OFFICIAL USE ONLY

ORNL-TM-920

Contract No. W-7405-eng-26

FUELS AND MATERIALS DEVELOPMENT PROGRAM QUARTERLY PROGRESS REPORT
FOR PERIOD ENDING JUNE 30, 1964

Compiled by

P. Patriarca

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

SEPTEMBER 1964

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

OFFICIAL USE ONLY

DISTRIBUTION OF THIS DOCUMENT UNLIMITED

106

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

FOREWORD

This is the first progress report describing work performed at the Oak Ridge National Laboratory for the Fuels and Materials Development Branch, Division of Reactor Development, U. S. Atomic Energy Commission. The specific programs covered are as follows:

Part I. Metals and Ceramics Division

<u>Program Title</u>	<u>Person in Charge</u>	<u>Principal Investigator(s)</u>
Fuel Element Development	G. M. Adamson, Jr.	C. F. Leitten, Jr. J. P. Hammond
Mechanical Properties	D. A. Douglas, Jr.	J. R. Weir
Nondestructive Test Development	D. A. Douglas, Jr.	R. W. McClung
Solid Reaction Studies	C. J. McHargue	T. S. Lundy
Zirconium Metallurgy	C. J. McHargue	M. L. Picklesimer

Part II. Solid State Division

Irradiation Effects on Alloys and Structural Materials	D. S. Billington	M. S. Wechsler
--	------------------	----------------

This report consists of selected portions of the annual reports of the Metals and Ceramics and Solid State Divisions for the periods ending June 30, 1964, and May 31, 1964, respectively. Future reports will be published on a quarterly basis.

TABLE OF CONTENTS

	Page
Summary	viii
Part I. Metals and Ceramics Division	
1. Fuel Element Development	3
Deposition of Refractory Uranium Compounds	3
Deposition of Tungsten Alloys	7
Thermochemical Preparation of Carbides	11
Fabrication of Aluminum-Base Irradiation Test Plates	15
Hydrogen-Absorption Studies in the Water-Vapor Aluminum System	19
Fabrication of Uranium Carbide with UBe_{13} Sintering Aid	19
Aided Sintering of Uranium Nitride	22
Dispersion Hardening of Molybdenum	23
2. Mechanical Properties	26
Effect of Hydrogen on the Mechanical Properties of Metals	26
Reactions of Type 304 Stainless Steel with Flowing CO_2 at Atmospheric Pressures and Elevated Temperatures	27
Radiation Effects on the Mechanical Properties of Stainless Steel	28
Influence of Preirradiated Heat Treatment on the Strength and Ductility of Irradiated Type 304 Stainless Steel	33
Neutron Flux Dosimetry	35
3. Nondestructive Test Development	37
Electromagnetic Test Methods	37
Ultrasonic Test Methods	40
Penetrating Radiation Methods	43
Low-Voltage Radiography and Microradiography	43
Gamma Scintillation Gaging	43
X-Ray Imaging with Closed-Circuit Television	44
Inspection Development of Problem Materials	46
Development of Remote Inspection Techniques	47
Third Geneva Conference Exhibits	48

4. Solid Reaction Studies	50
Diffusion in Body-Centered Cubic Metals	50
Diffusion of ^{44}Ti and ^{48}V in Titanium	51
Diffusion of ^{48}V in Vanadium	51
A Submicron Sectioning Technique for Analyzing Diffusion Specimens of Tantalum and Niobium	51
Diffusion of ^{95}Nb and ^{182}Ta in Niobium	52
Effect of Alpha Bombardment on the Diffusion of Lead in Silver	52
Thermal Diffusion of Antimony and Ruthenium in Silver	53
5. Zirconium Metallurgy	55
Zirconium Alloys	55
The Effect of Preferred Orientation and Stress on the Directional Precipitation of Hydrides in Zircaloy-2	57
Texture Determinations by Hardness Anisotropy in α -Zirconium Alloys	60
Determinations of Pole Figures by Quantitative Metallography	66
Oxide Film Studies	68
Preparation of Single Crystals of Zirconium and Zirconium Alloys	70
Zone Refining of Zirconium	74

