737-738 (1960), [Abstract].

During 1960, major emphasis was placed on the measurement of the saturation magnetization of Fe-V alloys, with the purpose of following the electronic effects that accompany the structural changes occurring in alloys in this composition range. The preliminary phases of this work were described in the 1959 Annual Report. The investigation began with the alloys in the form of the metastable bcc α phase, obtained by quenching from 1225°C or above. Then the magnetizations were redetermined after a series of anneals at 625°C, which yielded the stable sigma phase as the final product.

For the alloys rapidly quenched from high temperature and containing 60, 53 and 45 a/o Fe, values of $\sigma_{\infty,0}$ of 93.9, 62.8, and 42.0 cgs/gm, respectively, were determined. These data, together with the data of Fallot,²⁰ indicate that in the disordered bcc phase the linear relation between saturation moment and concentration of Fe atoms is retained at least to the vicinity of equiatomic composition and extrapolates to zero moment at 33 a/o Fe. The latter observation demonstrates that the effect of alloying Fe with V is not simply dilution of a constant Fe moment.

Annealing for several hours at 625°C lowered the saturation magnetization by about 20 per cent. Most of the decrease occurred prior to the observation of sigma-phase nucleation by X-ray diffraction or metallographic examination, but the decrease was concurrent with the appearance of (100) α , (111) α and (210) α superlattice lines in the bcc patterns. This CsCl-type ordering has been previously reported by Philip and Beck.²¹ The kinetics of CsCl-type ordering in the 53 atomic per cent Fe alloy is particularly rapid. In fact, it has been impossible to quench this alloy rapidly enough to avoid the presence of weak superlattice lines in its diffraction pattern. Our inability to prevent some ordering from taking place upon quenching results in an anomalously low value for the as-quenched magnetization of this alloy. Values of $\sigma_{\infty,0}$ for the 60, 53 and 45 a/o Fe alloys in the α' condition are 76.3, 49.7, and 34.2 cgs/gm, respectively.

²⁰ M. Fallot, Ferromagnetism in Alloys of Iron, Ann. Physique 6 305 (1936).

²¹ T. V. Philip and P. A. Beck, CsCl-type Ordered Structures in Binary Alloys of Transition Elements, AIME Trans. 209 1269 (1957).

The sigma phase formed by further annealing for several hundred hours at 625°C was found to be ferromagnetic, but with magnetizations lower than the disordered α by about a factor of three.

The data are now being analyzed in an effort to determine the nature of the electronic redistributions which produce the observed changes in the net unbalance of positive and negative spins.

2. Occurrence of the CsCl-type Structure in Transition Element Alloys (A. E. Dwight)

Those compounds of the CsCl-type structure which were discovered during 1960 are listed in Table XXXI. Lattice contractions, $D_{AB} - d_{AB}$, are plotted against radii ratios R_A/R_B in Figure 29. Although Y is not actually a lanthanide YAg is included. The contraction of YAg deviates from the lanthanide-Ag curve in a direction opposite to that of CeAg. It is noted that Ag forms CsCl structures with lanthanides ranging from La to Lu, but Cu and Au form only with the heavy lanthanides. It is also noted that Ag and Au which are fairly close in atomic radius, differ in their ability to contract, with Ag exhibiting the lower contraction. Further investigation is under way to determine what crystal structure takes precedence over the CsCl type in alloys of Au and Cu with the lighter lanthanides.

Table XXXI

LATTICE CONTRACTION IN EQUIATOMIC COMPOUNDS

AB	Structure	a_0 (Å)	$D_{AB} - d_{AB}$ (Å)	R_A/R_B
DyCu	bcc	3.461	0.0538	1.387
LuCu	CsCl	3.390	0.0763	1.357
LuAg	bcc	3.541	0.1115	1.201
ErAu	bcc	3.533	0.0984	1.223
LuAu	bcc	3.497	0.1426	1.207

Figure 29. Lattice Contractions in CsCl-type Compounds between Cu, Ag, Au and the Lanthanides.

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3. Studies on Transition Metal Intermediate Phases (A. E. Dwight, M. V. Nevitt and J. B. Darby, Jr.)

Publications:

1. A. E. Dwight, Factors Controlling the Occurrence of Laves Phases and AB_5 Compounds among Transition Elements, Trans. Amer. Soc. for Metals, Preprint 211, (1960).
2. A. E. Dwight, Positions of Thorium and Uranium in the Periodic Table, Nature (London) 187 (4736) 505-506, (1960).
3. M. V. Nevitt, Stabilization of Certain Ti_2Ni -Type Phases By Oxygen, AIME Trans. 218 327 (1960).
4. M. V. Nevitt, J. W. Downey and R. A. Morris, A Further Study of Ti_2Ni -Type Phases Containing Titanium, Zirconium and Hafnium, AIME Trans. 218 1019 (1960).
5. J. B. Darby, Jr., Miscible Laves-type Compounds in Ternary Systems, J. Metals 12 720 (1960) [Abstract].

6. A. E. Dwight, Occurrence of AB_3 Compounds in Binary and Ternary Transition Element Systems, J. Metals 12 721 (1960) [Abstract].
7. M. V. Nevitt and J. W. Downey, Zirconium-rich Corners of the Ternary Systems Zr-Co-O and Zr-Ni-O, J. Metals 12 721 (1960) [Abstract].

Laves-type Phases (Dwight): The first publication listed above covers the work on Laves phases up to the early part of 1960. It was found that Laves phases may form in the range of Goldschmidt radius ratios from 1.05 to 1.68 and that the radius ratio has little influence on the structure type. The positions of the partner elements in the periodic table are the dominant factor which controls the formation of any one of the three Laves phases, but the occurrence of the Laves phases as a group is dependent upon the ability of the partner atoms to undergo the necessary contraction or expansion required to approach the effective radius ratio 1.23.

During 1960, the crystal structures and lattice parameters have been determined for the Laves phases listed in Table XXXII.

Table XXXII

LAVES PHASES STUDIED DURING 1960*

A-Element		B-Element		Lattice Parameters			
A'	A''	B'	B''	$c_0, \text{\AA}$	$a_0, \text{\AA}$	c/a	Type
33.3 Nb	22.2 Zr	66.7 Cr	26.7 Co 33.3 Ni	8.04 7.94 7.850 8.06	6.98		MgCu ₂
33.3 Nb		66.7 Mn			4.90	1.64	MgZn ₂
33.3 Nb		66.7 Fe			4.84	1.64	"
33.3 Nb		40.0 Fe			4.822	1.628	"
33.3 Nb		33.3 V			4.92	1.64	"
33.3 Gd		66.7 Ru			5.275	1.687	"
33.3 Dy		66.7 Ru			5.255	1.683	"
33.3 Ho		66.7 Ru			5.244	1.680	"
33.3 Lu		66.7 Ru			5.210	1.674	"
11.1 Y		66.7 Ru					"
33.3 Zr		66.7 Ru			5.146	1.654	"
33.3 Lu		66.7 Os			5.261	1.648	"
33.3 Zr		66.7 Os			5.210	1.637	"
33.3 Lu		66.7 Mn			5.228	1.613	"
33.3 Ti		66.7 Mn			4.826	1.642	"
33.3 Zr	25.0 Hf	66.7 Mn			5.039	1.613	"
33.3 Th		66.7 Mn			5.476	1.631	"
33.3 Lu		66.7 Re			5.335	1.634	"
8.3 Ti		66.7 Re			5.241	1.637	"
33.3 Zr		66.7 Re			5.039	1.643	"
33.3 Sc		66.7 Al			7.579		MgCu ₂
33.3 Er		66.7 Al			7.795		"

* Data have been sent to GEORGE for parameter calculations.

Most of above parameters are approximations, obtained from the (220) and (206) lines. A revised table will be issued when parameters are received from the computer.

In addition, crystal structures have been determined for a family of Laves phases in which the A-element is Nb and the B-element is varied from Cr to Mn to Fe to Co, using binary and ternary alloys as shown in Figure 30.

Figure 30. Crystal Structure of Nb Laves Phases.

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(The structure of NbCo_2 is due to Saito and Beck.²²) It was found that the crystal structure varies from MgCu_2 -type to MgZn_2 -type and back to MgCu_2 -type, with the change in composition bracketed between certain ternary alloy compositions.

It is also of interest that a ternary $\text{Nb}(\text{VNi})_2$ phase exists with a MgZn_2 structure. Neither NbV_2 nor NbNi_2 are stable but each lies beyond a MgCu_2 zone of stability; hence, alloying two nonstable MgCu_2 -forming elements with Nb results in a stable MgZn_2 phase, when one element, V, is beyond the upper MgCu_2 zone and the other, Ni, is beyond the lower MgCu_2 zone.

More recently, work on Laves phases has been concentrated on those having the MgZn_2 structure, having as an objective the study of the factors controlling the c/a ratio. Preliminary findings are shown in Figure 31 from which the following observations are made:

1. When Ru is the B-element, c/a ratios range up to 1.687, compared to a maximum of 1.667 for all other MgZn_2 -forming B-elements.

²² S. Saito and P. A. Beck, Co-rich Intermediate Phases in the Cb-Co System, Trans. AIME 218 670 (1960).

2. When the B-element is Ru, Os, or Re, the c/a ratio increases with the R_A/R_B ratio, as long as the A-element is restricted to a single group of the periodic table.
3. The behavior of Mn as a B-element is anomalous, showing no predictable trend with variation in the R_A/R_B ratio.

Figure 31. Axial Ratios of $MgZn_2$ -Type Laves Phases.

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It was noted that $ZrRu_2$ is stable only at high temperature, and ternary additions of the heavy lanthanide Lu stabilize it to lower temperatures, while ternary additions of Nb destabilize it completely. In contrast, $HfRu_2$ is not stable at any temperature yet investigated and cannot be stabilized by Lu additions. The difference in alloying behavior between Zr and Hf will be investigated further.

AB_3 Compounds (Dwight): Crystal structure data on binary AB_3 compounds are given in Table XXXIII. Certain of these compounds have been discussed in the second publication listed above.

To demonstrate the effect of relative atomic size on occurrence of AB_3 compounds, the frequency of distribution plot shown in Figure 32 was prepared. Also included is the frequency of occurrence of ϵ compounds, discussed in the next section of this report. Only transition element compounds have been considered in which A and B lie on opposite sides of the Mn group.

Table XXXIII

BINARY AB₃ COMPOUNDS STUDIED DURING 1960

Composition	Structure Type	$c_0, \text{\AA}$	$a_0, \text{\AA}$	c/a
ScRh ₃	Cu ₃ Au		3.900	
YPd ₃	Cu ₃ Au		4.074	
LaPd ₃	Cu ₃ Au		4.235	
CePd ₃	Cu ₃ Au		4.136	
NdPd ₃	Cu ₃ Au		4.130	
GdPd ₃	Cu ₃ Au		4.090	
HoPd ₃	Cu ₃ Au		4.064	
ErPd ₃	Cu ₃ Au		4.056	
LuPd ₃	Cu ₃ Au		4.027	
HoPt ₃	Cu ₃ Au		4.063	
NbPd ₃	TiAl ₃	7.913	3.895	2.032

Figure 32. Effect of Size Factor on Frequency of Occurrence of Four AB₃ Compounds and on the ϵ Phase.

Figure 32 includes data for both newly discovered compounds and compounds reported by other investigators. It is apparent that the Cu_3Au -type structure can occur over a wide range of radius ratio. It is also apparent that the range of occurrence of the Cu_3Au -type overlaps that of the other four types. Among the other four, there is an apparent size effect, most noticeable between the two structures of lower symmetry: tetragonal TiAl_3 -type, and orthorhombic TiCu_3 -type. These two are stacking variants of the same ordered layers.

During the past year an investigation has been made of the c/a ratios of hexagonal TiNi_3 -type compounds. Figure 33 shows the parameters and c/a for the isomorphs involving Pd. Considering, first, the data for binary compounds, one sees that c_0 increases much more steeply than a_0 with increasing R_A , thus accounting for a rise in the c/a ratio. The points for the four elements of the Ti group lie on a smooth curve, with U deviating. When the electron concentration is presumably held constant by restricting the A-element to members of one group of the periodic table and the B-element to Pd, the c/a ratio is apparently dependent on the size factor.

Figure 33. Axial Ratios of TiNi_3 -Type APd_3 Compounds.

Micro 30544

Ternary alloys were then prepared in which a portion of the A-element was replaced by a neighboring element from the Sc or V groups; that is, in ZrPd_3 , part of the Zr was replaced first by Y, then by Nb. These data are also shown in Figure 33. It is apparent that Y lowered the c/a ratio in spite of the fact that the Y atom has a larger atomic radius than does Zr. It has already been shown that a large A atom tends to increase the c/a ratio; thus the effect of Y in decreasing the c/a ratio is not due to size. The substitution of Nb for part of the Zr slightly increases the c/a ratio, although the Nb atom is smaller than Zr. The data on ternary alloys imply that it is the electron concentrations of Y and Nb which affect the c/a ratio. The conclusion drawn from the study of TiNi_3 -type compounds is that the c/a ratio is dependent both on relative size and electron concentration, not on electron concentration alone.

It was noted that almost no Sc could be substituted for Ti in TiPd_3 , as Y was for Zr. As shown in Figure 34, a small amount of Sc is sufficient to stabilize the cubic ScPd_3 structure. The ternary sections shown in Figure 34 are typical of many which were investigated during the past year. As shown in the upper right section of this figure, a continuous series of solid solutions exists between the orthorhombic NbNi_3 and MoNi_3 compounds, and a portion of the Nb in NbNi_3 can be replaced by Zr. Lattice parameters were determined for this sequence of compounds, and the axial ratios are shown in Figure 35. The data prove that axial ratios of this sequence of TiCu_3 -type compounds are dependent upon position of the partner elements in the periodic table. Further work is under way to determine whether axial ratios are related to relative atomic size, to electron concentration, or to both.

Figure 34. Crystal Structures in Certain Ternary ANi_3 and APd_3 Alloys.

Micro 30546

Figure 35. Axial Ratios of TiCu_3 -type Compounds.

Micro 30542

Epsilon Phases (Dwight): It was found that addition of 10 a/o Ir to an NbNi_3 alloy transformed the structure from the distorted hexagonal (actually orthorhombic) TiCu_3 type to a true hexagonal structure having no apparent ordering. Further investigation revealed similar phases in other systems, as shown in Table XXXIV.

Table XXXIV

OCCURRENCE OF ϵ PHASES

Composition	c_0 (Å)	a_0 (Å)	c/a
Nb + 67.5 Ni + 10 Ru	4.256	2.617	1.626
Nb + 67.5 Ni + 10 Os	4.263	2.622	1.626
Nb + 67.5 Ni + 10 Ir	4.285	2.620	1.636
Nb + 50 Ni + 17.5 Co + 10 Ir	4.258	2.628	1.620
Nb + 67.5 Pd + 10 Ir	4.50	2.768	1.628
Ta + 67.5 Ni + 10 Os	4.26	2.61	1.63
Ta + 67.5 Ni + 10 Ir	4.26	2.60	1.64
Mo + 67.5 Ni + 10 Os	4.226	2.604	1.623
Mo + 60 Ni + 20 Ir	4.268	2.63	1.62

Because of the resemblance to the ϵ phase reported by Raub²³ in the Mo-Pt system, these ternary phases are denoted ϵ phases.

From the data in Table XXXIV it is noted:

1. All nine ϵ phases lie adjacent to an AB_3 compound of the $TiCu_3$ type or the $TiAl_3$ type.
2. All have c/a ratios fairly close to the ideal value of 1.633.

Alloying Behavior of Niobium (Dwight): An investigation was made of the intermetallic compounds which exist in binary systems of niobium with the transition elements. The data on Nb Laves phases and NbB_3 compounds was presented in earlier sections of this report. A compound $NbAu_2$ was discovered, having the AlB_2 -type structure, $c = 2.73$ Å, $a = 4.63$ Å, $c/a = 0.59$. In two binary systems, Nb-Re and Nb-Os, a chi phase (α -Mn structure) pre-empts the Laves phase at the $NbRe_2$ and $NbOs_2$ compositions. The two chi phases were studied in some detail, and lattice parameters are given in Figure 36, with recent data on Nb-Re by Knapton²⁴ for comparison.

Figure 36. Lattice Parameters of Chi Phases in Nb-Os and Nb-Re Systems.

Micro 30545

²³ E. Raub, Die Legierungen der Platin metalle mit Molybdän, Z. Metallk. 45 23 (1954)

²⁴ A. G. Knapton, The Niobium-Rhenium System, J. Less Common Metals 1 (6) 480 (1959)

It was found that, in binary diagrams where Nb was placed on the left, the phases occur from left to right in the following order: $bcc \rightarrow Cr_3O \rightarrow \sigma \rightarrow \text{Laves} \rightarrow \text{chi } (\alpha \text{ Mn}) \rightarrow \text{cp hex variant} \rightarrow \text{fc cube variant}$. No one system thus far known contains all these phases, but the order of occurrence is always followed.

A₂B Phases (Nevitt): During 1960, emphasis on A₂B phases shifted from compounds having the Ti₂Ni-type structure to a group of compounds having a structure isomorphous with Al₂Cu and another group which are believed to be isostructural with Si₂Mo. Essentially all of the work on Ti₂Ni-type phases which was described in earlier Annual Reports has now appeared in published form.

Our work with the Al₂Cu-type phases has demonstrated that transition metal binary systems may exhibit either a Ti₂Ni-type or an Al₂Cu-type phase at A₂B stoichiometry, depending upon an atomic size factor. In Figure 37 this effect is shown by means of a plot of the frequency of occurrence of these two structure types as a function of the radius ratio R_A/R_B . Values of the ratio fall between 1.07 and 1.50 for Al₂Cu-type phases, but are restricted to the narrower range 1.05 to 1.27 for Ti₂Ni-type phases. The ratios for Zr₂Co and Zr₂Ni (1.280 and 1.286, respectively) lie just outside the favorable range for the Ti₂Ni type but well within the range favorable for the Al₂Cu type.

Figure 37. Frequency of Occurrence of Al₂Cu-type and Ti₂Ni-type Phases as a Function of R_A/R_B .

Therefore the latter structure is found in both compounds. Since the tendency of O_2 to enhance the stability of Ti_2Ni -type phases is well known from previous work,²⁵ the occurrence of Ti_2Ni -type phases in the systems $Zr-Co-O$ and $Zr-Ni-O$ would not have been entirely unexpected. As indicated in the 1959 Annual Report, our work shows that they are absent, and we take this to mean that 1.27 is a critical ratio value which cannot be exceeded if a Ti_2Ni type is to occur. The study of Hf_2Ni has been significant because its radius ratio, 1.268, lies just at the critical value. We predicted and later established experimentally that it has the following behavior: Binary Hf_2Ni is an Al_2Cu -type phase, but in the ternary system with O this structure is not stable and, instead, a Ti_2Ni -type phase occurs at the composition Hf_4Ni_2O . These considerations together with the $950^\circ C$ isothermal sections of the Zr -rich corners of the $Zr-Co-O$ and $Zr-Ni-O$ systems are incorporated in a forthcoming paper.

The study of compounds having the Si_2Mo -type structure was initiated during 1960 as an outgrowth of an earlier observation that, contrary to several published statements, Ti_2Cu is not a Ti_2Ni -type phase. We concluded that Ti_2Cu has tetragonal symmetry but were unable to determine the structure by X-ray diffraction. However, Mueller and Knott,²⁶ using neutron diffraction, established that the compound is isostructural with Si_2Mo . In a systematic search for additional isomorphs involving transition metals, we have found compounds to which we have tentatively ascribed the Si_2Mo -type structure. Positive identification must await the determination of the z -parameters by X-ray or neutron diffraction. Our current results are given in Table XXXV.

Table XXXV

 Si_2Mo -TYPE COMPOUNDS

Compound	a_0 (Å)	c_0 (Å)
Ti_2Cu	2.944	10.782
Zr_2Cu	3.220	11.183
Hf_2Cu	3.170	11.133
Ti_2Pd	3.090	10.054
Zr_2Pd	3.306	10.984
Zr_2Ag	3.246	12.004
Zr_2Au	3.28	11.60
Hf_2Au	3.231	11.606

²⁵ M. V. Nevitt, J. W. Downey and R. A. Morris, A Further Study of Ti_2Ni -type Phases Containing Titanium, Zirconium and Hafnium, AIME Trans. 218, 1010 (1960)

²⁶ M. H. Mueller and H. W. Knott, Pittsburgh Diffraction Conference Abstracts, November 1960.

Miscible Laves Phases in Ternary Systems (Darby): An investigation of the miscibility of Laves-type phases in fifty-one ternary systems at a fixed temperature has been under way with the twofold objective of (a) seeking out those systems in which there is complete miscibility, and (b) determining the limits of solubility for those systems in which a miscibility gap exists between component compounds. The first goal should yield background information for further study of various properties over a wide composition range while maintaining a constant crystal structure. The second should provide qualitative information on the factors which limit the stability of Laves-type phases. In addition, a further check would be available on the observations of Dwight regarding the stability of Laves phases as a function of the position of the component elements in the periodic table.

The effort thus far can be divided arbitrarily in three parts: (a) ternary compounds in which the A-partner is uranium and the composite B-partners are transition elements from the three long periods [for example, $U(Fe,Co)_2$], (b) the composite A-partner is uranium and a transition element, and the B-partner is another transition element [for example, $(U,Zr)Co_2$], and (c) a miscellaneous group of ternary compounds each having a composite A-element involving transition metals from Groups IVB and VB, and a B-element which is either another transition metal or aluminum, [for example, $(Zr,Nb)Co_2$].

The twenty-three systems for which we have complete results are summarized in Table XXXVI.

Table XXXVI

OCCURRENCE AND RANGE OF MISCIBILITY OF
LAVES-TYPE COMPOUNDS

System	Temperature (°C)	Miscibility	System	Temperature (°C)	Miscibility
$U(Fe,Co)_2$	900	Complete	$(Hf,Zr)Co_2$	900	Complete
$U(Fe,Os)_2$	700	"	$(Hf,Nb)Co_2$	900	"
$U(Co,Mn)_2$	650	"	$(Hf,Ta)Co_2$	900	"
$U(Fe,Mn)_2$	650	"	$(Zr,Nb)Co_2$	900	"
$(U,Hf)Co_2$	1200	"	$(Zr,Ta)Co_2$	900	"
$(U,Zr)Co_2$	1200	"	$(Nb,Ta)Co_2$	900	"
$(U,Zr)Re_2$	1200	"	$(Hf,Zr)V_2$	900	"
$(U,Ti)Co_2$	800	"	$(Ti,Ta)Cr_2$	900	a gap
$(Zr,Ti)Co_2$	900	"	$(Hf,Zr)W_2$	900	Complete
$(Hf,Ti)Co_2$	900	"	$(Hf,Zr)Re_2$	900	"
$(Ti,Nb)Co_2$	900	"	$(Hf,Zr)Os_2$	900	"
$(Ti,Ta)Co_2$	900	"			

4. Calorimetric Studies of Intermetallic Compounds of Transition Elements (J. B. Darby, Jr. and D. B. Jugle)

Construction of Equipment (Darby): The design of a liquid-metal solution calorimeter of the twin design was completed and approximately 75% of the components have been machined. All auxiliary equipment has been acquired or designed and fabricated.

Considerable effort was expended in evaluating various design concepts related to the fabrication of thermal sensing elements and in selecting a suitable temperature-control system for the calorimeter. Also, an electronic integrator was designed and fabricated, in cooperation with the Electronics Division, to integrate the area under a curve which may be simultaneously plotted on a strip chart recorder. This instrumentation is expected to reduce sharply the labor normally required for graphical integration with equal, if not higher, accuracy.

Solution Rate Studies in Various Solvents (Jugle): Three metals, tin, aluminum and antimony, have been examined as possible solvents for the calorimeter. Ideally, since transition element intermetallic compounds are to be studied, it would be desirable to obtain solution rate data for these compounds and for the elements of which they are composed. The work during the past year has centered on determining the rates at which elemental Ti, V, Cr, Fe, Co, and Ni dissolve in liquid tin and liquid aluminum. Antimony was examined as a solvent because of its large solubility for the elements in question. However, even at a pressure slightly over one atmosphere of purified argon, sufficient antimony condensed on the cold regions of the apparatus to prohibit its use in the calorimeter.

In all tests, a sample of known weight and dimensions was rotated in the liquid metal at a constant rate for a constant time interval. The sample was then withdrawn to a cold portion of the furnace, cooled, and removed from the furnace. The adhering solvent (tin or aluminum) was selectively removed by chemical means, and the sample was weighed and dimensionally checked. The weight loss was divided by the average of the surface area difference before and after the run. This factor $\bar{C}$ (corrosion) was then plotted against time for the three temperatures of investigation, namely, 600, 700, and 800°C for tin as the solvent, and 700, 750 and 800°C for liquid aluminum. The data for the corrosion rates of the six elements in aluminum indicate a consistent increase in the rates with atomic number and temperature. The same trend is observed with tin as the solvent, with the exception that a minimum is observed with vanadium at the three temperatures investigated as one compares the data for Ti, V and Cr.

The data in Table XXXVII were derived by dividing the slope R_{Sn} of C vs. t for the tin system by the similar slope R_{Al} for the aluminum system. The data were interpolated to 700 and 800°C. The data show that the rate of corrosion of the above elements is faster in liquid tin, except in the case of vanadium.

Table XXXVII

RATIO OF CORROSION RATES IN
LIQUID TIN TO THAT IN
LIQUID ALUMINUM

Element	800°C R_{Sn}/R_{Al}	700°C R_{Sn}/R_{Al}
Ti	2.4	2.5
V	0.48	0.36
Cr	1.0	1.6
Fe	1.3	1.3
Co	1.7	2.8
Ni	-	5.0

A Filament Furnace for Melting-point Determinations of High-melting Compounds (Jugle): A filament furnace has been designed and fabricated for rapid determination of the melting points of high-melting compounds (up to melting point of tungsten). Temperature measurements are made by the following:

1. To 1700°C: Pt vs. Pt-10% Rh thermocouple.
2. From 1700 to 2400°C: W vs. Re thermocouple.
3. Above 2400°C: optical pyrometer.