Part II. Solid State Division

6. Irradiation Effects on Alloys and Structural Materials	81
Kinetics of Radiation-Enhanced Diffusion in Cu-Al	83
Effect of Deformation upon Neutron Radiation-Enhanced Diffusion in Cu-Al Alloys	88
Annealing of Cu-Ni Alloys Following Neutron Irradiation, Quenching, and Deformation	92
Resistivity Measurements in Fe-3.7 wt % Si Alloys	97
In-Reactor Internal Friction Measurements of Interstitial Rearrangements in Body-Centered Cubic Metals	100
Aging of the Nitrogen Peak in Fe-N Alloy	102
Breakup of Precipitates by Irradiation	105
Irradiation of Vanadium	106
Fission-Spectrum Irradiation Facility for the BSR	109

Crystallography of Dislocations and Dislocation Loops in Deformed Iron	112
Plastic Deformation of Iron and Its Alloys	112
Irradiation Effects on the Mechanical Properties of Iron and Iron Alloys	113
Reactor Pressure Vessel Materials	122
Impact Tests on Irradiated Pressure Vessel Steels	122
Charpy Impact Machine Calibration	125

SUMMARY

Part I. Metals and Ceramics Division

1. Fuel Element Development

We have shown vapor deposition, or pyrolytic decomposition, to be an effective and relatively simple technique for fabricating both fuel and cladding materials. Using this technique, high-purity UO_2 has been formed from UF_6 in a one-step conversion process. By the proper selection of variables, fine active powder, coarse high-density crystals, and bulk deposits were achieved. Many of the deposition parameters have been investigated.

Other vapor-deposition studies have led to the successful fabrication of high-quality tungsten tubing, rhenium and tungsten-rhenium alloy tubing, and boron carbide and silicon carbide bodies. While good quality tungsten-rhenium deposits were achieved, the composition and thickness varied. Boron-carbon alloys were deposited with a wide range of composition and properties. Near-stoichiometric deposits of silicon carbide were obtained both as tubing and as a thermal-cycle resistant coating on graphite or tungsten.

Miniature aluminum-base dispersion plates suitable for irradiation testing were fabricated from both U_3O_8 and niobium-coated UO_2 with excellent dimensional control and no cracking of the coating.

Fabrication techniques were developed by which both UC and UN were sintered to high theoretical densities at temperatures much below those usually used. Sintering the UC was improved by the addition of small quantities of UBe_{13} , which cleaned the surface of the UC particles. Conditions that permit sintering to 95% of theoretical density were established. Sintering of UN was improved by the selection of fine UN powder and the use of aluminum vapor as a scavenger.

We achieved dispersion hardening of molybdenum by colloidal chemistry techniques. Sols of thorium or zirconium oxide were dispersed in sols of molybdenum oxide, which was ultimately reduced to the metal.

2. Mechanical Properties

A hydrogen environment weakens some metals. It reduces the creep strength of Inconel, nickel, and copper but does not affect that of iron and austenitic stainless steel. The mechanism by which hydrogen affects these materials is not clear; but we have obtained evidence, using the electron microscope, that a hydrogen-dislocation interaction may be involved.

A carbon dioxide environment strengthens and reduces ductility of alloys at elevated temperatures by carburizing them. Carburization may be inhibited in the stainless steels by an increase in the chromium content to above 20% which leads to formation of a protective Cr_2O_3 film at the metal-oxide interface.

Irradiation at 200 to 400°C increases the strength and decreases the ductility of stainless steel tested in the same temperature range. We have verified that this effect, which is not observed when the irradiation or test temperature reaches 600°C, is caused by fast neutrons. Irradiation at higher temperatures decreases high-temperature ductility without affecting strength; this we have found is caused by thermal neutrons, very likely by the $^{10}\text{B}(n,\alpha)$ reaction introducing helium into the metal. We have found a preirradiation heat treatment that can significantly improve the low-temperature postirradiation ductility of stainless steel.