In checking out the furnace, the melting points of various transition elements were determined to within less than $\pm 15^\circ\text{C}$ and in some cases to less than $\pm 5^\circ\text{C}$. The furnace was also used to determine the liquidus temperature (1068°C) of U-5-w/o Fs alloy.

5. Electrical Resistivities of Alloys (D. B. Jugle)

This program was begun during 1960 and the major expenditure of effort has been directed to the construction of apparatus for measuring the electrical resistances of alloy specimens from room temperature to 1200°C , and to the preparation of suitable specimens from brittle intermetallic compounds.

The specimens, sealed in quartz tubes, will be maintained at temperatures constant to within 1°C in a furnace employing a massive nickel thermostat, heavy thermal lagging, and an enveloping secondary heater shell. The furnace is now ready for use. Current and potential leads will be resistance welded to the specimens, and the leads will be brought out through the wall of the quartz tubes.

The problem of sample preparation has been attacked by the development of a technique for injection casting of pins. By means of this method it has been possible to produce cylindrical rods of the compound AlFe having a diameter of 0.10 in. and lengths varying from $2\frac{1}{2}$ to 6 in. An important part of this program will be devoted to an exploration of possible atomic or magnetic order-disorder transformations in CsCl-type compounds by means of resistivity measurements. It is planned to correlate these measurements with high-temperature X-ray diffraction studies. Our first step in establishing the experimental procedures for such a correlation has been an extensive series of measurements of the lattice parameter of the CsCl-type compound TiCo from 25°C to approximately 900°C . The data are currently being examined for the presence of an inflection in the a_0 vs. temperature curve as evidence of transformation

E. X-ray and Neutron Diffraction Studies

1. Neutron Diffractometer (S. S. Sidhu, M. H. Mueller and L. Heaton)

The horizontal neutron spectrometer which was nearing completion at the end of 1959 is shown in Figure 38. After an initial alignment series of checks, debugging of the electronics, and a trial of several different monochromating crystals, such as Cu, Pb and Be, the instrument has been used very successfully as a diffractometer for gathering intensity data for the structure determination of the disodium ruthenium complex described elsewhere in this report. For this purpose a General Electric Single Crystal Orienter was supported on the θ table for holding the single crystal. To date, the intensities for 1400 reflections have been obtained.

Although the initial design of the instrument provided a continuous drive of the 2θ arm with a limited stepping device, it is now being modified to accommodate the more versatile stepping motor, described elsewhere in this report in connection with the XRD-5 X-ray Diffractometer.

As soon as funds become available, we are planning to add a similar stepping motor on the θ and 2θ motion about the pivot point located approximately 2 ft from the center of the table as shown in Figure 38. This arrangement will permit the use of the instrument for crystal dynamics studies involving a change of neutron energy.

It is also desired to design and construct other very necessary accessories, such as cryostat, furnace, and magnet for the horizontal spectrometer.

The plate, which is barely visible in the top of the shielding as shown in Figure 38, is intended to accommodate the vertical neutron diffractometer briefly described in the last annual report. The design for this instrument has been completed and construction is well under way. It is estimated that within two months we will be able to assemble and operate the diffractometer, including the electronic components. Within six months, construction on the single-crystal holder should be complete. This part of the instrument has been designed to move the crystal in any angular position. The crystal position can be moved remotely at the electronic rack by means of the dc stepping motor and the angular position accurately read by digitizers with visual read out at the rack.

It is highly desirable to automatize both the horizontal spectrometer and the vertical diffractometer as much as possible, both as a time-saving device and as a means of eliminating the need for continuous attendance at the instruments.

Figure 38. Neutron Spectrometer II at the CP-5 Reactor.

ANL Negative No. 106-5337

2. Stepping Mechanism for X-ray and Neutron Diffractometers and Spectrometers (M. H. Mueller, L. Heaton and E. W. Johanson)

In many applications in diffractometry and spectrometry it is particularly desirable to use an incremental stepping motion rather than a continuous drive. A relatively short time ago a motor, called Slo-Syn,^a which lends itself to the above application, became commercially available. This motor is a permanent magnet-type ac motor with two field windings. As an ac motor it has a speed of 72 rpm; however, when dc voltage is applied to the field windings, the motor will lock into a magnetic hold position, and if the voltage is then switched, the motor will advance $1/100$, $1/200$, or $1/400$ of the motor shaft revolution, depending upon the switching used.

There is no need for electrical or mechanical braking, since the claimed accuracy of positioning each step is extremely great, and any inaccuracy of positioning is nonaccumulative. It is stated that on a 1.8° step ($1/200$ of a shaft revolution) the positioning accuracy is $\pm 0.09^\circ$.

In order to control the amount of rotation of this type motor conveniently, a transistorized electronic stepping motor control was built at Argonne. The control consists of a preset counter and motor drive switching circuit. The preset counter counts the number of drive pulses delivered to the motor by the switching circuit, and hence the amount of rotation of the motor shaft. After reaching the preset amount of rotation, the control automatically stops itself and resets the preset counter to zero. This control can be started and stopped manually or automatically, and can also be driven continuously.

An application of this motor is shown in Figure 39: the motor has been coupled to the 2θ drive shaft of the General Electric XRD-5 X-ray Diffractometer. Since this shaft requires one revolution per 2θ degree, it was ideally suited for attaching to it one of these motors.

Figure 39

Stepping Motor with XRD-5 Diffractometer.

^aMade by the Superior Electric Co., Bristol, Conn.

A motor with a 150-oz-in. torque and 1/100 revolution per step was found to be suitable. As indicated in Figure 39, a bracket was designed to support the motor and a drive coupling was made to couple the motor to the indicating drum and shaft. According to the specifications indicated above, this arrangement should provide a stepping motion in increments of 0.01° for 2θ with an accuracy of $\pm 0.00025^\circ$ on each step, which is of considerably greater accuracy than claimed for the screw drive used on diffractometers. A more complete writeup of this instrument will be submitted to the Review of Scientific Instruments.

3. Precision Lattice Parameter Measurements (M. H. Mueller and L. Heaton)

Publications:

1. M. H. Mueller, L. Heaton and K. T. Miller, Determination of Lattice Parameters with the Aid of a Computer, Acta Cryst. 13 828-829 (1960).
2. M. H. Mueller and L. Heaton, Determination of Lattice Parameters with the Aid of a Computer, ANL-6176 (January 1961).

The first publication indicated above is a condensed description of the computer program as presented at the Lattice Parameter Conference held in Stockholm, Sweden, in 1959. In order to make the program available to others, the ANL report was written in order to describe the program adequately, give examples, and show the exact treatment given to the input data.

The present program permits the determination of lattice parameters and standard errors for the orthorhombic system and all other crystal systems of higher symmetry by a method of least squares. The angular measurements of lines or spots for several different wavelengths obtained from various types of cameras or a diffractometer may be used. Provision has been made for using as many as three separate correction terms for eccentricity, absorption, divergence, etc.; however, one, two, three, or none at all may be used. The exact trigonometric function or functions used in these correction terms may be selected from a number of those previously suggested. If desired, a subjective weighting factor and/or an analytical weighting may also be used for each reflection.

At the present time, a cooperative effort is being carried out with T. B. Massalski and H. W. King of the Mellon Institute to compare the lattice parameters of hexagonal crystals obtained by their recently proposed²⁷

²⁷T. B. Massalski and H. W. King, Tables of Crystallographic Functions for Calculating Lattice Parameters of H.C.P. Metals and Alloys from X-ray Diffraction Data, Mellon Institute (1960).

graphical extrapolation technique with the results from our computer program. In order to make this a valid comparison, the same starting data are being used.

Since, as indicated above, the present program will not handle monoclinic or triclinic crystal systems, a cooperative effort is being made with W. Greenhow of the Applied Mathematics Division to write a program which would be applicable to at least the monoclinic system and which would treat the data as in the previously described program. Such a program would be useful for powder diffraction data and probably even more applicable to single-crystal data, since the individual reflections are resolved much more readily from single crystals.

4. Crystallographic Structure of Alpha Uranium (M. H. Mueller)

Since precise lattice parameters for single crystals of alpha uranium have now become available from Bell Laboratories,²⁸ it is of interest to compare these results with our values obtained from polycrystalline material. These results are summarized below:

<u>Investigator</u>	<u>Lattice Parameters in Å</u>		
	<u>a₀</u>	<u>b₀</u>	<u>c₀</u>
Mueller (Polycrystalline)	2.8539 ±0.0001	5.8691 ±0.0001	4.9554 ±0.0001
Cooper ²⁸ (Single Crystal)	2.85376 ±0.00005	5.86986 ±0.00006	4.95582 ±0.00006

It would appear that there is probably very little significant difference between the polycrystalline results obtained by us and the latest results obtained from a single crystal.

In alpha uranium, whose structure belongs to space group D_{2h}^{17} Cmcm, there are uranium atoms located as follows:

$$4 \text{ U at } 0, y, \frac{1}{4}; \quad 0, \bar{y}, \frac{3}{4}; \quad \frac{1}{2}, \frac{1}{2} + y, \frac{1}{4}; \quad \frac{1}{2}, \frac{1}{2} - y, \frac{3}{4} \quad .$$

²⁸Mrs. Ann Cooper, Bell Laboratories, private communication.

The various reported values for the parameter y may be summarized as follows:

<u>Investigator</u>	<u>Material</u>	<u>Temperature</u>	<u>y</u>
Jacob and Warren ²⁹	Powder	Room	0.105 $\pm$ 0.005
Konobeevsky <u>et al.</u> ³⁰	Powder	20°C	0.107 $\pm$ 0.003
Konobeevsky <u>et al.</u> ³⁰	Powder	500°C	0.115 $\pm$ 0.003
Sturcken and Post ³¹	Single Crystal	25°C	0.1025 $\pm$ 0.0001
Mueller and Knott (ANL)	Single Crystal	25°C	0.1023 $\pm$ 0.0001
	Single Crystal	25°C	to 0.1025 $\pm$ 0.0001

As noted, there is good agreement among the results for single crystals. We have reported two separate values since the value of 0.1025 was obtained by a minimization of the R factor as used by Sturcken and Post and a value of 0.1023 using a computer least-squares program.

It has been believed for some time that this y coordinate may change with temperature. To obtain results from a single crystal, we have now mounted, in a special silver mount, the same crystal which we used for room-temperature measurements in the high-temperature X-ray diffractometer furnace described in the last annual report. Results to date indicate that the y parameter increases by about 0.002 from room temperature to 500°C, and the B, Debye-Waller temperature value, increases from approximately 0.2 to 0.9 over this same range. This result must be checked, however, since for some unexplained reason the y parameter at room temperature in the furnace is 0.1006 and at 500°C it is 0.1027; in other words there appears to have been a general shift downward.

5. Crystal Structure of CuTi₂ and Ti₂Ni (M. H. Mueller)

Publication:

1. M. H. Mueller and H. W. Knott, Pittsburgh Diffraction Conference Abstracts, November 1960.

The crystal structure of CuTi₂ has been determined and reported at the November 1960 Pittsburgh Diffraction Conference. It is tetragonal with

²⁹C. W. Jacob and B. E. Warren, J. Am. Chem. Soc. 59 2588 (1937).

³⁰S. T. Konobeevsky et al., Proceedings of the Second United Nations International Conference on Peaceful Uses of Atomic Energy, Geneva, Switzerland (1958), Vol. 6, p. 194.

³¹E. F. Sturcken and B. Post, Acta Cryst., 13 852 (1960).

an a_0 of $2.9438 \pm 0.0001 \text{ \AA}$ and a c_0 of $10.7861 \pm 0.0001 \text{ \AA}$, using a $\text{CuK}\alpha$ $\lambda = 1.54051 \text{ \AA}$, and expressing the probable error in terms of 95% confidence limits. There are 6 atoms per unit cell in space group $D_{4h}^{17} - I4/mmm$. This is the well-known C11b MoSi_2 -type structure. The atoms are located in this space group as follows:

$$2 \text{ Cu (a) } 000; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$$

$$4 \text{ Ti (b) } 00z; \frac{1}{2}, \frac{1}{2}, \frac{1}{2} + z$$

$$00\bar{z}; \frac{1}{2}, \frac{1}{2}, \frac{1}{2} - z$$

where

$$z = 0.341 \pm 0.001$$

Since the X-ray scattering amplitudes of Cu and Ti are nearly equal, it is not surprising that previous workers had difficulty in deciding the correct structure. The neutron scattering amplitudes of Cu and Ti, however, are very different and of opposite sign, thus making the CuTi_2 a very interesting compound to investigate by means of neutron diffraction.

The calculated intensities for both neutron and X-ray diffraction for the above structure are shown in Figure 40, plotted against $\sin \theta / \lambda$ in order to simplify the comparison of individual reflections. It is obvious that there is a striking difference between the X-ray and neutron patterns. It is also noted that in the X-ray pattern all the strong reflections are those for which $\ell = 3n$, which led previous workers to suggest a smaller face-centered tetragonal cell with a c_0 one-third of the above value and an a_0 which is $\sqrt{2}$ times the above a_0 . Since the neutron scattering amplitude of Cu is +0.76 and that of Ti is -0.34, and since they are present in the ratio of 1 to 2, respectively, this compound would be a near null-matrix which would be characterized by very weak Bragg peaks if the Cu and Ti were randomly statistically distributed. Since the neutron pattern shows very strong peaks, it is obvious that the Cu and Ti occupy different positions.

The z coordinate was determined from the neutron diffraction pattern by means of a least-squares crystallographic program. The final R value was 0.09, based on the calculated and observed intensities of neutron diffraction.

Approximately eighteen months ago, using 99 reflections, we found the structure of Ti_2Ni by trial and error to be cubic $\text{Fd}3m$, with atoms located as indicated in Table XXXVIII. Before we had an opportunity to refine the structure, Yurko, Barton and Parr³² published their results. We

³²G. A. Yurko, J. W. Barton and J. Gordon Parr, *Acta Cryst.* 12 909 (1959).

then took suitable reflections from both sets of data and, as noted in the table, confirmed their initial parameters by least squares. Our data produced a slightly higher R factor but a more realistic Debye-Waller temperature factor B. Due again to the negative scattering amplitude of Ti relative to the positive amplitude for Ni, the locations of Ti and Ni atoms were firmly established by neutron diffraction. The lattice parameter of 11.3231 ± 0.0004 Å, which we reported at Pittsburgh, is significantly different than the value of 11.278 ± 0.001 Å reported by Yurko, Barton and Parr. Solubility differences cannot explain this disagreement, since it is reported to be less than $\pm \frac{1}{2}\%$.

Figure 4c. Calculated Intensities for CuTi_2 .

ANL Negative No. 106-5597

It is now of interest to look at both Ti_2Ni and CuTi_2 in combination with oxygen, since both reportedly take in approximately 16 atom per cent oxygen and both have the Ti_2Ni structure. This structure in the presence of oxygen may be similar to the old reported parent structure of this type, $\text{Fe}_3\text{W}_3\text{C}$. Sufficient samples are now available from

Nevitt so that location of the oxygen can best be attempted with neutron diffraction powder techniques, and it may also be of interest to re-examine $\text{Fe}_3\text{W}_3\text{C}$.

Table XXXVIII

COMPARISON OF ATOMIC POSITIONAL PARAMETERS FOR Ti_2Ni ,
SPACE GROUP $\text{Fd}3\text{m}$ (ORIGIN AT CENTER)

Investigators	Number of Reflections	Positional Parameters			B	R	R- Based on I or F	Method of Determination
		(f) 48 Ti $X_1, \frac{1}{8}, \frac{1}{8}$	(e) 32 Ni X_2, X_2, X_2	(c) 16 Ti 0, 0, 0				
Yurko, Barton and Parr	43	0.810	0.215	0		0.10	I	Trial and Error
Mueller and Knott	99	0.813	0.208	0		0.32	I	Trial and Error
Yurko, Barton and Parr	19	0.811	0.215	0	-0.75	0.11	F	Least Squares
Mueller and Knott	18	0.812	0.213	0	0.24	0.17	F	Least Squares

6. A Single-crystal Neutron Diffraction Study of Disodium Tetranitritonitrosohydroxyruthenate (III) 2-Hydrate
(M. H. Mueller and S. H. Simonsen*)

There has been considerable interest in the nitrosylruthenium radical and its complexes and since several large crystals of disodium tetranitritonitrosohydroxyruthenate (III) 2-hydrate,

were available, it was decided to investigate the crystal structure by neutron diffraction. This compound is interesting since Fletcher *et al.*³³ showed that two of the nitrito groups were substitutionally more labile than the other two in that they were easily removed by weak acid hydrolysis. More recently, Murray³⁴ found that nuclear magnetic resonance spectra from an aqueous solution of the complex suggested ionic bonding by two of the nitrito groups and covalent bonding by the remaining two.

Not only did this crystal serve to align our neutron spectrometer accurately and develop our computer programs, but it is a desirable structure to investigate with neutron diffraction since, with X-rays, the Ru would serve as a heavy element to mask out details from the light

*Research Associate during the summer of 1960 from University of Texas.

³³J. M. Fletcher, I. L. Jenkins, F. M. Lever, F. S. Martin, A. R. Powell and R. Todd, *J. Inorg. Nucl.* 1, 378-401 (1955).

³⁴B. B. Murray, DP-391.

elements. By means of neutron diffraction it should be possible to locate these light atoms accurately as well as the waters of hydration and the hydroxyl group.

Preliminary X-ray investigation was carried out to establish that the unit cell is monoclinic with

$$a = 12.75 \text{ \AA}; \quad b = 14.52 \text{ \AA}; \quad c = 7.37 \text{ \AA}; \quad \beta = 121.2^\circ$$

At the present time, integrated intensities of 155 (hk0), 149 (h0l) and 93 (0kl) reflections have been measured by the moving-crystal, moving-counter technique. Patterson projections showing well-resolved peaks in both the positive and negative regions have been computed for each of the three axial zones. The statistical test of Howells, Phillips and Rogers³⁵ was applied to these zones, and the results indicate the space group C 2/m. The morphology of the crystal also suggests this space group. In addition, we have now collected approximately 1200 additional general (hkl) reflection intensities with about 200 more possible. After the determination of these are completed, it should be possible to proceed with the detailed structure analysis. It is also planned to collect three-dimensional X-ray data so that a comparison can be made between the neutron and X-ray results

A short communication describing this work has been submitted to *Acta Crystallographica*

7. The Use of Nuclear Null-matrix in Neutron Diffraction Studies of Magnetic Structures (S. S. Sidhu, L. Heaton, M. H. Mueller, F. Campos and D. Zaubers)

Nuclear null-matrices have been used to study magnetic moment alignments in magnetic structures, similarly as in the determination of light atom positions among heavy atoms in crystal structures^{36,37}. A null-matrix as defined here consists of two types of nuclei, one type scattering thermal neutrons 180° out of phase with the other. The atomic percentages and the amplitudes of randomly distributed atoms in a matrix are such that the crystal structure factor is given by

$$F_{hkl} = \sum_n (p_A b_A + p_B b_B) \exp [2\pi i(hu_n + kv_n + lw_n)] = 0$$

³⁵E. R. Howells, D. C. Phillips and D. Rogers, *Acta Cryst.* 3, 210 (1950)

³⁶S. S. Sidhu, LeRoy Heaton, and M. H. Mueller, Neutron Diffraction Techniques and Their Applications to Some Problems in Physics, *J. Appl. Phys.* 30, 1323-1340 (1959).

³⁷S. S. Sidhu, Use of Nuclear Null-Matrix in the Study of Hydrogen and Carbon Atoms in Metals, *Am. J. of Physics* 28, 413 (1960)

since

$$p_A b_A + p_B b_B = 0$$

Here p_A and p_B are the fractions of all sites occupied by A and B atoms, respectively, and b_A and b_B are the scattering amplitudes.

From the known amplitudes $\cdot \dot{x} \cdot$ of Mn, Co, and Cu nuclei

$$\cdot \dot{x} \cdot b_{\text{Mn}} = -0.36 \times 10^{-12} \text{ cm}; b_{\text{Co}} = 0.28 \times 10^{-12} \text{ cm}; \text{ and } b_{\text{Cu}} = 0.75 \times 10^{-12} \text{ cm},$$

the following null-matrices were prepared:

- (1) $M_{\text{Mn-Co}} = 44 \text{ a/o Mn and } 56 \text{ a/o Co.}$
- (2) $M_{\text{Mn-Cu}} = 69 \text{ a/o Mn and } 31 \text{ a/o Cu.}$

X-ray and neutron diffraction patterns of the $\text{M}_{\text{Mn-Co}}$ binary alloy are given in Figure 41. The crystal structure is fcc with $a_0 = 3.618 \text{ \AA}$ and the nearest distance of approach of metal-metal atoms is $2.558 \text{ \AA}$. The alloy is ductile and nonmagnetic, and since it forms a null-matrix the Mn and Co atoms occupy random positions in the crystal lattice.

Figure 41. Diffraction Patterns of $\text{M}_{0.7}\text{Co}_{0.3}$.

Fig. 41-a. Filtered Fe Radiation

Fig. 41-b. Neutrons, $\lambda = 1.078 \text{ \AA}$

ANL Negativ. No. 176-5-15

The matrix was alloyed with C and made into a ternary alloy of composition $\text{Mn}_{1.88}\text{Co}_{2.12}\text{C}$. The specific purposes were to study atomic ordering of Mn, Co, and C atoms and magnetic moment ordering of Mn and Co. X-ray and neutron diffraction patterns of the carbide of the null-matrix are given in Figure 42. The crystal structure (see Figure 43a) is ordered with Mn at $000, \frac{1}{2}\frac{1}{2}0$; Co at $\frac{1}{2}0\frac{1}{2}, 0\frac{1}{2}\frac{1}{2}$; and C at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. The lattice parameter is $a_0 = 3.787 \text{ \AA}$, with a metal-metal atom distance of $2.678 \text{ \AA}$. A tentative magnetic structure and the alignment of magnetic moments of Mn and Co atoms are given in Figure 43b. While the matrix alloy is ductile, nonmagnetic and disordered, its carbide is brittle, ferromagnetic,

and completely ordered. The results obtained here make it possible to explain the courses of embrittlement in the carbide, and the magnetic interactions between the central carbon atom and the metal atoms in the faces of the unit cell.

Figure 42. Diffraction Patterns of $\text{Mn}_{1.88}\text{Co}_{2.12}\text{C}$.

(a) Filter : Fe Radiation

(b) Neutron, $\lambda = 1.76 \text{ \AA}$

ANL Report No. 106-524.

Figure 43a. Ordered Crystal Structure of $\text{Mn}_{1.88}\text{Co}_{2.12}\text{C}$.

ANL Report No. 106-547

Figure 43b. Magnetic Cell and Magnetic Moment Alignment in $\text{Mn}_{1.88}\text{Co}_{2.12}\text{C}$.

A neutron diffraction pattern of $M_{69}Cu_{31}$ null-matrix (see Figure 44-2b) shows that the crystal structure³⁸ of the alloy is fcc_8 with $a_0 = 3.75$ Å, and the nearest distance of approach of atoms 2.65 Å.

Figure 44. Diffraction Patterns of 69 a/o Mn-31 a/o Cu.

ANL Negative No. 106-5465

There is a slight indication of the antiferromagnetic ordering of magnetic moments of Mn atoms, which becomes quite pronounced as the concentration of the Mn atom is increased. The magnetic structure that develops is shown in Figure 45.

Figure 45

Magnetic Cell and Magnetic Moment Alignment in 85 a/o Mn-15 a/o Cu.

ANL Negative No. 106-3958

The presence of weak nuclear peaks in the pattern indicates that the time given for homogenizing the sample was not sufficient and the sample was not entirely homogeneous.

³⁸David Meneghetti and S. S. Sidhu, Magnetic Structures in Copper-Manganese Alloys, Phys. Rev. 105, 130-135 (1957).

8. Neutron Coherent Scattering Amplitudes (M. H. Mueller and S. S. Sidhu)

Publication:

1. C. G. Shull,* M. K. Wilkinson,** and M. H. Mueller,
Slow Neutron Scattering by the Titanium Isotopes,
Phys. Rev. 118, 797-798 (1960).

The neutron coherent scattering amplitudes for the Ti isotopes as determined here at Argonne and at Oak Ridge have been reported in the above article. The results showed that the negative scattering amplitude of the element is the result of Ti^{48} which is normally present to the extent of 73.45%. All of the other isotopes exhibit conventional positive scattering amplitudes, with considerable variation in their magnitudes. Only Ti^{50} has a scattering cross section identifiable with nuclear potential scattering, which should be about 3.5 barns. The other values of the scattering amplitude are all smaller than pure potential scattering or are negative, suggesting the presence of resonance scattering at energies not too far removed from the neutron energy of about 0.07 ev used in obtaining the present data.

A sufficient sample of both K^{39} and Rb^{85} as the chlorides was obtained for a determination of the scattering amplitude of these two isotopes. Neutron diffraction patterns were also obtained for normal isotopic mixtures of these chlorides. The results are summarized briefly below.

Element or Nuclide	% Abundance	Scattering Amplitude (10^{-12} cm)	
		Present	Previous
K	100.0	+0.31	+0.35
K^{39}	93.3	0.35	-
Rb	100.0	+0.84	+0.55
Rb^{85}	72.3	0.79	-

As noted above, there is a considerable change in the scattering amplitude, especially for normal Rb, from the previously reported value. This increase is consistent with the observations made recently by Heaton and Gingrich on liquid rubidium. Before publishing the values summarized above, it is planned to use a least-squares computer program now available for the IBM-704 for rechecking.

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**Oak Ridge National Laboratory.

In line with the plan to continue to obtain neutron scattering data for isotopes as they become available, we have obtained neutron diffraction patterns for the dioxides of the following Zr isotopes: Zr^{90} , Zr^{91} , Zr^{92} , and Zr^{94} . In view of the complex neutron diffraction pattern obtained from these monoclinic structures, it will not be possible to use the least-squares program mentioned above, since very few peaks are resolved. However, since the crystal structure of ZrO_2 has recently been carefully worked out by McCullough and Trueblood,³⁹ it should be possible to use a modification of the above program in order to use a trial-and-error technique to find the best values for the scattering amplitudes.

9. State of Deuterium Atoms in Energetic Plasma Source
(S. S. Sidhu, F. Campos, and D. Zaubers)

Deuterated titanium has been used for a plasma source.⁴⁰ Titanium washers fully reacted with deuterium gas were interleaved with ceramic spacers and assembled into a cylinder with an internal diameter of $\frac{1}{2}$ in. An arc of several thousand amperes with a half-period of 5 μsec , when initiated within the washer stack, discharged D^+ ions from the washers into the space in the stack. Washers (a) fully reacted, (b) partly depleted, and (c) completely depleted were obtained from Livermore Laboratory⁴¹ and studied with neutron and X-ray diffraction and metallographic techniques to determine the state of deuterium atoms in the washers as treated above.

It was found that deuterium reacts with titanium and forms a metal deuteride which has an entirely different structure than that of the metal. The gas atoms are not adsorbed at the surface of the metal, nor do they go into the interstitial sites in the metal, as is commonly inferred, the extent of interstitial solid solution of deuterium in the metal at room temperature being extremely small, if any. In the deuteride structure, which may be formed at a nonstoichiometric ratio of metal : gas atoms, the atoms take definite positions with respect to their neighbors, and the bonds between metal-gas atoms are shorter than between metal-metal atoms. The deuterium atoms thus bonded in the deuteride structure leave the lattice only at the dissociation temperature and pressure of the deuteride.

An assembly of deuterated washers, as in a plasma source, loses deuterium from the parts that are heated to the dissociation temperature, leaving the unheated parts in the original state. The partly depleted portions of washers contain both the deuteride and the metal, but the completely depleted portions revert to the metallic state.

³⁹J. D. McCullough and K. N. Trueblood, *Acta Cryst.* 12 507-511 (1959).

⁴⁰F. H. Coensgen, W. F. Cummins and A. E. Sherman, Energetic Plasma Source, Bull. Am. Phys. Soc. 3, Series II, 412 (December 1958).

⁴¹Courtesy of Mr. Norman Milleron.

F. Problems in Metal Physics

1. Elastic Moduli Studies

Temperature Dependence of Elastic Moduli of Alpha-uranium Single Crystals (E. S. Fisher)

Publication:

1. H. J. McSkimin and E. S. Fisher, Temperature Dependence of the Adiabatic Elastic Moduli of Single-crystal Alpha Uranium, J. Appl. Phys. 31 1627-1639 (1960).

The temperature dependence of the elastic moduli of single crystals of alpha uranium between 78° and 300°K has been reported in the previous annual report (ANL-6099) and in the above publication. The striking feature of the data was the anomalous maximum in the modulus c_{11} at about 250°K and the accompanying continuous decrease in elastic stiffness in the [100] direction on cooling to 78°K.

During the past year, the wave velocity measurements for c_{11} have been extended down to 1.1°K, and the longitudinal wave velocity measurements in the [010] direction have been extended to 35°K, giving the value of c_{22} . Both sets of measurements indicate a sharp transition in the physical state of the crystals at some temperature between 41° and 43°K, as shown in Figure 46. The values of the moduli were obtained from the relations

$$c_{11} = \left[\frac{(bc)_r}{bc} \quad \frac{a}{a_r} \right] \left(\frac{f}{f_r} \right)^2 (c_{11})_r$$

$$c_{22} = \left[\frac{(ac)_r}{ac} \quad \frac{b}{b_r} \right] \left(\frac{f}{f_r} \right)^2 (c_{22})_r \quad ,$$

where a, b, and c refer to the lattice parameters of the crystal, and f is the frequency for a fixed integral number of waves in the specimen, as obtained by the phase comparison method.⁴² The subscript r denotes the values of the variables at the reference temperature, 78°K. The quantities in the square brackets are the thermal expansion corrections to the basic data, which were estimated by interpolation and extrapolation from the lattice parameter measurements of Bridge, Schwartz and Vaughan.⁴³

⁴²E. S. Fisher and H. J. McSkimin, The Adiabatic Elastic Moduli of Single Crystal Alpha Uranium, J. Appl. Phys. 29 1473-1484 (1958).

⁴³J. R. Bridge, C. M. Schwartz and D. A. Vaughan, X-ray Diffraction Determination of the Coefficients of Expansion of Alpha Uranium, Trans. A.I.M.E. 206 1282 (1956).

Figure 46. Plots of Data Showing the Temperature Dependence of c_{11} and c_{22} below 78°K.

This procedure is somewhat questionable because of the scarcity of measurements of lattice parameters below 63°K; however, since these corrections correspond to a maximum of 0.2% adjustment in the modulus, the errors are probably not sufficiently great to change the curves significantly.

In both sets of measurements, difficulties were encountered in the temperature range from 20 to 50°K, due to high energy losses either in the transducer-to-specimen seal or in the specimen itself. For the c_{11} measurements these losses were so great that the phase comparison method could not be used in this range. It was, however, possible to measure the time delay for a wave entering the specimen and returning to the transducer as the first echo. Although the latter data were subject to significantly greater error than the frequency measurements, the ratios of delay times relative to those at 78°K coincided within 1% of the frequency ratios where the 2 sets of data overlap, as shown in Figure 46. The delay-time measurements indicated an abrupt change in curvature between 39 and 43°K, although the minimum value of c_{11} cannot be estimated with reasonable accuracy. It appears to be at least 58% below that at 78°K. The value of c_{11} at 0°K was fairly well defined from the phase comparison data to be within $\frac{1}{2}\%$ of 1.13×10^{12} dynes/cm², which is about 52% of that at 300°K.

The temperature dependence of c_{22} also becomes anomalous below 58°K. It decreased with a decrease in temperature to about 42.5°K and increased abruptly at this point. It appears that c_{22} is affected by the same physical transition which causes the more spectacular effect on c_{11} . The only alternative explanation for the coincidence might be that the specimen used in the c_{22} measurements was widely misoriented from [010] toward [100]. This explanation seems unlikely, since the specimens were carefully oriented and the orientations carefully preserved during the facing process. The significant effects observed would require at least 5° misorientations, whereas the specimen was estimated to be within $\frac{1}{2}$ of arc from the [010] direction.

These studies are continuing with the intent of determining the temperature dependence of all 9 stiffness moduli on cooling to 1°K. The measurements will further define the transition temperature and perhaps assist in determining the nature of the physical change. It appears certain that the transition does not involve a crystal structure change, since the data are reproducible upon repeated heating and cooling through the temperature range. The drastic change in stiffness of the [100] direction probably correlates with a reversion in the temperature dependence of the a_0 parameter between 20 and 63°K, as indicated by the measurements of Bridge, Schwartz and Vaughan. To aid in clarifying the nature of the transition, magnetic susceptibility studies with single crystals are planned.

Theoretical Studies on the Elastic Moduli of Alpha Uranium (D. Van Ostenburg)

Publication:

1. D. Van Ostenburg, Lattice Dynamics of Alpha Uranium, Bull. Am. Phys. Soc. 5 421 (November 25-26, 1960).

Since the last annual report we have completely revised our calculations in the harmonic approximation of the lattice dynamics of α uranium. The structure of α uranium is viewed as a close-packed hexagonal lattice that has been distorted to orthorhombic symmetry. Choosing any particular atom as origin, it has two nearest, two second-nearest, four third-nearest, and four fourth-nearest neighbors. Following the method developed by Born and Begbie⁴⁴ and set forth in Born and Huang,⁴⁵ equations were developed which give the elastic constants in terms of linear combinations of the microscopic force constant. Interactions out to fourth nearest neighbors were included. Through symmetry considerations, nineteen atomic force constants enter into this force system. Greek letters are introduced for the force constants where the arguments 1, 2, 3, 4 denote, respectively, the first, second, third and fourth-nearest neighbors.

⁴⁴G. H. Begbie and M. Born, Proc. Roy. Soc. A188 179 (1947);
G. H. Begbie, Proc. Roy. Soc. A188 189 (1947).

⁴⁵M. Born and K. Huang, Dynamical Theory of Crystal Lattices, Oxford University Press, New York (1954) Chap. V.

We arrive at the following equations giving the elastic moduli as functions of the atomic force constants:

$$c_{11} = \frac{2a}{bc} \left[2\beta(2) + \beta(3) + \beta(4) - \frac{4}{\Gamma(\gamma)} \left\{ 2\delta(2) - \delta(3) + \epsilon(3) + 2\delta(4) \right\}^2 \right] \quad (1)$$

$$c_{22} = \frac{2b}{ac} \left[\gamma(3) + 8y^2\gamma(1) + 4B^2\gamma(4) - \frac{64}{\Gamma(\gamma)} \left\{ y\gamma(1) - B\gamma(4) \right\}^2 \right] \quad (2)$$

$$c_{33} = \frac{2c}{ab} \left[\frac{\alpha(1)}{2} + \alpha(4) - \frac{4}{\Gamma(\gamma)} \left\{ \mu(1) + 2\mu(4) \right\}^2 \right] \quad (3)$$

$$c_{66} = \frac{2b}{ac} \left[\beta(3) + 8y^2\beta(1) + 4B^2\beta(4) - \frac{64}{\Gamma(\beta)} \left\{ y\beta(1) - B\beta(4) \right\}^2 \right] \quad (4)$$

$$c_{55} = \frac{2a}{bc} \left[2\alpha(2) - \alpha(3) + \alpha(4) \right] \quad (5)$$

$$c_{44} = \frac{2c}{ab} \left[\frac{\gamma(1)}{2} + \gamma(4) - \frac{4}{\Gamma(\alpha)} \left\{ \mu(1) + 2\mu(4) \right\}^2 \right] \quad (6)$$

$$c_{13} = \frac{4}{b} \left[-\lambda(4) + \frac{2}{\Gamma(\gamma)} \left\{ \mu(1) + 2\mu(4) \right\} \left\{ 2\delta(2) - \delta(3) + \epsilon(3) + 2\delta(4) \right\} \right] \\ - \frac{2a}{bc} \left[2\alpha(2) + \alpha(3) + \alpha(4) \right] \quad (7)$$

$$c_{23} = \frac{8}{a} \left[y\mu(1) - B\mu(4) - \frac{4}{\Gamma(\gamma)} \left\{ y\gamma(1) - B\gamma(4) \right\} \left\{ \mu(1) + 2\mu(4) \right\} \right] \\ - \frac{2b}{ac} \left[\alpha(3) + 8y^2\alpha(1) + 4B^2\alpha(4) \right] \quad (8)$$

$$c_{12} = \frac{2}{c} \left[-\left\{ \delta(3) + \epsilon(3) \right\} + 4B\delta(4) + \frac{16}{\Gamma(\gamma)} \left\{ y\gamma(1) - B\gamma(4) \right\} \right. \\ \left. \left\{ 2\delta(2) + \epsilon(3) - \delta(3) + 2\delta(4) \right\} \right] - \frac{2a}{bc} \left[2\gamma(2) + \gamma(3) + \gamma(4) \right] \quad , \quad (9)$$

where

$$\Gamma(\alpha) = 2\alpha(1) + 4\alpha(4) \quad ,$$

$$\Gamma(\beta) = 2\beta(1) + 4\beta(4) \quad ,$$

and

$$\Gamma(\gamma) = 2\gamma(1) + 4\gamma(4) \quad .$$

Compatibility and invariance relations give us the following additional relations among the force constants:

$$\frac{2b}{ac} \left[\beta(3) + 8y^2\beta(1) + 4B^2\beta(4) \right] = \frac{2a}{bc} \left[2\gamma(2) + \gamma(3) + \gamma(4) \right] \quad (10)$$

$$\frac{2a}{bc} \left[2\alpha(2) + \alpha(3) + \alpha(4) \right] = \frac{2c}{ab} \left[\frac{\beta(1)}{2} + \beta(4) \right] \quad (11)$$

$$\frac{2b}{ac} \left[\alpha(3) + 8y^2\alpha(1) + 4B^2\alpha(4) \right] = \frac{2c}{ab} \left[\frac{\gamma(1)}{2} + \gamma(4) \right] \quad (12)$$

$$a \left[2\delta(2) + \epsilon(3) - \delta(3) - 2\delta(4) \right] = 4b \left[y\beta(1) - B\beta(4) \right] \quad (13)$$

$$4b \left[y\alpha(1) - B\alpha(4) \right] = c \left[\mu(1) + 2\mu(4) \right] \quad . \quad (14)$$

We have a total of nineteen atomic force constants with fourteen relations between them. Equations (3) and (6) are equivalent to a single relation for the fourth-nearest-neighbor model, since their ratio equals $\Gamma(\gamma)/\Gamma(\alpha)$. This reduces the number of independent equations to thirteen.

The model assumes that a solid is a collection of atoms coupled together by springs in which the spring constants play the role of the atomic bonds or atomic force constants. In view of this, the calculation expresses how the bond strengths and bond directions combine to give the various extensional and shear moduli. For example, c_{11} , which is the extensional modulus in the x-direction, depends upon atomic force constants of the second through fourth nearest neighbors. Intuitively, one expects a term relating the force in the x-direction on the second nearest neighbor due to a unit displacement of the origin atom in the x-direction. This is manifested through the appearance of $\beta(2)$. Similar arguments can be applied to the other linear terms appearing in this and the other elastic moduli.

Once the atomic force constants are known, we can determine the normal modes of vibration by solving the familiar secular equation and then the frequency distribution spectrum can be determined. It turns out to be impossible to do this entirely from elastic constant data when considering interactions out to fourth nearest neighbors, as the number of force constants exceed the number of equations. An independent determination of the atomic force constants is required before we can proceed with such an evaluation. In principle, it is possible to evaluate them according to various theoretical approaches and/or deduce them from experimental data obtained from long-wave-length neutron scattering.

For an evaluation of the order of magnitude of the atomic force constants, we have resorted to the quasicentral force approximation and the three-nearest-neighbor atom model. The elastic moduli c_{33} and c_{44} are each functions of the same argument. Consequently, the number of independent relations reduces to thirteen. The equation remaining serves as a cross check. In the numerical examples below the agreement with that equation was within an order of magnitude. It must also be noted that in the four-nearest-neighbor atom model, $\delta(3)$, $\epsilon(3)$, and $\delta(2)$ occur in such a way that all of them cannot be evaluated. This is a consequence of the fact that the dynamical matrices of the second and third nearest neighbors are not symmetric. It is sufficient for them to be symmetric but not necessary. Therefore, in the calculation we have assumed $\delta(3) = \epsilon(3)$. This reduces the number of force constants to thirteen. The elastic moduli were obtained from extrapolations of the temperature-dependent data⁴⁶ to 0°K.

To achieve the quasicentral force parameters, we set $\beta(1)$, $\gamma(2)$, $\alpha(2)$, $\delta(2)$, and $\alpha(3)$ equal to zero. The remaining force constants are altered from the general situation and this fact is denoted by an asterisk. The term central force is reserved for two-body forces which interact only along the line joining their centers. The results of the quasicentral force approximation and the three-nearest-neighbor atom model are given in Table XXXIX. In each example there is a trend for the magnitudes to

⁴⁶H. J. McSkimin and E. S. Fisher, J. Appl. Phys. 31 1627 (1960).

decrease as the neighbors become more distant, although the convergence is not rapid. Presumably, according to this model, atoms in α uranium possess long-range interactions. Their influence could be employed in the calculation by including fifth-nearest and higher-order neighbors and/or introducing a term into the equations of motion pertaining to the effects of the electron gas. However, in order to test the validity of such models, one would need data currently not available.

Theoretical work on the temperature dependence of the elastic moduli has been postponed until further experimental data is available. The recent results of E. S. Fisher and H. J. McSkimin reported in this annual report indicate that a second-order phase transition is responsible for the observed anomalous behavior of c_{11} . Magnetic susceptibility apparatus will be constructed and the susceptibilities of single crystals of α uranium will be measured over the same temperature region as that of the elastic constants. These measurements should reveal if the second-order transition is observable through magnetic measurements. If this turns out to be the case, we shall attempt a theoretical correlation between the magnetic and the elastic constant data.

Table XXXIX

NUMERICAL VALUES OF THE ATOMIC FORCE CONSTANTS

Quasicentral Atomic Force Constants in Units of 10^4 dynes/cm		
$\gamma^*(1) = 10.1$	$\beta^*(3) = 2.6$	$\gamma^*(4) = -1.9$
$\alpha^*(1) = 7.7$	$\gamma^*(3) = 15.2$	$\alpha^*(4) = 4.7$
$\mu^*(1) = -2.5$	$\epsilon^*(3) = \delta^*(3) = 1.08$	$\delta^*(4) = 1.9$
$\rho^*(2) = 4.9$	$\beta^*(4) = 1.6$	$\lambda^*(4) = -3.3$
		$\mu^*(4) = -0.048$
Atomic Force Constants Out to Third Nearest Neighbors in Units of 10^4 dynes/cm		
$\beta(1) = 3.1$	$\beta(2) = -4.5$	$\beta(3) = 1.9$
$\gamma(1) = -0.89$	$\gamma(2) = 3.4$	$\gamma(3) = 2.3$
$\alpha(1) = -5.7$	$\alpha(2) = 2.3$	$\alpha(3) = 0.19$
$\mu(1) = -2.8$	$\delta(2) = 1.4$	$\epsilon(3) = \delta(3) = -1.6$

Elastic Moduli of Single Crystals of Zirconium (E. S. Fisher and C. J. Renken, Jr.)

The anomalies in the temperature dependence of the elastic moduli for single crystals of alpha uranium,⁴⁷ palladium,⁴⁸ yttrium,⁴⁹ and for polycrystalline chromium⁵⁰ indicate that the interatomic binding energies in many of the transition metal structures are abnormally sensitive to temperature. Since the contributions to the binding in these elements are complicated by the unfilled electron shells in the free atoms, the temperature dependence of the elastic moduli may depend considerably on the electron configuration in the free atom. The present studies with alpha zirconium (hexagonal crystal structure) are part of a general program to determine whether systematic correlations exist between electron configurations and the temperature coefficients of the elastic moduli in unalloyed transition metals. Determinations of the 5 elastic moduli at 20°C have now been completed, and high-temperature measurements are in progress.

Measuring Method: The measurement of the ultrasonic wave velocities in a sufficient number of known directions in a single crystal makes possible the direct computation of the elastic moduli of the crystal. For specimens having linear dimensions on the order of 2 to 3 mm, phase comparison techniques have been found useful. The equipment described in this report is based on the technique developed by McSkimin.⁵¹ The measurement system is a type of acoustic interferometer adapted to small solid specimens, and it requires specialized electronic equipment which cannot be purchased off the shelf. Therefore this system was designed and constructed to include the features of convenience and flexibility necessary in a permanent piece of equipment.

Figure 47 shows a block diagram of the system. Briefly, radio-frequency (rf) pulses of a known frequency are generated and converted into pressure variations by a quartz crystal. These pressure waves propagate down a fused quartz buffer rod toward the specimen. The couplant between the buffer and specimen transmits part of the energy into the specimen; most of the remaining energy is reflected back from the buffer-couplant-specimen interface. The energy traveling in the specimen is reflected

⁴⁷H. J. McSkimin and E. S. Fisher, Temperature Dependence of the Adiabatic Elastic Moduli in Alpha Uranium, J. Appl. Phys. 31 1627-1639 (1960).

⁴⁸J. A. Rayne, Elastic Constants of Palladium from 4.2-300°K, Phys. Rev. 118 1545 (1960).

⁴⁹J. F. Smith and J. A. Gjerre, Elastic Constants of Yttrium Single Crystals, J. Appl. Phys. 31 645 (1960).

⁵⁰M. E. Fine, E. S. Greiner and W. C. Ellis, Transitions in Chromium, Trans. A.I.M.E. 191 56 (1951).

⁵¹H. J. McSkimin, Use of High Frequency Ultrasound for Determining Elastic Moduli of Small Specimens, I.R.E. Trans. P.G.U.E. 5 25-43 (1957).

back and forth between the specimen faces. During each round trip, part is transmitted back through the couplant into the buffer rod. At certain discrete frequencies, the specimen waves are all in phase, but they are out of phase with the interface reflection. When this occurs, the velocity of propagation is given by

$$v = \frac{2tf_n}{n + (\gamma/360)} \quad ,$$

where f_n is the frequency, n the number of waves, t the specimen thickness, and γ the couplant correction. The couplant correction may be determined from a knowledge of the magnitude of the interface reflection and first reflection from the far end of the specimen as they appear at the quartz crystal end of the buffer. This was shown in an analysis mentioned in Appendix B of the paper by McSkimin and Fisher.

Figure 47. Block Diagram of Measuring Apparatus

Several different couplant materials have been used for the room-temperature measurements with zirconium. These include Dow Corning resin 276-V9 and Nonaq. An aqueous solution of sodium silicate and calcium carbonate in suspension forms upon drying a solid which shows considerable promise as a high-temperature couplant. This material has been used for the high-temperature measurements made to date.

Results at 19.7°C: The single-crystal specimens of zirconium were made from pieces of crystal bar treated by the phase-change-anneal technique.⁵² Three specimens were used in the measurements; the orientations and dimensions of these are given in Table XL. Measurements were made for each of the 3 possible wave modes in crystals A and B and the 2 wave modes in crystal C. The corresponding propagation and displacement vectors are described in Table XLI. The propagated longitudinal wave frequencies ranged from 45 to 80 mc/sec; for shear waves,

⁵²J. Langeron and P. Lehr, On the Preparation of Large Crystals of Zirconium and the Determination of the Orientation of the Hydride of Zirconium, Comp. Rend. 243 151-154 (1956).

the measurements were confined to the 44-54 mc/sec range. In all cases the specimen temperature was maintained at $19.7^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$ by encasing the specimen and buffer rod in a water-cooled jacket.

Table XL

DESCRIPTION OF ZIRCONIUM CRYSTALS

Crystal	Deviation of Normal to Parallel Faces and [001] Direction	Thickness, cm	Lateral Dimensions, cm
A	$90^{\circ} \pm \frac{1}{2}^{\circ}$	$0.33505 \pm 0.03\%$	$\frac{1}{2} \times \frac{1}{2}$
B	$46^{\circ}50' \pm 10'$	0.31623	$1\frac{1}{2} \times \frac{3}{4}$
C	$0^{\circ} \pm \frac{1}{2}^{\circ}$	0.43256	$1 \times \frac{3}{4}$

Table XLI

SUMMARY OF RESULTS COMPUTED FROM WAVE VELOCITY DATA

Crystal	Type Mode	Direction of Particle Motion	Wave Velocity (in Units of 10^5 cm/sec)	Equation for ρV^2 (ρ density)
A	longitudinal	hk0	4 6970	c_{11}
	shear	001	2 2202	c_{44}
	shear	h'k'0	2 3356	$\frac{c_{11} - c_{12}}{2}$
B	quasi-longitudinal	hkl	4.6674	$1/2 (c_{33}C^2 + c_{11}S^2 + c_{44} + \sqrt{g(c_{13})})$
	quasi-shear	h'k'l'	2 6060	$1/2 (c_{33}C^2 + c_{11}S^2 + c_{44} - \sqrt{g(c_{13})})$
	shear	hk0	2 2824	$c_{44}C^2 + \frac{c_{11} - c_{12}}{2} S^2$
C	longitudinal	001	5 0350	c_{33}
	shear	hk0	2 2205	c_{44}

C - cosine of angle between propagation direction and [001] S - sine of angle between propagation direction and [001]
 $g(c_{13}) = [c_{11}S^2 - c_{33}C^2 + c_{44}(C^2 - S^2)]^2 + 4C^2S^2(c_{13} + c_{44})^2$

The measured wave velocities determined from the data and corrected for phase shift in the couplant are given in Table XLI together with the equations relating the velocities and the elastic moduli. A density of 6.505 gm/cm^3 , obtained from the X-ray data of Swanson and Fuyat,⁵³ was used to evaluate the moduli. The computed values of the elastic moduli are given in Table XLII. The probable errors therein indicated were estimated on the basis of 0.05% possible error in each wave velocity measurement, in addition to uncertainties in orientation and temperature. Table XLIII gives the elastic parameters computed from the stiffness moduli.

⁵³H. E. Swanson and R. K. Fuyat, Standard X-ray Diffraction Powder Patterns, NBS Circular 539, 2 11 (1953).

Table XLII

BEST VALUES OF ELASTIC MODULI FOR
ZIRCONIUM AT 19.7°C
(for Density of 6.505 gm/cm³)

$$\begin{aligned}c_{11} &= 1.435 \pm 0.002 \\c_{12} &= 0.725 \pm 0.002 \\c_{13} &= 0.654 \pm 0.002 \\c_{33} &= 1.649 \pm 0.002 \\c_{44} &= 0.3217 \pm 0.0003\end{aligned}$$

Table XLIII

ELASTIC PARAMETERS FOR ALPHA ZIRCONIUM AT 19.7°C

Compliances Moduli (in Units of 10 ⁻¹² cm ² /dyne)	Young's Moduli (in Units of 10 ¹² dynes/cm ²)	Compressibilities (in Units of 10 ⁻¹² cm ² /dyne)
$s_{11} = 1.009$	$E_{100} = 0.991$	$\beta_{100} = 0.367$
$s_{33} = 0.798$	$E_{001} = 1.253$	$\beta_{001} = 0.315$
$s_{12} = -0.400$	$E_{\text{min.}} = 0.890$	$\beta_{\text{vol.}} = 1.049$
$s_{13} = -0.242$	(at 52 $\frac{1}{2}^\circ$ from [001])	
$s_{44} = 3.1182$		
$s_{66} = 2.8184$		

After the initial set of measurements described above, the specimens were annealed in vacuum to remove and to measure the evolved hydrogen. No perceptible volume was obtained from crystal A; crystals B and C each produced about 10 ppm by weight of hydrogen. After cooling, the specimens were refaced and the wave velocity measurements were repeated at 19.7°C. The results were within the estimated error of those given in Table XLII, indicating that hydrogen in concentrations up to 10 ppm has no significant effect on the elastic moduli when the specimens are slowly cooled to permit precipitation of the hydride phase.