3. Nondestructive Test Development

We are developing new techniques and equipment for the non-destructive evaluation of materials and components. The major emphasis has been on eddy-current, ultrasonic, and penetrating-radiation methods.

Analytical methods have been developed and implemented with computer programming to calculate impedance of eddy-current coils to facilitate their design and application. Improved circuitry has been designed and fabricated to enhance the usefulness of the phase-sensitive eddy-current instrument. Detailed instructions have been prepared on the design and construction of coolant-channel spacing probes.

We have continued to study techniques for the detection of nonbond in clad structures and have designed and built a number of new experimental devices. Preliminary work shows promise for the ultrasonic evaluation of roll-swaged joints common to several fuel elements. New and improved instrumentation has been designed and built for the processing of ultrasonic data signals.

We have microradiographed minute specimens after in-pile testing. In continued studies on techniques and standards for the determination of fuel inhomogeneities in fuel plates and rods, we have provided design criteria for production scanners for the HFIR fuel plates. We are examining x-ray imaging television systems for use in hot cells. The method also shows promise for precision measurement of component expansion during thermal testing.

In our development on problem materials including molybdenum, tungsten, tantalum, and graphite, we are trying to use ultrasonics to measure the strength of graphite.

A principal part of the development of remote inspection techniques has been the work on radiography in the presence of a radiation background. Use of photographic reduction on the fogged film greatly increases the tolerance to background.

Five exhibits related to nondestructive testing developments were prepared for display at the Third Geneva Conference on Peaceful Uses for Atomic Energy.

4. Solid Reaction Studies

We found that Arrhenius-type expressions adequately describe the temperature variations of volume diffusion coefficients in niobium and tantalum but not in β -zirconium, β -titanium, or vanadium. Bombardment with 10^{11} 2.2-Mev alpha particles per square centimeter per second increases diffusion coefficients of lead in silver single crystals by 6×10^{-18} cm²/sec in the temperature range of 360 to 480°C. The thermal-gradient redistribution of antimony in silver can be described in terms of a kinetic theory and an unusually large negative heat of transport ($Q^* = -29 \pm 3$ kcal/mole).

5. Zirconium Metallurgy

The transformation kinetics in a series of Zr-Mo alloys and in a Zr-0.9 wt % Fe alloy were studied by electrical resistivity and metallography. The Zr-Mo alloys behaved much as the Zr-Nb alloys previously reported. The Zr-0.9 wt % Fe alloy results are difficult to interpret because three phases are observed over an appreciable temperature range.

The effect of applied stress on the preferred orientation of hydrides precipitated during cooling was examined. The data were analyzed by use of a hydride pole figure. Stress reorientation of hydrides occurred only if the applied elastic stress was parallel to a high concentration of basal poles. Plastic strain caused the hydrides to precipitate parallel to tensile strain components and perpendicular to the compressive strain components.

A technique for the rapid determination of an approximate (0001) crystallographic pole figure for Zircaloy-2 by use of Knoop microhardness measurements was developed. Only 36 impressions are required, if they are made in a specified pattern. The resulting pole figure is in excellent agreement with figures prepared from x-ray diffraction data.

A technique and an analysis were developed for rapidly determining hydride and crystallographic (0001) pole figures in Zircaloy-2 by the use of a polarized-light microscope and quantitative metallography.

The refractive indices were determined as a function of wavelength for the first time for anodized films formed on zirconium foil. The method also yielded accurate measurements of film thicknesses, but it failed for films formed by reaction with air, oxygen, or water, because these films intrinsically absorb in the ultraviolet and visible spectrum.

Single crystals of zirconium and Zircaloy-2 were grown in sizes up to 13 mm in diameter by 10 cm long by use of an electron-beam furnace. Many of the variables of the growth process were investigated, and most of the necessary requirements for reproducible growth of large quantities of single-crystal material are now determined.