High-temperature Measurements: Experiments are now being carried out to determine the temperature dependence of the elastic moduli of zirconium in the temperature range from 20°C to 850°C by means of the phase comparison technique described above and with the same specimens used for the 20°C measurements. The primary problem here is to

find a coupling material which will provide adequate ultrasonic energy transmission to the specimen at the high temperatures and which will permit separation of the specimen and buffer unit after the test, without destruction of either. On the basis of the experience to date, it appears that the aqueous mixture consisting of Na_2SiO_3 and CaCO_3 , which solidifies upon drying to a transparent glass, will prove suitable. Two tests carried out in air with a zirconium crystal coupled to a buffer unit showed that both shear waves and longitudinal waves can be transmitted through the material at temperatures at least up to 775°C . Similar tests with both uranium and zirconium in vacuum showed no damaging effects of low pressure up to temperatures of 650°C .

It appears that the glass coupling material, when given sufficient drying time, remains sufficiently stiff for transmitting a good share of the ultrasonic energy and is sufficiently plastic to accommodate the stresses set up by differences in thermal expansion between the specimen and buffer material. It also appears, however, that intermediate diffusion layers form at the couplant-buffer and couplant-specimen interfaces, which are brittle and, consequently, less resistant to fracture by thermal stresses. In the case of zirconium, this latter complication only restricts the time schedule permitted for a successful measuring run. It may be more restricting in the case of uranium, as indicated by difficulties in reproducing suitable coupling in successive tests.

2. Diffusion in Uranium (S. J. Rothman)

Publications:

1. S. J. Rothman, L. T. Lloyd and A. L. Harkness, Self-diffusion in Gamma Uranium, Trans. A.I.M.E. 218 605-607 (August 1960).
2. S. J. Rothman, J. Gray, Jr., J. P. Hughes and A. L. Harkness, Self-diffusion in Beta-Uranium, ANL-6126 (July 1960).
3. S. J. Rothman, The Diffusion of Gold in Gamma Uranium, ANL-6127 (May 1960).

The first paper is a publication based on the report Self-diffusion in Gamma Uranium, ANL-5971 (July 1959), which was discussed in last year's annual report (ANL-6099). The work on sintering of gamma uranium as a means of checking the diffusion mechanism, which was described in the previous annual report (ANL-6099), has proven unsuccessful because of oxidation of the uranium, and it has been temporarily discontinued.

Self-diffusion in Beta Phase: The second report describes the extension of the self-diffusion measurements into the beta-phase temperature range. The diffusion coefficient was found to drop by a factor of 150

on going from the body-centered-cubic gamma structure to the complex tetragonal and covalently bonded beta structure. Also, there were indications of grain boundary diffusion and anisotropic diffusion in the beta phase.

Tracer Element Diffusion in Gamma Phase: The third report is the first of a series on the diffusion of tracer elements in gamma uranium. It showed that the parameters for the diffusion of gold, a fairly "hard-sphere" atom, in the gamma uranium lattice were

$$D_0 = 4.86 \times 10^{-3} \text{ cm}^2/\text{sec}$$

$$Q = 30,400 \text{ cal/mol},$$

quite close to the parameters for self-diffusion.

Similar studies have been undertaken with lanthanum, iron, and chromium as tracer elements. The first two were unsuccessful because of oxidation of the lanthanum and insufficient evaporation of the iron. The study of the diffusion of chromium is almost finished; preliminary graphical estimates of the diffusion parameters are as follows:

$$D_0 = 2.2 \times 10^{-3} \text{ cm}^2/\text{sec}$$

and

$$Q = 22,000 \text{ cal/mol}.$$

These values are rather different from those reported by Mosse *et al.*,⁵⁴ namely, $D_0 = 0.7 \text{ cm}^2/\text{sec}$, and $Q = 32,000 \text{ cal/mol}$, although the D values do not differ by more than a factor of three.

Tracer Element Diffusion in Beta Phase: The diffusion coefficient (D) of chromium in the beta phase at 748°C was $1.7 \times 10^{-9} \text{ cm}^2/\text{sec}$, indicating a discontinuity in the plot of $\log D$ versus the reciprocal of the absolute temperature at the $\gamma \rightarrow \beta$ transformation temperature, as was the case in self-diffusion; however, D decreased by a factor of ten for the diffusion of chromium than it did for self-diffusion, and the diffusion coefficient of chromium in beta uranium was a hundred times greater than the self-diffusion coefficient. Further, the plot of the logarithm of the concentration versus the square of the penetration distance for the diffusion of chromium in beta uranium was a good straight line, whereas the plots for self-diffusion were curved.

Self-diffusion in Alpha Phase: Diffusion specimens have been prepared from three single crystals of highly depleted material with the

⁵⁴M. Mosse, V. Levy and Y. Adda, Diffusion de Quelques Metaux en Solution Dilute dans l'Uranium Gamma, Compt. Rend 250 3171 (1960).

diffusion directions along [100], [010], and [001] axes. The crystals contained a lineage structure. The samples have been diffusion annealed and are awaiting sectioning.

3. Interaction of Interstitial Solute Atoms with Dislocations (D. G. Westlake)

The study of the effects of hydrogen on the deformation modes of zirconium has been pursued in three directions: 1) a theoretical investigation of the mechanisms of twinning to aid in the interpretation of subsequent experimental results; 2) re-evaluation of the habit planes of zirconium hydride, as the information available in the literature is contradictory; and 3) preparation of single crystals of zirconium for measurements of the critical stress for slip between 77 and 300°K as a function of hydrogen content. The progress in these three endeavors is reported below.

Twinning in Zirconium: The twinning in zirconium may or may not be a dislocation mechanism. Rapperport⁵⁵ was able to determine the twin elements for three of the four modes of twinning which he observed. Dislocation models which satisfy three criteria have been proposed for these modes: the models are in accord with the dislocation theory of twinning as given by Cottrell and Bilby⁵⁶ and by Thompson and Millard;⁵⁷ they agree with experimental data;⁵⁵ and they satisfy Cahn's rule relating twin thickness and shear strain.⁵⁸

The twinning on (10.2) planes could be produced by a partial dislocation with a Burgers' vector equal to

$$\frac{3 - (c/a)^2}{3 + (c/a)^2} [\bar{2}\bar{1}1] \quad ,$$

where a and c are the hexagonal lattice parameters. Such a dislocation might originate as a result of the interaction of two minor unit dislocations

⁵⁵E. J. Rapperport, Room Temperature Deformation Processes in Zirconium, Acta Met. 7 254 (1959).

⁵⁶A. H. Cottrell and B. A. Bilby, A Mechanism for the Growth of Deformation Twins in Crystals, Phil. Mag. 42 573 (1951).

⁵⁷N. Thompson and D. J. Millard, Twin Formation in Cadmium, Phil. Mag. 43 422 (1952).

⁵⁸R. W. Cahn, Plastic Deformation of Uranium, United States Atomic Energy Commission Technical Information Service, AERE-M/R-740 (1951). (Originally published at Atomic Energy Research Establishment, Harwell, Berkshire, England.)

in a pile-up caused by slip. Equation 1 represents this interaction:

$$[\bar{1}00] + [\bar{1}\bar{1}0] \rightarrow [\bar{2}\bar{1}0] \rightarrow \frac{3 - (c/a)^2}{3 + (c/a)^2} [\bar{2}\bar{1}1] + [00\bar{1}]^* \quad (1)$$

The asterisk indicates that the indices refer to the lattice of the twin. The twinning dislocation would be zonal⁵⁹ and have a thickness

$$\frac{\sqrt{3} \ c}{\left(\frac{c^2}{a^2} + 3\right)^{1/2}}$$

corresponding with the fact that homogeneous shear occurs on only every second plane. The atom movements resulting from the passage of such a dislocation through the lattice seem obvious.

A very similar model was proposed for twinning on (11.2) planes. An interaction of a major and a minor unit dislocation could produce the twinning dislocation as shown in Equation 2:

$$[100] + [001] \rightarrow [101] \rightarrow \frac{(c^2/a^2 - 2)}{(c^2/a^2 + 1)} [\bar{1}\bar{1}1] + [210]^* \\ [210]^* \rightarrow [110]^* + [100]^* \quad (2)$$

The twinning dislocation would have a thickness equal to

$$\frac{3c}{2(c^2/a^2 + 1)^{1/2}} \quad .$$

Atom movements would be slightly more complex than for twinning on (10.2) planes, with strong indications of some movement out of the plane of shear.

Rapperport's experimental data indicate that homogeneous shear occurs on every seventeenth plane during twinning on (11.1) planes. The model that would produce a zonal dislocation more than three times as thick as those for (10.2) and (11.2) twinning requires a combination of 5 minor unit dislocations with one partial dislocation. A dissociation of

⁵⁹M. L. Kronberg, Atom Movements and Dislocation Structures for Plastic Slip in Single Crystals of β -Uranium, J. Nuclear Materials 1 85 (1959).

the zonal twinning dislocation into narrower ones would be necessary to give agreement with Cahn's rule. Atom movements are far from obvious. The model is complex enough to be questionable.

The various factors affecting the magnitude of the applied stress necessary to initiate twinning were considered, with the following conclusion: twinning, by a dislocation mechanism, would be nucleated at stress concentrations. The macroscopic applied stress would not be a measure of the nucleation stress; therefore, critical resolved shear stresses for twinning are not obtainable.

Identification of Zirconium Hydride Habit Planes: Kunz and Bibb⁶⁰ have reported that the habit planes of the hydride in zirconium crystals are the (10.2), (11.1), and (11.2) families (the twin planes). This was in contradiction to the findings of Langeron and Lehr⁶¹ who reported only the (10.0) family (the slip planes). Therefore, in order to interpret properly the effect of hydride plates on the mechanical properties, a study of the habit planes of hydride in zirconium has been made in collaboration with E.S. Fisher.

Two (10.0) faces, one (00.1) face, and one (11.0) face were developed on a zirconium crystal by grinding. Cold-worked material was removed from the surface by etching in a solution of 50 parts HNO₃, 50 parts H₂O, 8 parts HF. The crystal was charged with hydrogen to five different concentration levels in order to observe the effect of concentration on the mode of precipitation. Between chargings, the specimen was analyzed for hydrogen by collecting the gas evolved during an anneal at 800°C in a vacuum of 2×10^{-6} mm of mercury. Details of the charging operations and the analyses are given in Table XLIV.

Table XLIV
EXPERIMENTAL DATA FOR CHARGING A SINGLE CRYSTAL
OF ZIRCONIUM WITH HYDROGEN

Experiment	Hydrogen Charging Temp (°C)	Homogenizing Temp (°C)	Homogenizing Time (hr)	Cooling Rate (°C/hr)	Hydrogen Conc (ppm by weight)
1	480	700	16	100	10
2	480	700	40	100	40
3	480	700	48	100	60
4	480	480	24	100	20
5	530	530	168	100	~ 1000

⁶⁰F. W. Kunz and A. E. Bibb, Habit Plane of Hydride Precipitation in Zirconium and Zirconium-Uranium, Trans. A.I.M.E. 218 133-135 (1960).

⁶¹J. P. Langeron and P. Lehr, On the Preparation of Large Crystals of Zirconium and the Determination of the Orientation of the Hydride of Zirconium, Comptes Rendus 243 151-154 (1956).

After each charging, the specimen was chemically etched again and examined metallographically. Traces were observed in preferred directions on each face. These traces always disappeared after vacuum annealing, hence they can be assumed to be manifestations of hydride plates. The angles between traces and the edges common to the (00.1), (10.0), and (11.0) faces were measured. Stereographic analyses were used to determine which planes could produce the observed combination of traces. The results are summarized as follows:

- (1) By far the most common habit planes were the (10.0) family.
- (2) Some (10.5) habit planes have been observed at the lower hydrogen concentrations, and some (10.1) planes were seen at the 1000 ppm concentration level.
- (3) No combinations of traces have been observed which could be interpreted as manifestations of hydride plates parallel to a twinning plane.

Preparation of Zirconium Single Crystals: Attempts have been made to grow crystals which occupy the entire cross section near the center of zirconium tensile specimens, $\frac{1}{4} \times \frac{1}{4} \times 2$ in. The method, which consists of cycling through the $\alpha \rightarrow \beta \rightarrow \alpha$ transformation and annealing in the high alpha range for grain growth, was described by Langeron and Lehr.⁶¹

The bars of Westinghouse iodide zirconium which have been used vary in iron content from 100 ppm to 1000 ppm by weight. The phase diagram of the Zr-ZrFe₂ system is of the eutectoid type; therefore, iron stabilizes the beta phase. Specimens containing appreciable quantities of iron, when heated near the $\alpha \rightarrow \beta$ transformation temperature of pure zirconium, contain some beta-phase zirconium. One can avoid this by annealing below the eutectoid temperature of 800°C, but this is objectionable on two counts: the lowering of temperature, and the precipitation of ZrFe₂ reduce grain boundary motion.

All attempts have failed to grow large grains in crystal bar zirconium which exhibits a second phase (probably ZrFe₂) precipitated as a network within the grains; however, material which contains only very small quantities of the second phase in grain boundaries seems to be quite suitable. Large crystals were grown in eleven of the twelve tensile specimens cut from a single bar of iodide zirconium which had been judged metallographically clean. These and other similar specimens will be charged with various amounts of hydrogen, both in solid solution and precipitated as hydride, for an investigation of the effect of hydrogen on the deformation modes of zirconium.

⁶¹Op. Cit.

4. Nuclear Magnetic Resonance Studies (D. O. Van Ostenburg)

The Metallurgy Division has recently purchased nuclear magnetic resonance equipment to serve as a new investigative tool for the study of metal physics. The nuclear magnetic moments and nuclear electric quadrupole moments permit the use of nuclei as probes to explore internal magnetic and electric fields in solids. Information from the measurements is contained in the nuclear resonance absorption curve, which is essentially a plot of rate of energy absorption versus absorption frequency. The pertinent parameters of the line are its position, width, shape, and intensity. These factors depend upon the electric and magnetic fields at the positions of the nuclei whose spectrum is under investigation, and these fields in turn arise from neighboring atoms and densities of conduction electrons around the nuclei.

Some specific areas of metal physics in which nuclear magnetic resonance can give valuable information are: self-diffusion, electronic structure of metals and alloys, density and distribution of dislocations, density and distribution of vacancies and interstitials, lattice deformation and electron distribution around chemical impurities, order-disorder lattices, phase transformations, and radiation damage.

The first studies will be in the field of transition metal alloys and the general area of the electronic structure of the heavy elements.

G. Corrosion Research (J. E. Draley, et al.)1. Polarization in Distilled Water (F. E. DeBoer)

In the last annual report it was concluded that the apparatus for measuring polarization in pure water was working successfully. Since that report, the polarization behavior of many metals has been surveyed in boiling water. This should serve as an introduction to the detailed study of one metal. The data have been compiled in a paper which has been submitted for publication in the Journal of the Electrochemical Society.

The effect of applied current on the solution potential of 20 pure metals has been measured after exposing each to boiling distilled water for one day. These measurements were made by the interrupter method* with constantly increasing current from 0 to $35 \mu\text{amp}/\text{cm}^2$ in both the anodic and cathodic directions, as illustrated in Figures 48 and 49. There seems to be no simple relationship, such as the Tafel equation, of the results followed in these systems. Different rates of application of polarizing currents were used, and extrapolated to the hypothetical situation where no coulombs were passed in the measurement (thus avoiding changes in the interface induced by the current). Such curves are shown dashed. Many of the polarization curves are reliable and reproducible; however, for some the reproducibility is not reassuring. For a few metals, such as cobalt, the potential became more positive as anodic current was applied (normal behavior), then rose in an irregular and irreproducible manner at the higher currents (see Figure 49).

Figure 48. Polarization of Aluminum in Boiling Distilled Water.

ANL Neg. No 106-5844

Figure 49. Polarization of Cobalt in Boiling Distilled Water.

ANL Neg No 106-5852

*J. E. Draley, et al., J. Electrochem. Soc. 106 490 (1959).

2. Corrosion Mechanism in Zirconium (R. D. Misch)

The mechanism of zirconium corrosion is being studied from several different viewpoints. The three main approaches which serve to guide experimental work are:

I. Investigation of compensating effects which are theoretically possible in the corrosion product layer of ZrO_2

II. Investigation of additives which can promote electronic conductivity in ZrO_2 without accompanying deleterious effects on the film structure.

III. Investigation of additives which can catalyze the combination of hydrogen atoms.

Other factors may also influence the corrosion rate, and it is hoped that these will become evident when the more obvious factors have been isolated.

Compensating Additives Forming Rutile-type Oxides: Certain additives can be combined in ZrO_2 to produce a minimum disturbance in structure and number of defects. Low- and high-valence elements are required in such a ratio that the average valence is +4. As part of the structural approach, a series of ternary alloys were made with equimolar additives which can form oxides having the rutile structure. The oxides and lattice parameters are shown in Table XLV * Zirconium alloys were prepared containing the metallic elements of these combinations. All the alloys had 0.05 a/o A and 0.05 a/o B, where A and B form ABO_4 .

After arc melting, each button was partially flattened, vacuum annealed and cold rolled to $\frac{1}{16}$ -in. thickness. Half-inch diameter discs were stamped out and used for testing. These discs were tested as rolled or after vacuum annealing at 900°C for 16 hr, followed by either furnace cooling or water quenching.

A study was made of the oxidation rate in O_2 at 700°C , 1 atm, and in steam at 540°C , 600 psi, to compare these results with other data under similar conditions and to see whether corrosion hydrogen effects could be identified in some of the alloys more so than in others.

*K. Brandt, Structure Reports 9, 178 (1942-44)

Table XLV

SYNTHESIZED RUTILE COMPOUNDS (BRANDT)

Compound	a, Å	c, Å	c/a
CrTaO ₄	4.626	3.009	0.648
FeTaO ₄	4.672	3.042	0.652
RhTaO ₄	4.684	3.020	0.645
CrNbO ₄	4.635	3.005	0.647
FeNbO ₄	4.680	3.050	0.650
RhNbO ₄	4.686	3.014	0.642
AlSbO ₄	4.510	2.961	0.658
CrSbO ₄	4.577	3.042	0.664
FeSbO ₄	4.623	3.011	0.652
RhSbO ₄	4.601	3.100	0.673
GaSbO ₄	4.590	3.030	0.660
RhVO ₄	4.607	2.923	0.635
TiO ₂	4.5929	2.9591	0.644

The oxidation in dry O₂ was carried out for times up to 11,000 min. Under these conditions, only the FeSb and RhSb alloys were better than zirconium without additives. When the same alloys were put into steam at 540°C, 600 psi the sequence was different, and the RhV combination proved to be the best, with seven alloys better than zirconium. The RhNb and RhSb alloys (best except for RhV) were only good in the quenched condition, whereas RhV was the only alloy with good resistance in the cast and cold-rolled condition. These specimens were the only ones which survived well over 500 hr in steam at 540°C, 600 psi. At the end of December 1960, specimens of this composition have been in test for 3,194 hr. Weight gains cannot be given because of slight oxide flaking. Growth of the oxide layer is obviously slow and uniform. It is believed that all the other compositions would have disintegrated much earlier if they had not been removed when oxide flaking became appreciable.

Because of their opposite corrosion behavior in oxygen and steam, the FeSb and RhV alloys are of particular interest. It is suspected that the latter alloy has an oxide with lower electronic resistance. Measurements of emf are being made to test this hypothesis.

Compensating Additives Based on Scandium and Yttrium:

Another structural approach was based on an alloy series using scandium and yttrium in combination with elements having valences higher than +4. The Sc³⁺ or Y³⁺ would be compensated by such ions as Nb⁵⁺ or Mo⁶⁺.

After screening a large number of combinations, the most promising have proved to be scandium with Mo, Ta, or W, and yttrium with tantalum. Those alloys which are still in steam test without showing accelerated attack are the following:

Alloy		Hr in Steam at 540°C, 600 psi
0.13 a/o Y	0.16 a/o Ta	1214
0.13 a/o Sc	0.20 a/o Ta	3173
0.075 a/o Sc	0.23 a/o Ta	3173
0.05 a/o Sc	0.23 a/o Ta	3173
0.13 a/o Sc	0.20 a/o W	3173
0.07 a/o Sc	0.22 a/o W	3173
0.05 a/o Sc	0.23 a/o W	3173

The oxide layer for the times shown was grey and fairly uniform except at the edges, where the oxide had cracked. The oxide thickness was approximately 0.2 mm on the scandium alloys and 0.1 mm on the yttrium alloy.

It is significant that none of these alloys had developed areas of accelerated attack with accompanying hydride formation. Combinations of Sc and Mo were also promising as compared with a variety of other combinations, but were subject to slowly accelerating attack after long exposure in steam. A report on the Sc and Y alloys is in preparation.

Binary Alloys - emf Measurements: The second approach to a study of zirconium oxidation mechanisms has been based on measurements of the emf of the growing ZrO_2 scale. A low emf signifies a conducting scale, whereas a high emf indicates low conductivity. The study was made on a series of alloys containing 1, 2 and 4 atom per cent of the following elements: Al, Be, C, Co, Cr, Cu, Fe, Hf, Mo, Nb, Ni, Pb, Pt, Si, Sn, Ta, Ti, U, V, and W. These alloys were originally prepared for a study of dry oxidation by the Chemical Engineering Division at ANL and are described in ANL-6046. Specimens of each alloy were kindly provided by Dr. H. A. Porte for further study in water and steam. The analyzed and nominal contents were in reasonable agreement. The zirconium controls and the zirconium used as the base stock had the analyses shown in Table XLVI. The important differences were in Cu, Fe and Ni. Higher amounts of these elements in the ppm range improve corrosion resistance in water and this fact may have influenced the relative standing of the Zr control as shown later where corrosion data are presented.

The technique of emf measurement requires contact of the growing scale and an electronic conductor, in this case nickel oxide doped with lithium oxide. The procedure has been described in the previous annual report. The specimen is brought to temperature in one to two minutes by inserting the specimen after the system has come to temperature.

Table XLVI

ANALYSIS OF ZIRCONIUM

Chemical Analyses for C, H, N, O; All Other Elements
Determined by Spectrographic Analyses

Element	Zirconium Used in Oxidation Studies (ppm)	Zirconium Used as Base Metal for Alloys (ppm)
Ag	< 1	1
Al	10	< 10
B	< 0.1	0.5
C	79	19
Cr	1	5
Cu	5	100
Fe	800	80
H	-	0.6
Hf	< 1000	< 500
Mg	< 1	15
Mn	1	< 1
N	23	11
Ni	100	< 50
O	185	77
Pb	4	15
Si	50	50

Measurements were made on the 1- and 4-a/o alloys with the expectation that the 2-a/o alloy would be intermediate. The emf developed across the oxide on the alloys varied from 0 to above that on pure zirconium. It was possible to group the alloys into three classes, which are described below:

Class I: Al, Be, C, Hf, Pb, Si, Sn, Ta, and W. These alloys had similar maximum emf's in both the 1- and 4-a/o alloys, or the 4-a/o alloy was somewhat higher. Aluminum is a special case because the emf was higher than it is for pure zirconium. The remaining alloys had emf's below or comparable to pure zirconium.

Class II: Co, Cr, Cu, Fe, Mo, Nb, Ni, Pt, U, and V. The 4-a/o alloy had a lower emf than the 1-a/o alloy. In the case of chromium and copper, occasional emf maxima were higher than the maximum for pure zirconium. In the remaining cases, the emf's were always lower than the maximum for pure zirconium.

Class III: Ti. The emf was low in both the 1- and 4-a/o alloys. Only the titanium alloy had this property.

The data for five representative alloys are presented in Table XLVII. An additive such as titanium will form solid solutions in both the metal and the oxide. An additive such as platinum will be less soluble in the metal and probably insoluble in the oxide. Between these extremes can be found varying degrees of solution and compound formation.

Table XLVII
RESULTS OF emf MEASUREMENTS OF BINARY ZIRCONIUM ALLOYS
1 atm O₂ 700°C

Alloy		Test Time (min)	Induction Period (min)	Maximum Observed emf	emf at End	Resistance at End (ohms)	Comments on emf Curve	Appearance of Specimen after test
Element	Atomic %							
Al	1	147	24	1.48	1.44	5.9×10^4	Rapid rise, fluctuations for 21 min, then smooth	Uniform white
	4	103	38 (excluding small initial rise)	1.68	1.61	1.6×10^5	Smooth curve, no fluctuations	Glossy white coating with cracks
Ta	1	147	18	0.81	0.60	9.0×10^4	Small fluctuation for 26 min, then minor	Black with white specks
	4	100	45	0.85	0.85	Not measured	Very stable emf	All white, a thin white outer layer is flaking, darker underneath
Co	1	147	123 (excluding small initial rise)	1.0	1.0	3.3×10^4	Smooth curve except for one dip	Adherent, non-uniform grey
	4	100	-	0	0	3.3×10^2	No rise	Smooth, shiny dark grey
Pt	1	147	107	0.98	0.78	5.5×10^4	Maximum fluctuations to end	Shiny black, some peeling
	4	91	Intermediate	0.64	0	1.1×10^2	Slow rise with irregular variations between 0 and maximum	Dull black coating
Ti	1	147	42	0.15	0.15	2.3×10^2	Very slow emf rise	Shiny black, white on sharp edges
	4	103		0.03	0.03	1.5×10^4	Very slow rise	Shiny black, scattered white
Zr		115	4	1.32	1.15	Not measured	Sporadic fluctuations diminishing toward end of experiment	White oxide, some black patches

Higher than on zirconium

A gross measurement of film conductivity as made in the present study could not differentiate between conductivity produced by second-phase conducting particles and enhanced conductivity of the ZrO₂. In some cases the choice between these alternatives was clear, while in others a microscopic study would be necessary.

Binary Alloys - Corrosion Test Results: The same alloys were tested, first in degassed water at 350°C for a maximum time of 225 hr. The results made it possible to rate the alloys in order of increasing corrosion resistance. Promising alloys of the best 9 constituents were selected to go into steam at 540°C and 600 psi. Some of these compositions were shown to be poor within a short time, but others have shown good corrosion resistance. At the end of December 1960, the total test time was 2987 hr, and the following specimens were still in test: 1, 2, 4, a/o Co, 2, 4 a/o Cr, 2 a/o Fe, 1 a/o Mo, 1, 2, 4 a/o Nb (discontinued at this time), 2, 4 a/o Ni, 1, 2, 4 a/o Pt, 1 a/o U, 1, and 2 a/o W. On the basis of appearance, the Co alloys were the best and the Nb alloys were the worst. The survival of the 1-a/o U alloy was a surprise. All but the Nb alloys have been continued in test.

Weight gains for those alloys with negligible flaking are tabulated in Table XLVIII.

Table XLVIII

CORROSION WEIGHT GAINS OF BINARY ALLOYS
AFTER 2987 HR IN 540°C, 600 psi STEAM

Alloy	Wt Gain, mg/dm ²
2 a/o Fe	410
1 a/o Co	460
2 a/o Co	540
1 a/o Mo	1130
1 a/o U	1180
1 a/o Pt	1460
4 a/o Pt	2750
2 a/o Pt	3050

Discussion: Obviously these alloys do not all represent "good corrosion resistance," but they provide some clues to understanding the corrosion mechanism. The surviving alloys fall into two classes: cathode formers (Ni, Co, Fe, Pt), and noncathode formers (Cr, W, U, Mo, Nb). Class I are all hydrogenation catalysts, and Class II all have multiple valencies, a fact which indicates that they will contribute to the electronic conductivity of the ZrO₂ layer. This hypothesis was confirmed by the emf measurements in oxygen and will be evaluated in steam.

In the case of the uranium alloy it is thought that some favorable impurities, such as iron, may be present. This would be in agreement with the compensation mechanism which has been shown for certain alloys.

The factor of catalytic combination has not been studied directly but deserves consideration on the basis of certain alloy combinations which have shown good corrosion resistance. The alloy containing 0.05 a/o Rh and 0.05 a/o V was mentioned earlier in this section. Later work has shown that the alloy containing 0.05 a/o Pt and 0.05 a/o Ta is also a promising combination. In these combinations it is believed that the catalytic effect of Rh and Pt is enhanced by additives such as V and Ta, which can increase the conductivity of the ZrO_2 layer and thereby enhance the effectiveness of isolated particles of the noble metals.

According to theoretical considerations, a means by which the conductivity of ZrO_2 can be enhanced is to incorporate cations of valence higher than four. For example, each +5 cation will introduce one electron into the ZrO_2 lattice. Some likely additives and valences in which they are commonly found are as follows: P(3,5), S(2,4,6), V(2,4,5), Cr(2,3,6), Mn(2,4,6,7), As(3,5), Se(2,4,6), Nb(3,5), Mo(3,5,6), Tc(4,6,7), Ru(3,4,6,8), Sb(3,5), Te(2,4,6), Ta(5), W(3,5,6), Re(1,4,7), Os(4,6,8), Bi(3,5), and U(4,6). Several actinides could be listed also. Ruthenium and osmium are of particular interest because they should also be catalysts for hydrogen combination. However, these elements may have an unfavorable structural effect which would require compensation by another additive.

By extending the emf measurements to steam, it should be possible to resolve some of the questions of alloy effectiveness based on considerations of film conductivity. Structural studies are also planned to determine why, e.g., aluminum and titanium are such deleterious additives although they both lower the emf (raise the conductivity) of the growing ZrO_2 scale.

3 Corrosion of 1100 Aluminum in Water (S. Mori)

The eddy current thickness gage for corrosion specimens which was developed by Doe* has been improved to a point where it is almost as sensitive as measurements on the micro-balance. Sample corrosion (1100 aluminum) can be read to the nearest $4 \mu\text{gm}$ on the gage, with a reproducibility of about $40 \mu\text{gm}$. The devices for putting into position the unknown and standard samples have been improved so that both may be alternately centered inside the instrument with a minimum amount of required adjustment. The temperature gradient was decreased and the temperature stability was improved by proper lagging around the gage box and by circulating constant-temperature air inside the box. The gage has been used successfully for the past year.

Loss of Corrosion Product: Some of the solid product of the corrosion of aluminum in water is lost from the surface during the exposure. By adding fresh water continuously to the test chamber and allowing the

*William B. Doe, Eddy Current Type Diameter Gauge for Corrosion Measurements, ANL-5227 (September 1954).

overflow water to pass into an evaporator, it has been possible to analyze for aluminum. The aluminum content of the corrosion product lost from 1100 aluminum, by dissolution, peptization, or flaking has been determined as a function of time.

Figure 5 . Corrosion Product Lost from Specimens during Corrosion of 1100 Aluminum in Oxygen-saturated Water at 70°C.

Apparent breaks in such curves (see Figure 50) occur about at the time previously shown to correspond to the breakdown of an initial boehmite (AlOOH) film, with the formation of bayerite [$\text{Al}(\text{OH})_3$]. Note that an originally ground surface lost more product per unit apparent surface area than an originally etched surface. This is very possibly associated with the difference in real (microscopic) surface areas. The two curves cross after a few days, subsequent to which time the product is retained better on the ground specimen.

When considered with other measurements, these analyses make possible rather complete observations of the overall chemistry of the reaction. Such a summary for a single specimen is given in Figure 51. The dried specimen (containing corrosion product) was weighed periodically to give the gain in weight, G , as a function of time. At the same times, the amount of unreacted metal was measured on the eddy current thickness gage to give the total metal lost by corrosion, L . The aluminum lost to the solution was determined as before. From these, the atomic ratio of OH to Al in the adherent corrosion product was calculated, assuming the composition to be $\text{Al}(\text{OH})_n$. The oxide identified by X-ray diffraction was bayerite, $\text{Al}(\text{OH})_3$. The average composition, as prepared and examined, apparently varied with time from about $\text{Al}(\text{OH})_{2.3}$ to $\text{Al}(\text{OH})_{3.1}$.

Figure 51. Corrosion of 1100 Aluminum in Oxygen-saturated Water at 70°C.

Kinetics of Long-time Reaction: Using the eddy current thickness gage, the amount of corrosion has been determined as a function of time over a one-year period. The data for typical individual specimens

are shown in Figure 52 (annealed and etched 1100 Al, O_2 -saturated H_2O at $70^\circ C$), together with the gains in weight of the specimens. Two chambers were used, through which the refreshing water flowed in series; the fresh water was added to chamber II first, then it flowed through chamber I. It is typical that the specimen in the fresh water corroded less during the initial period than in the water which had been contaminated by corrosion product from samples in the first chamber. Subsequent to the initial period, the curves are parallel, indicating no contamination influence on corrosion rates.

Figure 52

Corrosion of 1100 Aluminum
in $70^\circ C$, Oxygen-saturated
Distilled Water.

Analysis of the shapes of the corrosion curves is proceeding. It is not yet possible to show results, but the kinetics of the reaction should provide insight into the mechanism.

pH Measurements Close to Corroding Surface: One of the unusual features of the corrosion of 1100 aluminum in water is the relatively great amount of attack which occurs during the initial exposure period, before the rate becomes quite small. We have felt that this is related to water contamination close to the surface of the corroding metal, and have been measuring the pH at such locations by means of specially developed miniature electrodes.

In Figures 53 and 54 are shown the pH at a distance of 1 mm from the 1100 aluminum surface as a function of time in water at $50^\circ C$. Several positions along the surface were measured, designated in terms of the distance from the edge of the specimen which was upstream with respect to the refreshing water.

In oxygen-saturated water the pH rose briefly, decreased to a minimum in the general region of 25 to 50 min, then gradually rose toward the pH of the bulk water. The most acid region (pH 4.3 at minimum) was toward the inlet region, where the oxygen concentration is presumed to be highest.

Figure 53

pH of Water 1 mm from Corroding
1100 Aluminum Surface. (50°C,
Oxygen-saturated)

In helium-saturated water, pH changes were generally smaller. Most observed values showed the water next to the corroding surface to be more alkaline than the bulk water.

These data should help point the way to a descriptive mechanism of the processes occurring.

Figure 54

pH of Water 1 mm from Corroding
1100 Aluminum Surface. (50°C,
Helium-saturated)

Corrosion in Copper Sulfate Solution: Aluminum alloys characteristically show severe pitting attack in copper salt solutions at temperatures below the boiling point. This has been thought to be related to the deposition of active copper cathodes. Recently developed nickel-bearing alloys are believed to have active cathodes "built in," and do not corrode unduly in pure water at ordinary temperatures. It was believed to be of interest to determine whether or not such alloys are susceptible to pitting in copper-containing solutions. Accordingly, the behaviors of four alloys were compared in oxygen-saturated copper sulfate solution (5 ppm Cu^{++}) at 50°C. The materials were pure aluminum (99.99+%), 1100 Al (0.5% Fe, 0.2% Si, 0.1-0.2% Cu), X8001 alloy (1100 Al + 1% Ni), and alloy A288C (pure Al + 1% Ni, 0.5% Fe, 0.1% Ti).

After a few days, severe pitting was observed on the two nickel-containing alloys and less severe pitting on the 1100 aluminum specimens. No pits were observed on the pure aluminum after a total exposure of 35 days. For the alloys, surface preparation influenced the severity of the pitting. Rough ground surfaces (240 grit) pitted more

severely than a somewhat finer surface (400 grit); however, electropolished surfaces were badly attacked. All pitted areas were accompanied by, and are apparently a result of, deposited copper.

The pits formed on the same alloys in the same concentration of helium-saturated copper sulfate solution were generally smaller and less deep than in the oxygen-saturated solution.

4. Mechanism of High-temperature Corrosion of Aluminum Alloys (W. E. Ruther)

Water: Aqueous attack on the family of corrosion-resistant, low-silicon, aluminum-nickel alloys results in the formation of a multi-layered protective coating. The location of the corrosion-rate-determining barrier has been experimentally determined for attack at a temperature of 350°C. Pieces of a 1 w/o Ni-0.1 w/o Ti alloy were carefully ground flat, corroded for 27 days at 350°C, then returned to the shop for regrinding. The amount to be removed was determined by sectioning a sample. Some specimens had the outer one-third of the adherent layer removed and others had the outer two-thirds removed. These reground specimens and controls were then returned to the corrosion test for another two months. The amounts of corrosion were identical for all specimens, indicating that the barrier is close to the metal-oxide interface.

At 260°C, the corrosion rate is higher and the corrosion product different in character and composition. The experiment is being repeated at this temperature.

Superheated Steam: The corrosion of many aluminum alloys in superheated steam (540°C, 600 psig) is characterized by an increase in the hydrogen content and the formation of voids within the metal. Also characteristic is a sudden penetrating attack which rapidly destroys a sample after hours, days, or even months of extremely slow corrosive attack. A partially destroyed specimen was carefully sectioned and examined optically and with the electron microscope and its associated selected area diffraction camera.

Based on the micrographs and diffraction patterns the following mechanism for the reaction has been proposed.

The predominant oxides which form on a pure aluminum surface exposed to superheated steam at 540°C, 600 psi (α -Al₂O₃ and members of the γ series of Al₂O₃) appear to form thin, protective films. A portion of the hydrogen produced by the surface reaction with steam enters the metal and produces gas-filled blisters. As long as the interior of the blister is isolated from the steam, the corrosion appears to be limited to the very slow exterior surface reaction.

Eventually mechanical failure or continued corrosion opens a fissure to the interior of the blisters. Depending on the particular alloy and strain in the sample, this might occur in a few minutes, hours, or years. Film-free aluminum is then exposed in a predominantly hydrogen atmosphere containing some water vapor. The corrosion product formed under these conditions appears to be a hydrated aluminum oxide, probably diaspoire, and relatively nonprotective. More corrosion-produced hydrogen enters the metal, produces new blisters, and continues the cycle at an accelerating pace. New film-free aluminum surface is exposed to the hydrogen-steam at an increasing rate, and the sample is rapidly destroyed.

It has not been determined whether the oxide formed on the interior of the blister is nonprotective because of the environment in which it is formed (hydrogen-steam) or because of the geometry which tends to expose fresh metal. In either event, the hypothesis offers explanations for the various experimental observations described in ANL-6207.

The penetrating attack of aluminum and many of its alloys in liquid water is in many ways similar to the behavior in steam. This suggests that the same method of propagation might be operative in water at lower temperatures as well as in superheated steam. Thus, aqueous grain-boundary attack of pure aluminum and of common alloys above 200°C might proceed rapidly because the hydrogen-water vapor atmosphere is formed and reacts at such locations.

5. Corrosion Studies by Electron Microscopy (R. K. Hart)

Electron Optical Investigation of Particulate Material in Al-1 w/o Ni Alloys

Since the last annual report was written it has been possible to obtain a number of good electrothinned specimens of both A255* alloy and X8001* alloy for direct transmission examination. The two alloys were supplied in 0.005-in.-thick sheet which had been cold rolled from 0.125-in.-thick stock. These sheets were then heat treated for 4 hr at 530°C and water quenched. Some of the quenched material was then aged for 1 day at 150°C. Thin metal foils were then prepared from these sheets by electropolishing at 15°C in perchloric acid-acetic acid (1:9) at 30 to 40 volts. Typical examples of micrographs obtained from these specimens are shown in Figures 55 to 58.

*A255 series alloy was made from 99.99% aluminum stock to which was added 1.0% nickel and 0.1% titanium.

X8001 alloy is a commercial alloy supplied by Alcoa, and the following is a typical analysis:

nickel	0.89%	silicon	0.11%
copper	0.13%	manganese	0.01%
iron	0.48%	titanium	0.02%

Figure 55. Precipitates in A255 Alloy before Heat Treatment.

Micro 100533

80,000-X

As-rolled Alloys: Figure 55 is a micrograph obtained from as-rolled A255 alloy foil. Many of the precipitates in the $1\text{-}\mu$ range were of the form shown by the large particle in this figure. These precipitates consisted of a core which appeared to have a continuous structure and an outer casing composed of crystallites several hundred Angstroms in diameter.

Larger precipitates were similar in appearance to the core of the precipitate shown in Figure 55, whereas smaller precipitates generally consisted of crystal aggregates.

In as-rolled X8001 alloy the precipitates were all of the continuous type similar to those shown in Figures 57 and 58.

Figure 55. Precipitates and Dislocations in A255 Alloy after Aging 1 Day at 150°C.

Micro 100777

40,000-X

Quenched Alloys: All specimens after quenching or quenching and aging contained precipitates similar to those shown in Figures 56 to 58. In many of the micrographs, structures within the precipitates were clearly visible. The dark spots within these precipitates are most likely related to smaller precipitates from which these larger precipitates grew. Thus it would appear that the diffusion of nickel in these precipitates is neither uniform nor complete. This observation was verified in the case of one sample of X8001 alloy which was submitted for electron microprobe analysis. The analysis showed a varying distribution of nickel within a precipitate and that a high concentration of nickel remained around its edge. Both with the quenched, and quenched and aged, specimens the concentration of precipitates was greater within the grains than at boundaries, and there was no indication of any long range strain associated with these precipitates.

Figure 57. Precipitates and Dislocations in X8001 Alloy after Heat Treatment for 4 Hours at 530°C.

Micro 100623

40,000-X

Both Figures 56 and 57 show a variety of dislocations, some associated with precipitates while others lie within the matrix. Once a dislocation makes contact with a precipitate, it appears to be locked at the point of contact. Heating of the foil by the electron beam showed that many of the dislocations in the matrix were free and that a constant source of them were grain boundaries. The grain boundary in Figure 56 is acting as a donor. Some line dislocations after being locked to precipitates form dislocation loops as shown at A in Figure 56. These loops are probably the result of the collapse of aggregated vacancies. A complex network of dislocations can be seen at A in Figure 57. The cause of these networks is still unknown.

Examination of Alcoa Powder Product S171303: This material contained 1.39 w/o Fe, 0.08 w/o Si, 0.04 w/o Mn, 1.37 w/o Ni, 0.05 w/o Cr, and 0.26 w/o oxide. It was compacted and extruded into a $\frac{3}{4}$ -in.-dia rod at Alcoa. A piece of this rod was rolled into 0.005-in. sheet and electrothinned as described above.

Figure 56 Large Precipitate in X₅ Alloy after Heat Treatment for 1 Hour at 53 °C.

Micro 100622

40,000-X

The structure of these foils was found to be appreciably different from that of the cold-rolled and heat-treated aluminum-nickel alloys which has been described above. A typical transmission micrograph of this material is shown in Figure 59. The general appearance of these foils was closely similar to that of a vacuum evaporated film. Individual grains were generally 1μ or less in diameter and contained many dislocations. Subgraining was also prevalent. Selected area diffraction patterns showed that the aluminum grains were rotationally disoriented. The precipitates were well dispersed and appreciably smaller (0.2 to 1μ) than in the other alloys. The composition of these precipitates was FeNiAl_9 .

Figure 59. Electrothinned Alcoa Powder Product (S171303).

Micro 100862

20,000-X

Examination of Corrosion Films on Aluminum and Iron

Film Growth on Aluminum in High-temperature Water: Work on the aluminum-water systems of current interest has continued. The results of these investigations have been reported in ANL-6230 and thus only a summary will be given here.

Film growth on aluminum and two aluminum-1 w/o nickel alloys in water at 250°C and at 350°C has been studied. It has been found that oxide growth does not advance on a uniform front but, to the contrary, the advancing surface contains many outcrops in the form of thin platelets, chunky outcrops, and whiskers. In the cases of both the pure metal and the alloys considerable intergranular attack was observed. The general corrosion product was usually more uniform in crystal size when formed on the pure metal, but variations in crystal size were observed on both

aluminum and alloys with varying features of the metal surface. The roughness of the general oxide surface (including outcrops) was found to increase rapidly to about 0.2μ and then remain relatively constant with increasing film thickness. The composition of films formed under all investigated conditions, except one, was found to be boehmite ($\alpha\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$). This exception was films carried by the alloy specimens after testing for 32 days at 350°C . In this case the main corrosion film was still boehmite, but in addition the outer surface supported long needles of diasporite ($\beta\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$).

The Morphology of Surface Reaction Products on Aluminum:

The morphology of film growth produced on aluminum and aluminum-1 w/o nickel alloys by heating in vacuo and dry air at 350°C and at 540°C , in water vapor at 350°C , in superheated steam at 540°C and 600 psi, and by anodic oxidation in ammonium tartrate has been studied.

The oxide growths, viewed electron optically in silhouette, were found to take various shapes such as "chunky" outcrops, platelets, and whiskers. These outcrops nearly always consisted of well-crystallized material, often single crystals, which was in contrast to the structure of the general surface films.

Besides there occurring "amorphous" and gamma alumina ($\gamma\text{-Al}_2\text{O}_3$), films of a lambda phase (orthorhombic, pseudo-tetragonal, $a = b = 7.63 \text{ \AA}$, $c = 2.89 \text{ \AA}$) were found on the Al-Ni alloy at 540°C in vacuo, and a θ phase (monoclinic, $a = 5.7 \text{ \AA}$, $b = 2.92 \text{ \AA}$, $c = 11.9 \text{ \AA}$) was found on both aluminum and the Al-Ni alloy when heated in dry air at 350°C and at 540°C .

Reaction of these materials with steam led to the formation of both corundum ($\alpha\text{-Al}_2\text{O}_3$) and gamma alumina.

A summary of the observed oxide growths is given in Table XLIX.

Table XLIX
OXIDE GROWTH OBSERVED ON OXIDIZED ALUMINUM

	Vacuo	Dry Air	Water Vapor	Steam	Anodic Oxidation
Al	Smooth except for occasional outcrop and whisker; gamma alumina.	Smooth except for occasional outcrop; theta alumina.	Slightly roughened and dome shaped platelets gamma alumina.	Smooth except for platelets after 6 hr. Platelets and whiskers after 24 hr. Corundum plus gamma alumina. Pure aluminum less rapidly attacked.	Outcrops rare; gamma type alumina.
A255	Smooth except for occasional outcrop and whisker; lambda alumina.	Slightly rougher surface than pure aluminum; occasional outcrop of theta alumina.	Same as for pure aluminum.	6 hr - Platelets and outcrops built up of small crystallites; Corundum plus gamma alumina. 24 hr - Slight increase in roughness; Corundum plates abundant; few filaments.	Considerable outcropping; gamma type alumina.

Film Growth on Iron in High-temperature Water: Preliminary experiments have been carried out on the corrosion of pure iron under the following conditions:

- a) water containing 30 ppm O_2 for 26 days at $260^\circ C$, and
- b) water containing 530 ppm O_2 for 67 hr at $180^\circ C$.

These conditions were the first set in a continuing series of experiments.

The electrolytic iron foil (0.005 in. thick) used to prepare the disc specimens was hydrogen annealed for 1 hr at $800^\circ C$ and then furnace cooled in argon. Specimens in the form of drilled discs were made from this sheet and were electropolished immediately prior to use. These specimens were corroded in a refreshed autoclave, the water feed being 8 cc/min.

Pure iron reacted with water under conditions (a) above to produce outcrops in a variety of forms. The three most prevalent forms observed were platelets, filaments consisting of bundles of fibres, and dendritic structures. Selected area diffraction patterns showed the structures of these outcrops to be different.

The general surface, which consisted mainly of dendritic growths, (see Figure 60), was found to be $\gamma\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$. The filamentary growths shown in Figure 61 were composed of many fibres of $\alpha\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$. These fibres yielded diffraction patterns which were textured, the $[010]\alpha\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ being parallel to the long fibre axis. Platelets on the other hand were found to be $\gamma\text{-Fe}_2\text{O}_3$ with the $[111]\gamma\text{-Fe}_2\text{O}_3$ parallel to the beam.

After iron discs were corroded in water containing 530 ppm O_2 for 67 hr at $180^\circ C$, isolated "chunky" outcrops, as shown in Figure 62, were observed to protrude from an otherwise smooth surface. This type of outcropping was similar in many respects to that observed on aluminum-nickel alloys after very short exposures to water at $250^\circ C$. Selected area diffraction patterns from these outcrops were because of their thickness of poor quality. However, the diffractions which were measured agreed reasonably well with the diffraction data for $\gamma\text{-Fe}_2\text{O}_3$.

Optically, these surfaces displayed brilliant interference colors due to anisotropic film growth on metal grains of varying orientations. It was found that the outer surfaces of these corroded specimens were smooth enough to replicate, and a typical micrograph is shown in Figure 63

Some of the corrosion product films were stripped from the metal in methanol/iodine stripping solution and then viewed electron optically by direct transmission. The oxide structure was found to be similar to that obtained by replication, i.e., as in Figure 63. These films proved to be very useful, as they gave very good diffraction patterns, which corresponded to α - Fe_2O_3 - ASTM card 6-0502. The occurrence of long arcs on the spotty rings of these patterns confirmed that the film material was preferentially oriented with respect to the underlying metal.

Figure 60. Iron Disc after Corrosion for 26 Days at 260°C
in Water Containing 30 ppm O_2 .

Micro 100573 8000-X
Dendritic growth of $\gamma\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (lepidocrocite).

Figure 61. Iron Disc after Corrosion for 26 Days at 260°C
in Water Containing 30 ppm O₂.

Micro 100570

12,000-X

Circle is the image of selected area aperture. The corrosion product on the surface was $\gamma\text{-Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$ (lepidocrocite) and the filamentary growth consisted of fiber textured $\alpha\text{-Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$ (goethite).

Figure 62. Outcropping on Pure Iron Disc after Corrosion in Water Containing 530 ppm O_2 for 67 Hr at $180^\circ C$.

Micro 100790

16,000-X

Figure 63. Carbon Replica Preshadowed with Pt-Pd of the Outer Surface of Film on Iron after Corrosion in Water Containing 530 ppm O_2 for 67 Hours at 180°C.

Micro 100801

6000-X

H. Irradiation Effects

1. Fission Gas Research (B. A. Loomis)

It is generally accepted that swelling of fissionable materials upon neutron irradiation is the result of agglomeration of krypton and xenon fission product gas atoms in small bubbles within the metal matrix. The manner in which the bubbles nucleate and the mechanism of their growth, however, are not clearly understood; nor have the factors been defined which influence the magnitude of swelling. In the studies described below, an experimental survey has been made of the swelling behavior of unalloyed high-purity uranium and of some selected uranium alloys after postirradiation annealing. Some of the variables studied included the annealing temperature, time at temperature, microstructure, thermal cycling, and burnup.

Materials and Experimental Procedure

Castings of high-purity uranium and of high-purity uranium alloyed with either titanium, zirconium, niobium, molybdenum, carbon, or nitrogen were prepared from electrolytic uranium. The uranium was enriched with 1.7 w/o U^{235} . The castings, which were $\frac{3}{4}$ -in. in diameter, were extruded to $\frac{3}{8}$ -in.-diameter rods. The extruded rods of the unalloyed uranium and of the alloys containing carbon or nitrogen were annealed at 725°C for ten minutes, water quenched, and then reannealed at 620°C for 1 hr and furnace cooled to room temperature. The extruded rods of the other alloys were annealed at 800°C for three days, furnace cooled to 525°C, annealed at 525°C for fourteen days, and furnace cooled to room temperature.

Specimens, $\frac{1}{4}$ -in. in diameter and $\frac{1}{2}$ -in. long, were cut from the heat-treated materials for irradiation. The samples were irradiated under total volumetric restraint in stainless steel capsules ($\frac{3}{32}$ -in. wall thickness). The capsules were irradiated in the Materials Test Reactor at a calculated central metal temperature of about 300°C. After irradiation, the stainless steel jackets were removed, and the specimens were annealed at different temperatures and for various periods of time in an evacuated tube. The samples were heated to and cooled from the annealing temperatures at 4°C/min. The amount of swelling which occurred as a result of a given annealing treatment was obtained by measuring the room-temperature densities of the specimens.

No accurate burnup analyses are available as yet; the burnups given below are tentative and are based on the quoted thermal flux.

Results

Unalloyed Uranium: The swelling of unalloyed uranium irradiated to approximately 0.5 a/o burnup upon subsequent annealing is shown in Figures 64, 65, and 66.

Figure 64. The Effect of Annealing on the Swelling of Uranium Irradiated to about 0.5 a/o Burnup

Figure 65. The Effect of Annealing Temperature on the Swelling of Uranium Irradiated to about 0.5 a/o Burnup

Figure 66. Effect of Annealing Temperature on the Swelling of Irradiated Uranium

In Figure 64, the per cent decrease in density is plotted as a function of annealing time at various temperatures. Each curve represents a single specimen; the annealing times shown do not include the periods required for cooling to room temperature to make the density measurements, nor the reheating to the annealing temperature. The data is replotted in Figure 65 as a function of the annealing temperatures for four annealing intervals: 30 min, 3 hr, 10 hr, and 15 hr.

The effect of burnup is illustrated in Figure 66. Curves I and III are for specimens which received approximately 0.5 and 0.25 a/o burnup, respectively. The points on each curve represent the cumulative decreases in density of a specimen as a result of annealing 30 min at successively higher temperatures. In Curve II, each point represents a separate specimen which was annealed for 30 min at the indicated temperature.

Uranium Alloys: The swelling behavior of irradiated uranium alloys upon annealing is shown in Figures 67, 68, and 69. In Figure 67, the per cent decrease in density is plotted against the annealing temperature for specimens which received approximately 0.25 a/o burnup. Each curve represents a single specimen which has been heated for 30 min at consecutively higher temperatures. In Figure 68, similar data are plotted for alloyed uranium specimens which received approximately 0.5 a/o burnup. For comparison purposes, data for unalloyed uranium are also included in Figures 67 and 68. The temperatures at which phase changes occur in the alloys are indicated by vertical dashed lines on each of the curves. In Figure 69 the decreases in density of several uranium alloys are plotted as a function of annealing time at 620°C

Figure 67. The Effect of Annealing Temperature on the Swelling of Specimens Irradiated to about 0.25 a/o Burnup

Figure 68. The Effect of Annealing Temperature on the Swelling of Specimens Irradiated to about 0.5 a/o Burnup

Figure 69. The Effect of Annealing at 620°C on the Swelling of Specimens Irradiated to about 0.5 a/o Burnup

High Zirconium-Uranium Alloys: Investigation of postirradiation annealing of specimens of zirconium-uranium alloys was made for annealing temperatures up to 900°C. The alloys were rectangular specimens cut from zirconium-clad, zirconium-uranium rolled fuel plates containing 3, 6, and 14 w/o highly enriched uranium. The specimens were cut from the fuel plates in such a manner that the alloy core was exposed on two sides. The alloys received burnups ranging up to 2.7% of the total atoms. The experimental data are plotted in Figures 70 and 71. Each curve represents the accumulated decrease in density of a single specimen annealed at successively higher temperatures. The annealing time at each temperature was only five minutes.

Figure 70. The Effect of Annealing Temperature on the Swelling of Irradiated Zirconium-Uranium Alloys

Figure 71. The Effect of Annealing Temperature on the Swelling of Irradiated Zirconium-Uranium Alloys

Figure 72. The Effect of Thermal Cycling between 600 and 700°C on the Swelling of Specimens Irradiated to about 0.5 a/o Burnup

Thermal Cycling: The effect of thermal cycling on some of the specimens between 600 and 700°C is shown in Figure 72, in which the percent decrease in density is plotted against the number of thermal cycles. The thermal cycle consisted of heating the sample at 4°C/min to 700°C and holding for 30 min, and then cooling the sample at 4°C/min to 600°C and holding for 10 min.

Discussion

The high-purity uranium decreased in density less than 1% upon annealing for extended periods of time at temperatures up to about

575°C. Burnup variations up to 0.5 a/o had no appreciable effect in this temperature range. Above this temperature and up to the $\alpha \rightarrow \beta$ transformation temperature, the magnitude of swelling increased sharply with increasing temperatures, as did the swelling rate at a given temperature; as shown in Figure 64, the swelling rate at 620°C is more than twice that at 595°C. The extent of swelling in this temperature range was also influenced by the burnup (see Figure 66).

The striking lowering of the swelling rate on annealing in the β -phase region is illustrated in Figures 64, 65 and 66. As shown in Figure 64, the swelling rate at 700°C is nearly constant for extended periods of annealing time. The indicated similar behavior at 653°C, which is normally below the $\alpha \rightarrow \beta$ transformation temperature, is probably due to a lowering of the transition temperature resulting from the presence of fission products in the material. The lowering of the swelling rate in the β phase is undoubtedly related, at least in part, to its increased strength or creep resistance as compared with the high-temperature alpha phase, although other factors may also be operative, such as the kinetics of bubble growth in this structurally complex phase.

Annealing in the gamma phase resulted in very large swelling rates. A specimen held for only 30 min at about 850°C decreased in density about 8%; on holding for 15 hr at temperature, the decrease in density was nearly 19%.

As for the behavior of the alloys, several observations are pertinent. As in the case of unalloyed uranium, decreases in density upon annealing at temperatures up to about 575°C were less than 2%. At some critical temperature level above this temperature there is a sharp increase in swelling, and in some of the alloys in this range the extent of swelling was even greater than for unalloyed uranium (see Figure 68). This critical temperature range resulting in large sudden density decreases can be associated in general with heating through a region of phase transformation (see Figures 67 and 68).

The distribution of the second phase in the alloys appears to have a significant effect on the swelling behavior of the alloys shown in Figure 69. The preirradiation microstructure of the U-4 w/o Nb alloy contained a finely dispersed second phase, whereas all the other alloys had generally coarser second-phase distributions. The distribution of the second phase, however, obviously cannot be the only factor which affected the magnitude of swelling, since the high-purity uranium specimen contained relatively little second phase, yet it swelled more than the U-4 w/o Nb alloy.

2. Electron Microscopic Studies of Fission Fragment Damage (K. L. Merkle and R. K. Hart)

A program was initiated during the past year to study the nature of fission fragment damage in thin foils by electron transmission microscopy. It is planned to irradiate vacuum evaporated films of Au, Ag, Cu, and Al, and thicker foils that have to be electrothinned to a suitable thickness for transmission electron microscopy. To date, only evaporated films of gold have been irradiated. Some of the results are described below.

Preparation of Gold Films: For irradiation purposes it is desirable to start with very clean films which contain as few faults as possible. By varying the amount of gold, the evaporation rate, and the substrate temperature, we were able to produce films which were suitable if viewed at a high magnification. The best films were obtained by evaporating 0.2 gm of gold at 10 cm distance from the substrate onto the (001) cleavage plane of rock salt maintained at 480°C. The evaporation time was three minutes. After evaporation, the gold films were floated from the rock salt onto a water surface and then picked up onto copper microscope grids. The films were textured with the [001] direction normal to the film surface. Individual crystallites within these films ranged from <0.1 micron to more than 10 microns in size. Typical structures of the evaporated films are shown in Figures 73, 74, and 75.

Figures 74 and 75 show that the monocrystalline regions of these films still contain many stacking faults (see ① in Figure 74). It is interesting to note that the stacking faults often have one straight boundary and one "wavy" boundary. The "wavy" boundary outlines the top surface topography of the film; the straight boundary is in the surface adjacent to the rock salt. The parallel lines within a stacking fault, as shown by ① in Figures 78, 79, and 81, result from a phase difference in electron waves diffracted from opposite sides of a fault. This difference exists because the two parts of the crystal separated by the fault are displaced relative to each other parallel to the fault plane. Stacking faults were only observed in the $<110>$ directions. The films also contained holes, several of which are indicated by ④ in Figure 78. The cause of these holes is thought to be adsorbed gases on the rock salt surface interfering with the gold nucleation process.

Irradiation: The fission fragment source was natural uranium. The irradiations were performed in the isotope tray of CP-5 at an estimated ambient temperature of about 50 to 60°C. After excessive radioactivity had decayed, the samples were observed in the electron microscope. In the first experiments a 0.001-in. uranium foil was placed in contact with the gold film, contained in an aluminum holder. After irradiation, the films showed black spots of 20 Å to 300 Å in diameter (see Figure 78).

Figure 73. Gold Film No. 26 Evaporated onto Rock Salt at 480°C. Time of evaporation 2 min and 20 sec.

Micro 101164

20,000-X

Figure 74. Gold Film Evaporated onto (001) Rock Salt at 480°C. Monocrystalline Area Showing Stacking Faults and Small Holes Time of evaporation 3 min.

Micro 101065

20,000-X

Figure- 75. Same Film as in Figure- 74 but Different Area, Illustrating Effect of Local Substrate Condition or Stacking Fault Concentration. Time of Evaporation min.

Micro 101066

20,000-X

Figures 76 and 77 show the same area of a film before and after irradiation. A few of the damage spots are identified by ③ in Figure 77. The lines designated by ① and ② in Figures 76 and 77 are dislocation lines.* The difference in contrast in grain A of Figures 76 and 77 has probably been caused by slight bending of the film. Some of the observed damage has the appearance of dislocation loops, as shown at ② in Figure 78, whereas other damage spots appear to have more complex structures (see ③ in Figure 78). The density of the spots is approximately 8.6×10^{16} per cm^3 for an irradiation of 4×10^{16} n/ cm^2 .

*One end of the dislocations shown at ② appears to have been locked at a grain boundary.

Figure 76. Gold Film No. 5.
Selected Area prior to irradiation.

Micro 100893

160,000-X

Figure 77. Same Area as Shown in Figure 76 after Irradiation with Fission Fragments from Uranium Foil. $\text{rvf} = 10^{15} \text{ n/cm}^2$.

Micro 100924

160,000-X

Figure 78. Gold Film, 500 Å Thick. Irradiated with Fission Fragments from Uranium Foil $nvt = 4 \times 10^{16} \text{ n/cm}^2$.

This density is an order of magnitude larger than the density of fission fragments in the film. If one assumes that the results can be applied to bulk gold, then one fission fragment produces approximately 10 damage spots along its entire path. The micrographs show that many of the spots do, in fact, occur in clusters, as can be seen by ③ in Figure 79 and ② in Figure 81. It is assumed that the clusters represent areas in the metal in which a fission fragment has produced several primary knockouts, each of which had sufficient energy to produce a black spot.

To obtain electron micrographs of high resolution of detail, the film thickness had to be kept below 600 Å. This is only 1/100-th the range of a fission fragment in gold. To observe all the damage produced over its entire range, a fission fragment must travel parallel, or at a very low angle, to the film surface. Two different methods were employed to obtain this condition. The fission fragment source in both cases was vacuum evaporated uranium; diffraction analysis showed the resulting films to be uranium dioxide. In the first method an approximately 50-Å thick uranium dioxide film was evaporated onto a small circular area in the center of a gold film. Figure 80 shows a region inside that area after irradiation, and ④ indicates tracks of fission fragments which traveled parallel to the surface. The tracks show as light lines since the fission fragments remove some of the UO_2 along their path. In the area shown in Figure 80, the UO_2 film was too thick to permit observation of the damage in the underlying gold film. The ideal situation would be to have a sharp edge boundary of UO_2 on a gold film. The edge of the circular areas of the evaporated uranium dioxide was found, however, to be too diffuse for high magnification viewing. By using electron bombardment techniques it is hoped to get sharper edge boundaries.

The second method investigated was to evaporate uranium dioxide directly onto the mounting surface of specimen grids and then to mount the gold film in the usual way, the gold film being in intimate contact with the uranium dioxide. Figure 81 shows a region of gold film after irradiation which is adjacent to grid wire carrying uranium dioxide. The edge of the grid is indicated by vertical arrows.

3. Anisotropy Effects in Single Crystals of Uranium under Irradiation (K. L. Merkle)

A program was undertaken to determine whether the fission process in single crystals of uranium is associated with anisotropic effects regarding the direction and range of fission fragments and of knocked-on uranium atoms.

In the experiments regarding the anisotropy of fission fragments, the tracks of fission fragments that escaped from a uranium surface of pre-determined orientation were recorded on a nuclear plate.

Figure 79. Gold Film, 500 Å Thick, Irradiated with Fission Fragments from Uranium Foil. $nvt = 4 \times 10^{15} \text{ n/cm}^2$.

Micro 101151

160,000-X

Figure 80. Epitaxially Grown Gold Film, 300 Å Thick, with Uranium Dioxide Evaporated onto it, after Irradiation. $nvt = 2.7 \times 10^{16} \text{ n/cm}^2$. (Note Light Tracks of Fission Fragments. Dark Bands are Stacking Faults in Gold.)

Micro 100983

160,000-X

Figure 81. Gold Film near Grid Wire (arrows) onto which 1.8×10^{-4} g/cm² of Natural Uranium was Evaporated, after Irradiation. nvt = 5×10^{17} n/cm². (Note Stacking Faults ① and Defect Clusters ②.)

Mirco 101177

160,000-X

Large grains (several mm in diameter) in polycrystalline samples of high-purity natural uranium were selected and their orientations determined from X-ray Laue back-reflection photograms. Four different specimens, each of which contained one large grain, were ground and mechanically and electrically polished in such a way that the crystallographic (001), (010), (100), and (101) planes of the selected grains coincided with the plane surfaces of the four samples. The four specimens were then mounted together so that all planes were coplanar. An Ilford K-2 nuclear photographic plate, sensitive only to the highly ionizing fission fragments, was mounted onto the sample. The irradiation was performed in the J 10 stringer of the Argonaut reactor. Fission tracks were counted in the areas that corresponded to the oriented grains. Besides counting the number of tracks, a

statistical analysis of the angular distribution of the projections of the tracks on the film plane was made. To date, the data indicate that the anisotropy is less than 15%. It is not certain at present whether this is a true anisotropic effect.

In one experiment the uranium atoms that escaped from the uranium surface under irradiation were collected on aluminum foils. Two small, single crystalline discs with [001] and [010] surface normals were irradiated in CP-5 for 12 days to an integrated flux of 1.7×10^{18} n/cm². After irradiation, the aluminum foils showed a visible deposit. As yet we have not been able to determine the amount of uranium quantitatively, but we hope to be able to do this in the future.

I. Ceramic Materials Research

1. Sintering Mechanism of Al_2O_3 Single Crystals (G. C. Kuczynski*)

The rates of sintering of single-crystal spheres of Al_2O_3 in various oxidizing atmospheres have been studied in order to establish the atomistic mechanism of diffusion in this oxide. The results led to a very surprising dependence of diffusion coefficient D upon oxygen pressure:

$$D = 5 \times 10^8 p_{\text{O}_2}^{1/2} e^{-150,000/RT} \quad (1)$$

The activation energy, 150,000 cal/mol, agrees well with that (152,000 cal/mole) obtained by Y. Oishi and W. D. Kingery⁶² from measurements of oxygen diffusion in Al_2O_3 by ion exchange methods. This would seem to indicate that the rate-controlling mechanism in sintering of Al_2O_3 , is the diffusion of oxygen.

The diffusion coefficient obtained from sintering rate measurements at atmospheric pressure seems to be about 10^5 times higher than that obtained by ion exchange methods. Moreover, its indicated dependence on oxygen pressure would exclude the vacancy mechanism in oxidizing atmospheres, because with increasing p_{O_2} the number of oxygen vacancies should decrease. Also, if we consider the activation energy of 200,000 cal/mol obtained from sintering of Al_2O_3 spheres in pure H_2 as corresponding to the oxygen diffusion by vacancies created by reduction of the oxide with H_2 , the migration of oxygen in Al_2O_3 in oxidizing atmospheres would seem to be either by interstitials or a ring diffusion mechanism.

2. Sintering Mechanisms in Nonstoichiometric Oxides (P. F. Stablein)

Sintering experiments with systems of known initial geometry (spheres-to-spheres, spheres-to-plate) have continued with uranium dioxide to determine the mechanism involved. Although a number of techniques have been tried to reduce the excessive evaporation which takes place in UO_2 at temperatures above 1700°C , it has been found impossible to induce sintering in these simplified systems. Placing the spheres between two UO_2 plates so that the vapor is contained has not helped, nor has the use of powdered UO_2 sprinkled over the spheres and plate. In view of these difficulties, efforts in this direction have been temporarily discontinued.

In connection with the above work, a sphere grinder was designed and built to produce the required spheres, and a new tungsten filament furnace was built to carry out the sintering studies.

* The University of Notre Dame, Consultant to ANL Metallurgy Division.

⁶² Y. Oishi and W. D. Kingery, J. Chem. Phys. 33 480 (1960).

The furnace is a double-wall water-cooled vacuum shell with a gas train attached for introducing pure gases. The volume of the furnace, 2.1 liters, is small. The furnace can be used with almost any atmosphere or in vacuum. Platinum, tantalum, and tungsten heaters have been tested. Water-cooled copper electrodes hold the heaters in place and provide excellent electrical contacts. The furnace has a 4-kw power supply; a total radiation pyrometer serves as a sensing element to control a saturable reactor which, in turn, feeds a low-voltage multitapped transformer. An alternative sensing device, which measures the voltage drop across the electrodes and the heater, can be connected into the system while the furnace is operating to provide control if a window becomes fogged.

The sphere grinding device has four parts, which are shown in Figure 82. The principle involved is that if a particle is set spinning it will rotate about its centroid; when the particle hits an abrasive surface, the points farthest away from the centroid will be abraded away and eventually a sphere will be produced. At the left of Figure 82 is a Lucite cover plate which has a hole at the center for an air outlet. Next, the abrasive is a short section of ceramic tube (Norton RA 98) which is $1\frac{1}{2}$ in. ID x $\frac{1}{4}$ in. wall x $\frac{3}{4}$ in length. The air inlet consists of two plates fastened together. The air jet plate contains six 0.030-in.-dia holes tangent to and located on a circle slightly smaller than the internal diameter of the ceramic tube. The holes tip up at an angle of 5° from the surface of the plate. These are the jets which rotate the sample. They are connected through larger holes to the opposite side of the plate and match a raceway in the air-supply plate, shown at the right of the figure, which has a threaded hole for attaching fittings to the air line.

The air enters through the jets tangent to the internal surface of the abrasive tube and blows the sample around the inside of the cavity rapidly (500-3000 rpm), then exhausts through the outlet hole. The sample is abraded continually by the ceramic tube. The speed is controlled by a needle valve or pressure regulator. The required pressure (range of 10-50 psi) depends on the size and shape of the particles to be ground. Loose particles produced by excessive pressures erode the abrasive tube and do not improve the grinding characteristics.

Several materials have been successfully tested: UO_2 , ThO_2 , MgO , and Al_2O_3 (sapphire). Figure 83 shows spheres obtained from sintered compacts of a 90 w/o ThO_2 -10 w/o UO_2 solid solution. Any shape has been found suitable as a starting material. Spheres have been produced as small as 0.3 mm diameter and as large as 10 mm. In general, the spheres vary in diameter by less than 5%. On a microscopic scale the surfaces are not smooth; thus far no successful method has been found to improve the surfaces in this type of apparatus.

Figure 82. Parts of Sphere Grinding Apparatus.

From left to right: cover plate, ceramic tube, air jet plate, and air inlet plate.

Micro 30529

Figure 83. Spheres of 90 w/o ThO_2 -10 w/o UO_2 Solid Solution Made in Sphere Grinding Device.

Rulings: 1 mm square

Micro 30530

Usually one sphere is ground at a time. It is possible to produce more than one sphere at a time, but the yield is considerably lower. Ten to thirty minutes are required to produce a UO_2 sphere. A single ceramic tube can be used to produce hundreds of small spheres before wearing out. While air is the most convenient propellant, any inert gas or even a fluid can be used to grind solids which oxidize excessively or are pyrophoric.

3. Mechanism of Solid-Gas Reactions (M. L. Volpe)

Since the last annual report, changes in the apparatus have improved the reproducibility of the results. With these changes, after the third or fourth consecutive run, the rates became essentially constant. This enabled us to obtain consistent data by selecting the last of a series of three or more identical runs for the evaluation of rate constants. In this way we have studied, during the past year, the reduction of uranium oxides of compositions between U_3O_8 and UO_2 by carbon monoxide and hydrogen. Rates were measured at essentially constant composition; reaction temperatures ranged from 600 to 900°C, and initial pressures were varied from 300 to 600 microns. The effect of oxide composition and sample weight were also investigated.

The experimental method consisted in the addition of a small quantity of gas to a closed, all-glass system containing the oxide powder. A liquid nitrogen trap condensed out the reaction product, and the progressive decrease in reductant pressure with time was recorded on a chart. Except for a few runs with U_3O_8 , oxide samples were reduced by excess hydrogen or carbon monoxide to uranium dioxide before they were oxidized to the desired O/U ratio with a known quantity of oxygen. The amount of carbon monoxide used was calculated from the pressure, temperature, and volume of the carbon dioxide produced. This amount was found to be within 2% of that calculated for the transformation of pure U_3O_8 to pure UO_2 . Naturally, the magnitude of the observed pressure decrease depended upon system constants, such as temperature gradients, volumes, and room temperatures. The relationship between our data given as dP/dt and dC/dt , the rate in units of mol fraction of oxide reacted per unit time (which is independent of apparatus constants), is

$$\frac{\alpha V}{R x a t} \frac{dp}{dt} = \frac{dC}{dt} \quad , \quad (1)$$

where α is the expansion ratio of the gas being introduced from the volume V (at room temperature T) into the reaction vessel. It was measured for each run. In equation (1) R is the gas constant and " a " is the moles of UO_{2+x} originally present.

Results: For all O, U ratios, initial pressures, and temperatures, the pressure dependence of the reaction rate, here taken to be dP/dt , was found to be given by the equation

$$dP/dt = -kP \text{ (integrated form: } \ln(P/P_0) = -kt) \quad (2)$$

for reduction by hydrogen, and by

$$dP/dt = -kP^{2/3} \text{ (integrated form: } P^{1/3} = P_0^{1/3} [1 - (kt/3)] \quad (3)$$

for carbon monoxide. In these equations, P is the pressure at time t , and P_0 is the initial pressure. The value of the "apparent rate constant" k reflects the dependence of the rate upon such factors as O/U ratio, surface area, temperature, sample weight, and packing density. All of these have been studied except the effect of surface area. Figure 84 shows representative data for both hydrogen and carbon monoxide reductions plotted as $\log P$ vs. t . The hydrogen data form straight lines while the carbon monoxide runs do not. The reverse is seen to be the case in Figure 85, where the same data are plotted as $P^{1/3}$ vs. t . Tables L and LI list the observed rate constants for various experimental conditions.

The effect of temperature was investigated for both hydrogen and carbon monoxide. For hydrogen reduction of $UO_{2.2}$, an apparent activation energy of about 34 kcal/mol was obtained, a value which agrees well with Kuhlman's⁶³ 34 kcal/mol, and less well with DeMarco's⁶⁴ 39 kcal/mol, and Belle's⁶⁵ 25 kcal/mol. For carbon monoxide, the surprisingly low value of 5 kcal/mol was found for the reduction of U_3O_8 , $UO_{2.4}$, or $UO_{2.2}$. These results are illustrated in Figure 86.

For hydrogen, the data of Table L show that the rate constant is almost directly proportional to the $\frac{2}{3}$ power of the sample weight, whereas for carbon monoxide the dependence is much less, being only the $\frac{1}{3}$ power of sample weight. For carbon monoxide, a comparison of runs No. 1, 2, 3, 4, 5 for $UO_{2.2}$ with No. 10 for $UO_{2.4}$, and No. 13, 14, 15 for U_3O_8 show little or no dependence of rate upon overall oxide composition, although qualitatively a maximum rate at O/U ratio 2.4 is indicated. Runs No. 20 through 23 used U_3O_8 which had not been previously reduced to UO_2 , whereas all the others had this treatment. Since such a reduction followed by oxidation could quite possibly influence the observed rate, the unreduced samples should not be compared with the others. Unfortunately, the U_3O_8 samples of runs No. 9 and 10 (Table L) for hydrogen were also used without previous reduction. Nevertheless, for hydrogen reduction, the rate is again essentially independent of overall composition.

⁶³ C. W. Kuhlman, Reduction of Uranium Trioxide with Hydrogen-Nitrogen Mixtures, MCW-216 (1945)

⁶⁴ R. E. DeMarco and M. G. Mendel, The Reduction of High Surface Area Uranium Trioxide, J. Phys. Chem. **6** 132-133 (1959); U. S. Notz and M. G. Mendel, X-ray and Kinetic Study of the Hydrogen Reduction of γ - UO_3 , J. Inorg. and Nuc. Chem. **14** 55.65 (1960).

⁶⁵ J. Belle and L. J. Jones, Resume of Uranium Oxide Data, VIII, WAPD-PWR-PMM-904 (1956).

Figure 84. Rate Data Plotted as Log P vs. T.

Micro 29515

Figure 85. Rate Data Plotted as $P^{1/3}$ vs. T.

Micro 29513

Table L

HYDROGEN REDUCTION OF URANIUM OXIDES

Experiment Number	Sample Weight (gm)	Nominal Composition	Temperature (°C)	P ₀ (μ)	Rate Constant k (min ⁻¹)
1	2.03	UO _{2.2}	639	540	0.0124
2	2.04	UO _{2.2}	687	610	0.043
3	2.04	UO _{2.2}	688	590	0.041
4	2.04	UO _{2.2}	687	545	0.043
5	2.04	UO _{2.2}	738	545	0.076
6	1.11	UO _{2.2}	690	600	0.028
7	1.11	UO _{2.2}	690	365	0.024
8	1.11	UO _{2.2}	690	540	0.032
9	1.11	U ₃ O ₈	691	600	0.044
10	1.11	U ₃ O ₈	690	620	0.051

Table LI

REDUCTION OF URANIUM OXIDES WITH CARBON MONOXIDE

Experiment Number	Sample Weight (gm)	Nominal Composition	Temperature (°C)	P ₀ (μ)	Rate Constant k (min ⁻¹)
1	1.73	UO _{2.20}	686	630	1.86
2	1.73	UO _{2.2}	686	308	1.82
3	1.71	UO _{2.2}	690	650	1.80
4	1.71	UO _{2.2}	690	619	1.80
5	1.71	UO _{2.2}	689	636	1.99
6	1.71	UO _{2.2}	640	600	1.50
7	1.71	UO _{2.2}	738	606	2.19
8	1.71	UO _{2.2}	788	606	2.37
9	1.71	UO _{2.2}	889	619	3.12
10	1.71	UO _{2.4}	689	631	2.13
11	1.71	UO _{2.4}	639	644	1.98
12	1.71	UO _{2.4}	739	662	2.64
13	1.73	U ₃ O ₈	686	659	2.19
14	1.73	U ₃ O ₈	688	650	2.03
15	1.71	U ₃ O ₈	690	612	1.98
16	1.73	U ₃ O ₈	637	656	1.92
17	1.71	U ₃ O ₈	737	612	2.22
18	1.73	U ₃ O ₈	736	631	2.91
19	1.71	U ₃ O ₈	787		2.49
20	1.89	U ₃ O ₈	691	612	2.79
21	0.725	U ₃ O ₈	690	631	2.10
22	0.761	U ₃ O ₈	689	612	2.10
23	3.15	U ₃ O ₈	690	619	3.33

Figure 86. Activation Energy Plots.

Micro 30522

The sample of run No. 22 in Table LI was U_3O_8 which was formed into a pellet under a pressure of 4000 lb/sq in. Comparison of the rate constant for that run with No. 21, in which the sample was a loose powder, shows that the reaction rate is independent of the degree of compaction of the powder.

To summarize: the results of this research show that for reduction by hydrogen:

$$dP/dt = k_1 g^{2/3} e^{-33 \times 10^3/RT} P; \quad (4)$$

$$k_1 = 9.2 \times 10^5 \text{ g}^{-2/3} \text{ min}^{-1}$$

g = weight of sample in grams,

whereas for carbon monoxide:

$$dP/dt = k_1 g^{1/3} e^{-4 \times 10^3/RT} P^{2/3} ; \quad (5)$$

$$k_1 = 12.6 \text{ g}^{-1/3} P^{1/3} \text{ min}^{-1} \text{ for } \text{UO}_{2.2}$$

$$k_1 = 14 \text{ g}^{-1/3} P^{1/3} \text{ min}^{-1} \text{ for } \text{U}_3\text{O}_8 \text{ and } \text{UO}_{2.4}$$

g = weight of sample in grams

for any constant composition between U_3O_8 and $\text{UO}_{2.15}$. The dependence of the rate upon sample weight may not be safely taken as an indication of the influence of surface area, since the change in specific surface area with composition, temperature, and sample history has not yet been studied.

Discussion

Hydrogen Reduction: The rate equation (equation 4) for hydrogen was used to compare our results with those of other experimenters^{63,64,65} whose reaction rate data were obtained by measuring oxide weight-loss at constant pressure. The pressures they used were much higher than ours, their temperatures were generally lower, and they used different methods for the preparation and treatment of their oxides. Our data were used to calculate dC/dt for their conditions of temperature, pressure, and sample weight, and then compared with dC/dt calculated from their rate data for $C = 0$.

Kuhlman,⁶³ working at pressures between one-tenth and one atmosphere, and at temperatures ranging from 450 to 575°C described his results on U_3O_8 by the equation

$$dC/dt = kP(1-C), \quad (6)$$

where P is the pressure and k the rate constant. At 500°C and one atmosphere his rate was found to be 0.15 min^{-1} for $C = 0$; ours is 0.39 min^{-1} . Belle and Jones⁶⁵ reported for the same oxide.

$$dC/dt = k(1-C)^{2/3} . \quad (7)$$

They worked only at one pressure, 100 mm Hg. For 701°C they get for k 0.12 min^{-1} ; we calculate 0.26 min^{-1} . For $\text{UO}_{2.56}$ DeMarco and Mendel⁶⁴ reported the rate to be independent of the degree of reaction, proportional to the sample surface area, and proportional to the 0.43 power of the hydrogen pressure. For 402°C and one atmosphere, they get $k = 0.024 \text{ min}^{-1}$; we calculate 0.033 min^{-1} . When DeMarco's pressure dependence and activation energy were used to convert his data to our experimental conditions, there resulted the value 6.5 min^{-1} at 687°C and 600 microns Hg. The true value is 0.038 min^{-1} .

Apparently, then, equation (4) is valid for pressures from a few hundred microns Hg to one atmosphere within a temperature range from 400 to 800°C. Comparison of the results on $\text{UO}_{2.2}$ with those of U_3O_8 showed little or no dependence of the rate upon composition, but this point should be checked, as well as the effect of surface area.

With respect to reaction mechanism, our conclusion, concurring with that of DeMarco and others, is that a surface reaction, not diffusion, is rate controlling. Our "pre-exponential factor" k_1 coincides very closely with the expected collision rate between hydrogen and oxide calculated from simple kinetic theory. Thus, the reaction rate is simply the rate of collision with the oxide of those hydrogen molecules which have the energy needed to react, namely the activation energy, in this case 34 kcal/mol.

This is in contradiction to Belle's conclusion that the rate-controlling process is a phase transformation, insofar as such a transformation takes place by diffusion. However, his equation (equation 7) also results (for constant pressure and varying composition) from the assumption that the rate-controlling step is a reaction between hydrogen and oxide at the $\text{U}_3\text{O}_8\text{-UO}_2$ interface. The reaction rate will then be given by the rate of collision of hydrogen molecules with the interface, the area of which will decrease as the reaction proceeds. If this is true, when both the composition and pressure vary, the rate should be given by our equation (4) multiplied by the factor $(1-C)^{2/3}$; the conclusions could be easily tested with our apparatus using high pressures and small sample weights.

Carbon Monoxide Reduction: There have been no data published on carbon monoxide reduction with which to compare our results. We find the surprisingly low value of 5 kcal/mol for the activation energy for reaction with carbon monoxide. In addition, the pre-exponential factor k_1 in equation (5) is much too large unless the surface area assigned to our samples is made improbably low (of the order of one square centimeter). It is tempting to consider the low apparent activation energy as a combination of the true activation energy for the rate-controlling process with the free energy for some equilibrium step in the reaction mechanism. One would expect that step to be the creation of some crystal defect by reaction of CO with oxide. Unfortunately, all of the reactions of this type that we have considered result in either the wrong pressure dependence or in a pressure dependence which would vary with oxide composition. One mechanism of a different type is the following, (using the nomenclature of Rees⁶⁶):

⁶⁶A. L. G. Rees, Chemistry of the Defect Solid State, Methuen and Co., London (1954).

with equation (9) being rate determining. (The symbol $\square$ denotes a vacancy; the subscript s indicates a surface vacancy.) It is assumed that reaction (8) has a high negative free energy so that at any pressure all of the available surface sites are used up. Thus $(\text{CO}/\square^-)$ will be independent of pressure. Furthermore, it is postulated that $(\text{CO}/\square^-)$ diffuses much faster than $(\text{U}^{+6}/\square^+)$. Then reaction (9) would take place at the interface, and its rate would be proportional to the interfacial area. Finally, in order to have a $\frac{2}{3}$ pressure dependence it must be postulated that almost every carbon monoxide molecule which hits the surface must stick. Thus the composition of the particles at the sample surface will vary considerably; Belle's equation will hold for them. The low pre-exponential factor will be explained on the basis that the sample surface area rather than the total surface area is available to the gas.

APPENDIX A

NEW CONSTRUCTION AND FACILITIES

Construction and Occupancy of Building 212

Wings A-E: Construction work on Wings A-E, the administrative and physical metallurgy laboratory areas, was completed during the year except for the shakedown of building equipment. Occupancy by Metallurgy Division personnel began with the administrative areas in Wing A early in the last quarter of 1960. A contractor, Phillips-Getschow Co., is engaged in extending services and helping to install equipment in the laboratory areas under the direction of the Plant Engineering Group. As of the end of the year, several staff personnel have moved from the East Area and significant progress has been made toward total occupancy of the laboratories in Wings C, D, and E. This work is expected to continue at least through the first three quarters of 1961.

Wing F: Beneficial occupancy of Wing F occurred during December, 1960. The first significant purchase orders for handling equipment for the cave will be processed early in 1961, and the installation of these items will proceed as rapidly as permitted by delivery dates. Negotiations are under way to extend the contract for the installation of equipment in Wings A-E to cover the work required in Wing F. This work is expected to take well over a year to accomplish.

Wings G and H: Beneficial occupancy of Wings G and H occurred late in 1960, and final acceptance of the entire area is anticipated early in 1961. As in Wing F, negotiations are under way to extend the contract for the installation of equipment for Wings A-E. The first major piece of equipment, the 1250-ton extrusion press, is expected to arrive the first week in January, 1961. Occupancy of these wings will proceed as rapidly as the manpower to perform the work is available. Since the occupancy of these areas involves the installation of major equipment, the time to perform the work will exceed one year; however, most of the personnel should be located in their permanent space inside of this time.

Facilities for Plutonium Work in Wing D of Building 212

Following is a brief summary of some developments during 1960 and of the status at the end of the year of major facilities being provided in Wing D for research and development of plutonium-containing materials.

Plutonium Equipment Services and Utilities: Experience in the Building 40A plutonium metallurgy laboratory indicated the desirability of bringing standard utilities to glovebox equipment by means of headers located above the false ceilings and connecting to the gloveboxes overhead. This not

only affords the maximum flexibility for free-standing gloveboxes, but also affords some protection of the piping against contamination in the event of a spill, because of the flow of room air through the false ceiling into the room. Based on this, a system of headers and connection stations has been installed in Wing D for overhead connection to laboratory equipment of glovebox nitrogen, equipment vent, recirculated chilled water, plant air, and electricity. The waffle-iron grid pattern of the floor permits bringing services, such as high-amperage leads from generators in the ground floor, through the thin parts of the floor directly to the glovebox equipment.

Nitrogen Gas for Glovebox Atmosphere: A low-flow, once-through nitrogen-atmosphere system was developed and used during the past year in Building 40A plutonium gloveboxes. It has worked extremely well so we are installing a similar system for all gloveboxes in Wing D. The nitrogen is supplied to the gloveboxes by evaporation of liquid nitrogen from a central storage Dewar. The pressure in the gloveboxes is maintained at -0.5-in. water column very simply by a differential pressure controller on the exhaust header common to all gloveboxes. For flow rates of only 0.2 cfm for a 100-cubic-foot glovebox, the oxygen level and the moisture level are maintained at about 200 ppm.

The main purpose of the nitrogen system is to provide an atmosphere that will not support combustion, thereby reducing fire and explosion hazards. A lower moisture level can be had readily in any glovebox by the use of a small dryer. Where an atmosphere other than nitrogen is desired, the glovebox can be valved off from the nitrogen supply, and any other gas can be provided.

A system for detecting and pinpointing leaky gloveboxes has also been developed and tested, and is now being installed in Wing D. It consists of a simple piping system that permits monitoring the glovebox exhaust subheaders for significant increases in oxygen content and then sampling individual gloveboxes.

Extruded Aluminum-frame Gloveboxes: Extremely tight, inexpensive gloveboxes have been developed to enclose metallurgy and ceramics research equipment. They consist of extruded aluminum frames with O-ring-gasketed aluminum panels and laminated safety glass windows. Perfect O-ring grooves are included in the extrusion to reduce costly machining, and a "T" slot in the extrusion accommodates bolt heads, thus eliminating the usual welding of studs or the costly drilling and tapping of holes to permit clamping of the windows and panels.

The fabrication of these gloveboxes by General American Transportation Corporation was delayed because it was found that the 6062 aluminum alloy is susceptible to fine cracks adjacent to the welds. A study was made

which led to the selection of 5456 aluminum alloy (with 5.25% Mg). Extrusions of this alloy have been made and gloveboxes are being fabricated for delivery during the first quarter of 1961.

All of the ancillary glovebox components, such as stands, windows, glove and pouch rings, entry ports, filters, lead-throughs for services, filters, are on hand.

Plastic Gloveboxes: Gloveboxes made of fiberglass-reinforced polyester resin (Hetron 92 + 5% antimony trioxide for fire resistance) have been developed to enclose analytical chemistry equipment where corrosion resistance is needed. The gloveboxes have been made by Ceilcote Company, Inc. and are now being delivered.

Plutonium Melting and Casting Laboratory

Induction Melting Top Pour Furnace: 250-gm capacity; all parts on order for delivery during first quarter of 1961.

Injection Casting Furnace and Bottom Pour Furnace: 500-gm capacity each; all parts on order for delivery during first quarter of 1961.

Arc Melting Button Furnaces: Interchangeable hearth; existing 200-amp furnace will be relocated from Plutonium Metallurgy Laboratory in Building 200. Furnaces of 1200- and 600-amp capacity are designed and will be ordered during the first quarter of 1961.

Resistance Melting Furnace (NRC): Tantalum resistance furnace of 500-gm capacity; all equipment on hand, modified, installed, and tested.

Plutonium Machine Shop Laboratory

All machining equipment is on hand and ready for installation in gloveboxes.

High Speed Lathe (Hardinge): 10-in. swing.

Precision Tool Makers Lathe (Schaublin SV-70): With variable speed drive, $5\frac{1}{2}$ -in. swing.

Screw Cutting Lathe (Atlas): Back geared with 6-in. swing.

Vertical Precision Mill (Elgin): With variable speed drive, 10-in. horizontal and 7-in. vertical travel.

Tool Grinder (Hammond): 6-in. wheels.

Ultrasonic Drilling Machine (Raytheon): 100 watts; equipment tested and in glovebox in Building 40A.

Hand Press (Carver): 10-ton hydraulic.

Power Hack Saw: 3 x 3-in. cut size.

Abrasive Cut-off Wheel: 9-in. disc.

AC-DC Welder (Miller): Current range: 3-400 amp.

Plutonium Fabrication Laboratory

All fabrication equipment is on hand and is now being installed.

Vertical Press (Lake Erie): 100 ton, single action, 21-in. square platens, 12-in. stroke.

Rolling Mill (Loma): 2 high-4 high, 6-in. diameter by 8-in. wide rolls, rounding rolls from 1 to $\frac{1}{4}$ -in. diameter rod.

Swager (Fenn No. 2F): Two-die rotary, $\frac{3}{8}$ to $\frac{1}{10}$ -in. diameter dies.

Plutonium Ceramics and Powder Metallurgy Laboratory

Horizontal Tube Resistance Vacuum Sintering Furnace: Tantalum tube element capable of 2200°C; has been used for plutonium program work during past year in Building 40 A and will be relocated.

Powder Preparation Equipment: 1-quart-size ball mill, sieve shaker, mortar and crusher; equipment on hand.

Vacuum Drying Oven: On hand.

Hand Press (Carver): 12-ton hydraulic; on hand.

Remotely Operated Press: 10-ton hydraulic; ordered for delivery first quarter 1961.

Vertical Tube Resistance Sintering Furnace: Tantalum or tungsten tube capable of up to 2500°C; specifications submitted for bids.

Density: On hand.

High-temperature Dilatometer: Being designed.

High-temperature Thermal Analysis Equipment: Specifications submitted for bids.

High-purity Plutonium Laboratory

Liquation Resistance Furnace: Will be relocated from Building 200 Plutonium Metallurgy Laboratory.

Electrolytic Crystal Line: Equipment assembled in gloveboxes in Building 40A and ready for preliminary tests.

Plutonium Metallography Laboratory

Metallography Line No. 1: Complete metallography line equipped for mounting, mechanical grinding and polishing, chemical polishing and etching, and examining and photographing with Leitz bench microscope, and American Optical metallograph; has been in use for the past year in Building 40A and will be relocated.

Metallography Line No. 2: Similar to Line No. 1 but with improvements. Bausch and Lomb research metallograph; major components on hand and balance ordered for delivery first quarter in 1961.

Sonic Jackhammer: Parts on hand and being assembled.

Microhardness Tester (Kentron): Has been in use for the past year in Building 40A and will be relocated.

Plutonium X-ray Diffraction Laboratory

All X-ray diffraction equipment is on hand.

X-ray Diffractometer (GE-XRD-5)

Two X-ray Diffraction Film Units (Norelco)

Plutonium Heat Treat Laboratory

24 Vertical Resistance Tube Quenching Furnaces: 16 being used for plutonium work in Buildings 200 and 40A will be relocated. Balance on order for delivery during first quarter of 1961.

Vertical Tube Resistance Vacuum Quenching Furnace: Tantalum tube element for up to 2200°C and tungsten tube for up to 2500°C; has been assembled and tested with tantalum and is ready for enclosure in a glovebox. Tungsten tube element being fabricated.

Vertical Resistance Wire Vacuum Quenching Furnace: Tantalum wire element for up to 1450°C; assembled and being tested.

High-temperature Precision Furnaces: Three being specified.

Thermal-cycling Equipment: Delivery of components due in first quarter of 1961.

Plutonium Physical Properties Laboratory

Dilatometers: Existing quartz pushrod type with dial indicator pickup will be relocated from Building 200. Parts ordered for recording dial gage dilatometers. Recording quartz pushrod dilatometer with differential transformer pickup tested and being modified for glovebox operation. Plans for a higher temperature (up to 1500°C) dilatometer are being made.

Thermal Conductivity Equipment: Comparative type, $\frac{3}{4}$ -in.-diameter by 2-in.-long specimen; components assembled and being tested.

Calorimeter: Drop type, copper block, 200 cal/°C of temperature rise; prototype tested. Components for plutonium calorimeter on hand and ready for assembly.

Thermal Analysis Equipment: Differential type; being designed.

Plutonium Mechanical Properties Laboratory

Impact Testing Machine (Hounsfield): Small size; on hand.

Tensile Testing Machine (Riehle): 20,000-lb capacity, screw power, modified and equipped for tensile testing to 1200°C; ordered for delivery first quarter of 1961.

Hardness Tester (Kentrall): Combination regular and superficial for all scales of Rockwell tests, motorized; on hand.

Vickers Pyramid Hardness Tester: Modified for operation to 1000°C; on hand and being modified for glovebox operation.

Plutonium Corrosion Laboratory

All corrosion equipment is on hand and being assembled and tested.

Examination Equipment: Balance, ultrasonic cleaner, and bench microscope.

Autoclaves and Furnaces

Refreshed System

Steam System

Plutonium Chemical Analysis Laboratories

The analytical chemistry facilities are equipped to handle most of the Metallurgy Division's analytical needs for plutonium-containing materials, including the following types of analyses: wet chemistry, radiochemistry, X-ray fluorescence spectrometry, spectrographic, and gas.

Practically all equipment is on hand. Corrosion and fire-resistant fiberglass-reinforced polyester resin gloveboxes and fumehoods will be delivered during the first quarter of 1961.

Several methods were examined for ventilating chemistry gloveboxes which may be subjected to high concentrations of acid fumes. A major difficulty was the clogging by acids of the high-efficiency exhaust filters which are needed to remove particulate matter. Also, high acid concentration in the exhaust gases would be expected to corrode the fans as well as the short sections of aluminum ducts in the fan loft. This problem is being handled by recycling the air through scrubbers to remove acid fumes, thus permitting a simple low-flow, once-through ventilation of the gloveboxes.

Alpha-Gamma Cave Facility

Specifications for the alpha-gamma cave called for a soap bubble leak test to be performed by the contractor and a helium leak test (which was performed by personnel of the Engineering Irradiation Group) of the inner steel shell. By the end of February 1960, construction had reached the stage where leak testing was practical. First, the soap bubble test was applied by the contractor to the welds on the inner shell of the cave, both in the inert gas cell and the air cells. Many leaks were found and repaired. The welders exhibited quite a bit of skepticism that any additional leaks would be found by helium leak testing. But, after a few diametric illustrations using the audio indicator, they became fully cooperative in reworking the leaking welds.

In order to avoid interfering with the progress of construction, the major part of the helium leak testing program was confined to the off-shift hours between 4:00 PM and 8:00 AM. Testing of the inner shell was conducted on a two-shift, six-day week basis for four weeks during March. Several additional days in April were spent retesting repaired welds. The major effort was devoted to making a thorough and complete examination of

all the welds in the inert-gas cell. This involved testing 1,061 ft of linear welds and 372 shell penetrations, including plug welds, ceiling studs, and ports. In all, 109 leaks were located and repaired in the inert-gas cell. In addition, 28 leaks were found in those portions of the air side of the cave tested. Usually, welds were repaired after one or two attempts, but in a few instances 5, 6, and 7 rewelds had to be made.

The alpha-gamma cave is expected to be put into operation about the middle of 1962. Equipment, such as windows and manipulators, needed to make the facility completely usable is being designed and procured by the Remote Control Division. The decision has been made to use mechanical master-slave manipulators in the original equipment instead of electronic manipulators. Design of the internal shielding doors and drives has been completed and specifications are being prepared. Other items, such as alpha seals, windows, and rectilinear manipulators, are in various advanced stages of design, and procurement is expected during 1961.

Plutonium Fabrication Facility Modifications and Operation (Building 350)

Facility 350 technical services, including the helium atmosphere recirculating-purifying system and appurtenances, negative pressure system, hooded equipment and controls systems, fire alarm systems and all technical operating machinery, are operated and maintained by the Metallurgy Plutonium Fabrication Group with assistance from Plant Services Division.

Often overlooked is the fact that equipment, as procured and contractor installed, is not ready for operation. The operational shakedown, modification and testing of this equipment, and the development of satisfactory operating procedures has occupied a vast number of both staff and technician hours. This work is essentially complete, if, in fact, completion can ever be achieved. However, because much of this equipment (ventilation systems and controllers, helium atmosphere systems, coolant systems, etc.) must operate 24 hr per day, 8,700 hr per yr, scheduled maintenance and rebuilding operations will continue to require a certain amount of time if the facility is to function properly.

Helium Atmosphere System: Teflon O-rings in the high-pressure (140 psi) section of the helium-purification system failed under service conditions. They were replaced with a specially compounded silicone O-ring material that has so far proven to be effective.

The Gardner-Denver two-stage (140 psi) helium compressor was furnished with graphite rings, seals and pistons, which failed after approximately 300 hr of operation. The defective rings were replaced with a second set of similar rings, which failed after approximately 600 hr of operation. The second set was replaced with fiberglass-reinforced Teflon rings and

the graphite pistons (both stages) replaced with aluminum. By January, 1961, approximately 3,500 hr of continuous operation have been completed without incident. Soon after the first of the year, a shutdown will be scheduled and the compressor torn down to inspect and rotate the rings as recommended by the manufacturer.

Low-temperature Freon System: Helium in the purifying system is chilled to approximately -60°F at 140 psi using a direct-expansion Freon 22 refrigeration system. Because of the low temperatures involved, the system is not what might be termed "conventional," and a delicate balance of the system and proper operation of the Worthington two-stage Freon compressor is imperative if the desired results are to be obtained.

The compressor failed toward the end of the year. With the aid of the Worthington service engineer, the unit was completely rebuilt. Complete operational instructions were obtained, and flow diagrams were made and approved in an attempt to avoid any further mishaps with the system.

Limited operational experience with the rebuilt system has indicated that continual uninterrupted service of the unit is impossible for at least two reasons. First, the estimated temperatures of the Freon-helium heat exchanger is approximately -70 to -85°F . At this low temperature, the moisture content of the 140-psi helium should be maintained at 5 ppm or less to avoid frosting. The limit of absorption of the drying towers at best is less than 10 ppm. After several days of operation, changes in the behavior of the Freon compressor indicates that the load on the exchanger has changed due to frosting, and the Freon unit must be shut down until all evidence of frost is removed from the heat exchanger. This is accomplished by continuing the flow of room-temperature helium through the heat exchanger, which results in defrosting as the exchanger warms up.

The second factor that complicates continual operation of the Freon compressor is again a moisture problem. When a drying tower becomes saturated, it must be regenerated with hot helium. During this operation, approximately one-half of the two-stage helium compressor output is diverted through a gas heater and then through the saturated tower and back into the system. The balance of the helium output of the compressor follows the normal path through the heat exchanger. This change from normal load to approximately one-half load will affect the Freon compressor and, unless accomplished quickly (which is impractical), will necessitate a shutdown of the Freon unit until the regeneration cycle has been completed.

Atmosphere Sampling for Analysis of O_2 and Moisture: Oxygen and moisture contents of the helium atmosphere are monitored constantly by a Beckman Oxygen Analyzer and moisture hydrometer. Both of these units have been troublesome from two standpoints: (1) actual operation, calibration and adjustment of the basic units, and (2) improper techniques in the

sampling system. Both of these conditions have been rectified with the expenditure of a large number of man-hours. The sampling system was completely revised including calibration of all helium flow meters, etc. The basic units have been studied intensively and correct operation carefully analyzed. Both units are extremely sensitive due to the desired operating range of moisture and oxygen - less than 100 ppm in either case.

Miscellaneous Equipment: Other units associated with the helium-circulating-purifying system have at times been troublesome. Controls on chilled water systems and evaporative condensers have failed. There have been two instances of electric motor failure. In all instances, the interlocking controls have functioned to isolate the high-pressure system and have prevented dumping of helium or pressurizing of hoods.

Operational Results of the Helium Atmosphere System: The virtues of a tight hood, duct and piping system, wherein an inert atmosphere system is employed, have been clearly demonstrated during the past year's operation. Under normal operation of the system, helium consumption has been much less than the anticipated four tanks per week.

The design of the overall system has been proven satisfactory to accomplish the circulation and purification of the helium atmosphere. The moisture content in the helium from the driers can be held to less than 10 ppm, while the return averages between 50-100 ppm. The oxygen content in the supply can be held below 500 ppm, but so far has generally averaged 750-1500 ppm. The activated carbon towers have been effectively dried out and now show a ratio of volume of O_2 absorbed to volume of carbon of approximately 1 at room temperature, which can be improved by a factor of 3 to $3\frac{1}{2}$ at low-temperature operation.

Studies of the activated carbon absorption of O_2 from helium are in process and will soon be completed and combined with earlier data for publication in 1961.

During the past year, four more helium hoods were leak checked, leak rate tested, filled with helium, and placed "on stream." Hood Lines PF-14 and 25, the final two, are scheduled for "on stream" operation in January or early February of 1961.

Ventilation Systems: The building ventilation master control station in Basement B has proven quite effective. The pushbutton operation of the room-area ventilation systems required accurate sequencing of the fans during startup to prevent pressure excursions that could prove damaging. Studies further indicated that the existing fan control was not adequate, and during the year the existing pilot positioners were replaced with precision units to provide the required control.

The outside atmosphere reference tips, pioneered for the Facility 350 control system, have proven satisfactory with proper adjustment, and are now being employed elsewhere at the Laboratory.

Fire Detection System: The fire alarm system was placed in operation on March 28, 1960. The units were intentionally set on the sensitive side and, as a consequence, numerous false alarms occurred. The systems have been readjusted and frequently checked, and now appear to work in a very satisfactory manner. Careful control of pressures and temperatures in the various areas helped materially in stabilizing the detectors and preventing spurious signals to the Fire Department.

Extrusion Press Line for Plutonium Fuels Fabrication Facility

The following items of equipment have been designed and were delivered during 1960:

- a. A 600-ton, direct/indirect, laboratory-type extrusion press.
- b. Induction billet-heating equipment.
- c. A furnace for evacuation, heating, outgassing, and sealing composite billets.
- d. A 25-ton stretcher-detwister-straightener.
- e. An extrusion cutting saw.
- f. A 2-ton hoist with motorized trolley, turntable, and monorails.
- g. A one-ton hoist, motorized trolley and monorail.
- h. A saw for cutting extrusions.
- i. Miscellaneous equipment for heating dies, handling billets, etc.
- j. Gloveboxes to allow extrusion of plutonium in an inert atmosphere.

All of the above items have been received with the exception of the stretcher-detwister-straightener and the induction billet heater.

The extrusion press line will be housed in a 2,600-cubic-feet, inert-atmosphere-supplied glovebox attached to station PF-10 of the conveyor. The enclosed space is broken down into three interconnected glovebox suites. One hood, measuring 4 ft wide x 8 ft high x 18 ft long, will connect to the conveyor by the sealing door and transition. A hood, measuring 54 in. wide x 10 ft 6 in. high x 15 ft 9 in. long, housing the extrusion press is to be attached to the service hood by means of an overhead transition housing. The stretcher straightener hood is 4 ft wide x 6 ft high x 36 ft long and will attach to the end of the extrusion press glovebox line.

The extrusion press, manufactured by the Sutton Engineering Company, at Bellefonte, Pa., was specifically designed for in-hood operations. The hoods will gasket to a machined surface on the extrusion press base. All hydraulic lines were brought to the extrusion press through seals in the extrusion press base. The extrusion press was designed for maximum frame stress of 8,000 lb/in.² and with a narrower frame to allow access from the glove ports in the side of the glovebox. The die slide operates vertically rather than horizontally, and the press will be fed from the top. The two-ton crane and hoist was designed for in-hood use above the extrusion press with maximum clearances.

The stretcher-detwister-straightener consists of two horizontal box columns mounted one above the other. Two large gripping jaws are carried between these two columns. The stretch head may be moved for a distance of 27 in. and at 3,000 lb/in.² gage will exert a 50,000-lb pull. The second head may be rotated by means of a worm gear with a twist capacity of 1,800 pound-feet. The head and rotary mechanism are mounted on a carriage which may be propelled over a distance of 22 ft along the columns by a means of a continuous heavy-duty roller chain on sprockets driven by a hydraulic motor. The one-ton hoist and rail was designed for use over the stretcher-detwister-straightener.

None of the commercially available induction billet heaters would meet our budget limitation. An induction coil furnace was designed to be powered by an existing 10,000-cycle, 30-kva motor generator and was entered for Central Shop fabrication.

A complete set of installation drawings were prepared along with the Bills of Material, and all installation items were ordered with the exception of ventilation ductwork. Approximately 90% of this material has been received. Installation of the extrusion press has been held up pending completion of EBR-I Core IV, described in Part I, Section B.

APPENDIX B - PUBLICATIONS AND REPORTS

Publications

- Arenberg, Arne and Witten, Leon, Arneleon, Brit. J. of Photog., 597-598 (November 4, 1960). [Not based on ANL work]
- Ayer, J. E., Schmitt, D. R. and Mayfield, R. M., Permeation of Water Vapor through Polymeric Films, J. Appl. Polymer Sci. 3 (7) 1-10 (January-February 1960).
- Ayer, J. E., Mayfield, R. M. and Schmitt, D. R., The Engineering Aspects of the Water Vapor Permeability of Glove Materials, Nuc. Sci. and Engr. 8 (3) 274-276 (September 1960).
- Baskin, Y., Harada, Y., and Handwerk, J. H., Some Physical Properties of Thoria Reinforced by Metal Fibers J. Am. Cer. Soc. 43 (9) 489-493 (September 1960).
- Bean, C. H., McCuaig, F. D. and Handwerk, J. H., The Fabrication of the Fuel Elements for the Transient Reactor Test, Nuc. Sci. Abstr. 14 (4) 485 (February 29, 1960). [Abstract]
- Berger, H. and Crooks, R. K., An Analysis of a Magnetoresistive Voltage Regulator, Proc. Inst. of Radio Engrs. 48 (12) 2041 (December 1960). [Not based on ANL work.]
- Blumenthal, Bernhard, The Transformation Temperatures of High Purity Uranium, J. Nuc. Materials 2 (1) 23-30 (March 1960).
- Blumenthal, Bernhard, Constitution of Low Carbon U-C Alloys, J. Nuc. Materials 2 (3) 197-208 (September 1960).
- Burt, W. R., Jr., The Manufacture of the Fuel and Blanket for the Argonne Fast Source Reactor, Trans. Am. Nuc. Soc. 3 (1) 129-130 (June 1960). [Abstract]
- Chiswik, H. H., Nuclear Metallurgy, J. Metals 12 (3) 236 (March 1960).
- Clayton, Glen T. and Heaton, LeRoy, Neutron Diffraction Study of Krypton in the Liquid State, Phys. Rev. Letters 5 (11) 527-528 (December 1, 1960). [Abstract]
- Clayton, Glen T. and Heaton, LeRoy, Sample Assembly for Neutron Diffraction Studies of Liquefied Gases, Rev. Sci. Instr. 31 (12) 1355-1356 (December 1960).

- Coffinberry, A. S. (LASL), Schonfeld, F. W. (LASL), Waber, J. T. (LASL), Kelman, L. R. (ANL), and Tipton, C. R., Jr. (BMI), "Plutonium and Its Alloys," REACTOR HANDBOOK, 2nd Edition, Vol. 1, Materials, Chapt. 11, pp. 248-290. Interscience Publishers, Inc., New York, N.Y., 1960.
- Darby, J. B., Jr., Miscible Laves-type Compounds in Ternary Systems, J. Metals 12 720 (September 1960). [Abstract]
- DeBoer, F. E., Purification of Metals by Gas Chromatography, Nature 185 915 (March 26, 1960). [Letter]
- DeMastry, J. A., Shober, F. R. (BMI) and Smith, K. F. (ANL), High-strength Niobium-base Alloys for Application in the EBR-II, Trans. Am. Nuc. Soc. 3 (2) 446-447 (December 1960). [Abstract]
- Draley, J. E., Greenberg, Sherman and Ruther, W. E., The High-temperature Aqueous Corrosion Resistance of the Uranium-5% Zirconium-1 1/2% Niobium Alloy, J. Electrochem. Soc. 107 (9) 732-740 (September 1960).
- Draley, J. E. and Greenberg, S., "Corrosion of Uranium Alloys," REACTOR HANDBOOK, 2nd Edition, Vol. 1, Materials, Chapt. 8, Uranium Alloys, Section 8.5, pp. 183-191. Interscience Publishers, Inc., New York, N. Y., 1960.
- Draley, J. E., Breden, C. R., Ruther, W. E. and Grant, N. R., "High Temperature Aqueous Corrosion of Aluminum Alloys," Prog. in Nuc. Energy, Series IV, Vol. 2, Technology, Engineering and Safety, pp. 284-300, Pergamon Press, 1960.
- Dwight, Austin E., The Uranium-Molybdenum Equilibrium Diagram below 900°C, J. Nuc. Materials 2 (1) 81-87 (March 1960).
- Dwight, A. E., Positions of Thorium and Uranium in the Periodic Table, Nature 187 505-506 (August 6, 1960). [Letter]
- Dwight, A. E., Occurrence of AB₃ Compounds in Binary and Ternary Transition Element Systems, J. Metals 12 721 (September 1960). [Abstract]
- Dwight, A. E., Factors Controlling the Occurrence of Laves Phases and AB₅ Compounds among Transition Elements, Trans. ASM Preprint No. 211, 477-499 (1960).
- Handwerk, J. H., McCuaig, F. D. and Bean, C. H., The Fabrication of the Graphite-Urania Fuel for the Transient Reactor Test, Nuc. Sci. Abstr. 14 (5) 580-581 (March 15, 1960). [Abstract]

- Handwerk, J. H., Book Review: Materials for Nuclear Reactors by Bernard Kopelman, J. Am. Cer. Soc. 43 (10) 247 (October 1960).
- Handwerk, J. H., Introduction to Chapter on "Symposium on Ceramics in Nuclear Energy," ASTM Special Technical Publication No. 276, MATERIALS IN NUCLEAR APPLICATIONS, pp. 291-292 (1960).
- Horak, J. A. and Kittel, J. H., Irradiation Behavior of Restrained and Vented Uranium-2 w/o Zirconium Alloy, Trans. Am. Nuc. Soc. 3 (2) 540-541 (December 1960). [Abstract]
- Hymes, L. C., Consulting Editor, Air Weapons Materials Application Handbook - Metals and Alloys, ARDC TR59-66, Syracuse University Research Institute (December 1959).
- Iskenderian, H. P., Reinke, C. F., and Charak, I., Possible Effects of Scale Deposits on Fuel Plates of EBWR Core during 100 Mw (Planned) Operation, Trans. Am. Nuc. Soc. 3 (2) 380-381 (December 1960). [Abstract]
- Keeler, J. R. (BMI) and Smith, K. F. (ANL), "Vanadium and Its Alloys," REACTOR HANDBOOK, 2nd Edition, Vol. 1, Materials, Chapt. 31, pp. 697-707. Interscience Publishers, Inc., New York, N. Y. (1960).
- Kingery, W. D., Hill, D. C. and Nelson, R. P., Oxygen Mobility in Polycrystalline NiCr_2O_4 and Alpha Fe_2O_3 , J. Am. Cer. Soc. 43 (9) 473-476 (September 1960). [Not based on ANL work.]
- Lloyd, Lowell T., Recrystallization of Deformed Alpha-uranium Single Crystals, J. Nuc. Materials 2 (2) 141-146 (June 1960).
- Lloyd, Lowell T., "Physical and Mechanical Properties of Uranium," REACTOR HANDBOOK, 2nd Edition, Vol. 1, Materials, Chapt. 7, Uranium, Section 7.7, pp. 111-127. Interscience Publishers, Inc., New York, N. Y. (1960).
- Lynch, E. D., Handwerk, J. H. and Hoenig, C. L., Oxidation Studies of Urania-Thoria Solid Solutions, J. Am. Cer. Soc. 43 (10) 520-524 (October 1960).
- McSkimin, H. J. and Fisher, E. S., Temperature Dependence of the Adiabatic Elastic Moduli of Single-crystal Alpha Uranium, J. App. Phys. 31 1627-1639 (September 1960).
- Mueller, M. H., Heaton, LeRoy and Miller, K. T., Determination of Lattice Parameters with the Aid of a Computer, Acta Cryst. 13 828-829 (October 1960).

- Nevitt, M. V., Magnetization of the Compound TiFe, J. App. Phys. 31 155-157 (January 1960).
- Nevitt, M. V., Stabilization of Certain Ti₂Ni-type Phases by Oxygen, Trans. AIME 218 327-331 (April 1960).
- Nevitt, M. V., Magnetization of the Alpha and Sigma Phases in Several Fe-V Alloys, J. Metals 12 737-738 (September 1960). [Abstract]
- Nevitt, M. V. and Downey, J. W., The Zirconium-rich Corners of the Ternary Systems Zr-Co-O and Zr-Ni-O. J. Metals 12 721 (September 1960). [Abstract]
- Nevitt, M. V., Downey, J. W. and Morris, R. A., A Further Study of Ti₂Ni-type Phases Containing Titanium, Zirconium or Hafnium, Trans. AIME 218 1019-1023 (1960).
- Noland, R. A., Walker, D. E. and Hymes, L. C., "Fabrication of U₃O₈-Aluminum Dispersion Fuel Elements by Extrusion," ASTM Special Technical Publication No. 276, MATERIALS IN NUCLEAR APPLICATIONS, pp. 336-344 (June 1960).
- Paine, S. H. and Kittel, J. H., "Irradiation Effects," REACTOR HANDBOOK, 2nd Edition, Vol. 1, Materials, Chapt. 8, Uranium Alloys, Section 8.6, pp. 191-204. Interscience Publishers, Inc., New York, N. Y., 1960.
- Paine, S. Hugh, "Effects of Irradiation on Thorium," REACTOR HANDBOOK, 2nd Edition, Vol. 1, Materials, Chapt. 9, Thorium, Section 9.8, pp. 224-226. Interscience Publishers, Inc., New York, N. Y., 1960.
- Paine, S. Hugh, "Irradiation Effects," REACTOR HANDBOOK, 2nd Edition, Vol. 1, Materials, Chapt. 10, Thorium Alloys, Section 10.4-8, p. 238. Interscience Publishers, Inc., New York, N. Y., 1960.
- Renken, C. J., A Through Transmission System Using Pulsed Eddy Current Fields, J. Soc. for Nondestruc. Testing XVIII (4) 234-236 (July-August 1960).
- Rothman, S. J., Lloyd, L. T. and Harkness, A. L., Self-diffusion in Gamma Uranium, Trans. AIME 218 605-607 (August 1960).
- Salley, R. L. and Bean, C. H., Assembly, Sodium Bonding, and Inspection of EBR-II Blanket Rods, Trans. Am. Nuc. Soc. 3 (2) 448-449 (December 1960). [Abstract]
- Shull, C. G. and Wilkinson, M. K. (ORNL) and Mueller, M. H. (ANL), Slow Neutron Scattering by the Titanium Isotopes, Phys. Rev. 118 797-798 (May 1960).

- Sidhu, S. S., Campos, F. P. and Zauberis, D. D., Neutron Diffraction Study of the Magnetic Structure of $(\text{Mn},\text{CO})_4\text{C}$, Bull. Am. Phys. Soc. 5 58-59 (January 1960). [Abstract]
- Sidhu, S. S., Use of Nuclear Null-Matrix in the Study of Hydrogen and Carbon Atoms in Metals, Am. J. Phys. 28 413 (April 1960). [Abstract]
- Sidhu, S. S., State of Deuterium Atoms in Energetic Plasma Sources, Bull. Am. Phys. Soc. 5, Series II, 319 (April 1960). [Abstract]
- Sidhu, S. S., Heaton, LeRoy and Mueller, M. H., The Use of Nuclear Null-Matrix in Neutron Diffraction Studies of Crystal Structures and Magnetic Structures, Acta Cryst. 13 (12) 1086 (December 1960). [Abstract]
- Sidhu, S. S., Heaton, LeRoy and Mueller, M. H., Neutron Diffraction Studies of the Zirconium-Deuterium Systems, Bull. Am. Phys. Soc. 5, Series II, (6) 461 (November 1960). [Abstract]
- Smaardyk, A., Brubaker, R., Hummel, H. H., Kittel, J. H. and McCarthy, A., A Design Concept of a Fast Fuel Test Reactor (FFTR), Trans. Am. Nuc. Soc. 3 (2) 556-557 (December 1960). [Abstract]
- Smith, Karl F., "Stainless Steels," REACTOR HANDBOOK, 2nd Edition, Vol. 1, Materials, Chapt. 23, pp. 563-589. Interscience Publishers, Inc., New York, N. Y., 1960.
- Smith, K. F., "Structural Steels," REACTOR HANDBOOK, 2nd Edition, Vol. 1, Materials, Chapt. 33, Special-Purpose Alloys, Section 33.3, pp. 759-760. Interscience Publishers, Inc., New York, N. Y., 1960.
- Smith, K. F., "Cadmium," REACTOR HANDBOOK, 2nd Edition, Vol. 1, Materials, Chapt. 38, pp. 806-809. Interscience Publishers, Inc., New York, N. Y., 1960.
- Van Ostenburg, D. O., Lattice Dynamics of Alpha Uranium, Bull. Am. Phys. Soc. 5 (6) 421 (November 25, 1960). [Abstract]
- Woyci, Jerome, Hicks, Victor and Sidhu, S. S., Neutron Diffraction Study of $\text{Zn}_x\text{-Mn}_{1-x}\text{Fe}_2\text{O}_4$, Bull. Am. Phys. Soc. 5, Series II (6) 458 (November 1960). [Abstract]

Reports

- ANL-5611 Zegler, S. T. and Nevitt, M. V., Apparatus for Measuring the Thermal Conductivities of Metals, (October 1959).
- ANL-5640 Kittel, J. H. and Smith, K. F., Effects of Irradiation on Some Corrosion Resistant Fuel Alloys, (May 1960).
- ANL-5724 Yaggee, F. L., The Manufacture of Centrifugally Cast Alloy Fuel Slugs (Mark-II Fuel Loading for EBR-I), (July 1960).
- ANL-5918 Kittel, J. H., Irradiation of Extrusion-clad Uranium-2 w/o Zirconium Alloy for EBR-I, Mark-III, (October 1959).
- ANL-5944 McGonnagle, W. J. and Perry, R. B., Analysis of Fuel Element Core Blanks for Argonne Low Power Reactor by Gamma Counting, (December 1959).
- ANL-5950 Salley, R. L. and Burt, W. R., Jr., Casting and Fabrication of Core Material for Argonne Low Power Reactor Fuel Elements, (December 1959).
- ANL-5957 Blumenthal, B., Baumrucker, J. E. and Lloyd, L. T., The Transformation Temperatures of High Purity Uranium, (June 1960).
- ANL-5960 Lied, R. C. and Handwerk, J. H., Fuel Development for the TREAT Reactor, (January 1960).
- ANL-5963 Handwerk, J. H. and Lied, R. C., The Manufacture of the Graphite-Urania Fuel Matrix for TREAT, (January 1960).
- ANL-6070 Greenberg, S. and Ruther, W. E., Aqueous Corrosion of Magnesium Alloys, (May 1960).
- ANL-6091 Reinke, C. F. and Carlander, R., Examination of Irradiated EBWR Core-I Fuel Elements, (July 1960).
- ANL-6096 Fisher, E. S., The Adiabatic Elastic Moduli of Single-crystal Alpha Uranium at 25°C, (June 1960).
- ANL-6102 Paine, S. H., Murphy, W. F. and Hackett, D. W., A Study of Irradiation Effects in Type 'A' Nickel and Type 347 Stainless Steel Tensile Specimens (July 1960).
- ANL-6126 Rothman, S. J., Gray, J., Jr., Hughes, J. P. and Harkness, A. L., Self-diffusion in Beta Uranium, (July 1960).

- ANL-6127 Rothman, S. J., The Diffusion of Gold in Gamma Uranium, (May 1960).
- ANL-6141 Dunworth, R. J. and Macherey, R. E., The Drip Casting of Zirconium Metal, (October 1960).
- ANL-6144 Hart, Raymond K. and Heyduk, M. J., Metallography of Aluminum and Some Aluminum-1 w/o Nickel Alloys (June 1960).
- ANL-6149 Misch, R. D., Characteristics of Anodic and Corrosion Films on Zirconium (May 1960).
- ANL-6151 Crothers, Charles C., Chemical Decontamination of the ANL-2 High Pressure Water Loop, (July 1960).
- ANL-6164 Lied, R. C., Preparation of Magnesium Oxide Refractories, (July 1960).
- ANL-6180 Gavin, A. P. (RE) and Crothers, C. C., Irradiation of an Aluminum Alloy Clad Aluminum-Uranium Alloy Fuel Plate, (July 1960).
- ANL-6194 Brubaker, R., Hummel, H. H., Kittel, J. H., McCarthy, A. and Smaardyk, A., Fast Fuel Test Reactor - FFTR Conceptual Design Study, (August 1960).
- TID-7502 [Pt. I]
[Del. 2] Kelman, L. R. and Wilkinson, W. D., "Properties of Uranium-Plutonium Alloys," Proceedings of the Metallurgy Information Meeting Held at Oak Ridge, April 11-13, 1955, pp. 195-203 (1960).
- Stone, C. C. and Noland, R. A., Motor Arc-Welding Process, pp. 522-533, *ibid.*
- TID-7502 [Pt. II]
[Del. 2] Bean, C. H., Lindgren, J. R. and Macherey, R. E., "Fabrication of Roll-Clad Uranium Alloy Fuel Elements for the Argonne Boiling Experimental Reactor," Proceedings of the Metallurgy Information Meeting Held at Oak Ridge, April 11-13, 1955, pp. 863-874 (1960).
- Chiswik, H. H., Some Relationships between Thermal Cycling and Irradiation Behavior of Uranium: Effect of Grain Size and Preferred Orientation, pp. 572-578, *ibid.*
- Chiswik, H. H. and Dwight, A. E., Heat Treatment of Some Uranium-Zirconium and Uranium-Zirconium-Niobium Alloys for Irradiation, pp. 581-595, *ibid.*
- Draley, J. E. and Greenberg, S., Aqueous Corrosion of 5 w/o Zr-1-1/2 w/o Nb-Uranium Alloy, pp. 640-652, *ibid.*

- TID-7502 Draley, J. E. and Ruther, W. E., Corrosion of Aluminum and Its Alloys at Elevated Temperatures, pp. 669-680, *ibid.*
Pt. II
Del. 2
(Cont'd.) Foote, F. G., Argonne National Laboratory, pp. 734-740, *ibid.*
- Kittel, J. H., Dimensional Stability of Fuel Alloys under Irradiation, pp. 596-607, *ibid.*
- Murphy, W. F., Klank, A. C. and Paine, S. H., Radiation Damage to Fuel from the First Loading of EBR-I, pp. 543-563, *ibid.*
- TID-7587 Draley, J. E., "Aqueous Corrosion of 1100 Aluminum and of Aluminum-Nickel Alloys," AEC-Euratom Conference on Aqueous Corrosion of Reactor Materials, Brussels, Belgium, October 14-17, 1959, pp. 165-187 (July 1960).
- Draley, J. E., High Temperature Aqueous Corrosion of Uranium Alloys Containing Minor Amounts of Alloying Elements, pp. 390-404, *ibid.*
- TID-7589 Lied, R. C., "Uranium and Plutonium Carbide Development at Argonne," Progress in Carbide Fuels [Notes from the Second AEC Uranium Carbide Meeting Held at Battelle Memorial Institute, March 22 and 23, 1960] pp. 3-4 (1960).
- NMI-1220 Misch, R. D. and Greenberg, S., "Corrosion of Zirconium Alloys in Superheated Steam," Proceedings of the Ninth Annual AEC Corrosion Symposium, May 10-12, 1960, Held at Boston, Massachusetts, p. 21 (1960). [Abstract]
- Draley, J. E., Hart, R. K. and Ruther, W. E., Aluminum Corrosion in High Temperature Water: Mechanism Experiments, p. 31, *ibid.* [Abstract]
- DeBoer, F. E., Draley, J. E., Ruther, W. E. and Youngdahl, C. A., Polarization of Metals in High Purity Water, p. 36, *ibid.* [Abstract]

Patents

McCuaig, Franklin D. and Misch, Robert D., Method and Alloy for Bonding to Zirconium, Patent No. 2,932,887 (April 19, 1960).

Noland, Robert A. and Stone, Cecil C., Apparatus and Method for Arc Welding, Patent No. 2,936,363 (May 10, 1960).

Foote, Frank G., Ternary Alloys of Uranium, Columbium and Zirconium, Patent No. 2,947,621 (August 2, 1960).

Shuck, Arthur B., Apparatus and Method for Injection Casting, Patent No. 2,952,056 (September 13, 1960).