As-deposited bars of zirconium and titanium as large as 0.5 in. in diameter were successfully zone melted as many as ten successive passes. Appreciable purification was obtained in as few as four passes, and resistivity ratios as high as 450 were measured.

Part II. Solid State Division

6. Radiation Metallurgy

The relative kinetics of the resistivity change of first and second runs for Cu-15 at. % Al were analyzed. The kinetics of the resistivity change for an interrupted irradiation were also treated. The results suggest that interstitials rather than vacancies are responsible for enhancement of diffusion in this alloy.

The effect of prior cold working to 0 to 54% reduction in area on the rate of short-range ordering during irradiation at 100°C was determined for Cu-15 at. % Al. The decrease in ordering rate with increasing amounts of cold work is interpreted in terms of the introduction of sinks for radiation-produced point defects.

The isochronal annealing of copper-nickel alloys containing 25 to 65 wt % Cu was studied following neutron irradiation at -180°C. The largest decrease in resistivity, indicative of radiation-enhanced segregation, was observed for Ni-40 wt % Cu. The isochronal annealing of this alloy was also investigated following quenching from 600 to 1050°C and deformation at below -100°C.

Preliminary measurements are described of the resistivity of Fe-3.7 wt % Si as a function of temperature from -196 to 1050°C and of the change in resistivity upon quenching from temperatures up to 850°C.

In-reactor measurements of low-frequency internal friction were used to study the radiation-accelerated loss of nitrogen from solid solution in quenched Fe-0.015 wt % N alloys. No evidence for the resolution of precipitates was observed upon irradiating aged samples. Measurements of internal friction during irradiation were also made for vanadium containing nitrogen and oxygen.

The preliminary design of a facility for the BSR is described that will provide a flux of neutrons whose energy distribution conforms closely to a fission spectrum. For a total flux of about 10^{12} neutrons/cm²-sec, the heat load is about 15 kw.

Plans are discussed to use etch pitting, electron transmission microscopy, and tensile tests at various temperatures and strain rates to study the plastic deformation of unirradiated and irradiated iron and its alloys. The theory of electron diffraction contrast is applied in a crystallographic analysis of dislocations and dislocation loops in deformed iron.

An irradiation of tensile samples of iron and steel is described that is part of a program to study the effect of dose, dose rate, and irradiation temperature on mechanical properties.

The characteristics of nuclear reactor pressure vessels are described and a discussion is given of the use of prestressed concrete, stainless steel, ferritic steel, and low-alloy high-strength steel as materials of construction. Impact samples of pressure vessel steel characteristic of weld heat-affected zones have been irradiated at elevated temperatures in the ORR. In two experiments, the anticipated irradiation temperature of 550°F (288°C) was exceeded. A third experiment has been operating satisfactorily for seven weeks. The status of attempts to calibrate Charpy impact machines in accordance with the specifications of two standard agencies is discussed.

~~OFFICIAL USE ONLY~~

PART I.

METALS AND CERAMICS DIVISION

~~OFFICIAL USE ONLY~~

1. FUEL ELEMENT DEVELOPMENT

G. M. Adamson, Jr.

The objective of the Fuel Element Development program remains the development of new or improved fabrication techniques for complete fuel elements and for fuel and cladding materials. We are studying a variety of materials, selected to include the best ones for use at temperatures over a wide range.

We are presently emphasizing vapor deposition as a fabrication technique for fuel element materials. Our ultimate goal is the fabrication of a fuel element by a one-step conversion process followed by forming an integral clad, both using the vapor-deposition method. To achieve this goal, efforts have been directed toward the preparation of UO_2 and refractory metals such as tungsten and tungsten alloys in shapes suitable for fuel element applications.

The vapor-deposition process consists essentially of the pyrolytic decomposition or thermochemical reduction of volatile compounds on a heated surface. Since many metal halides are sufficiently volatile to be transferred as gases at low temperatures, these compounds are well suited to use in vapor-deposition techniques. Particular advantages of vapor deposition are the relatively low temperatures and simple equipment that are required as compared to those required for the usual fabrication procedures for refractory metals and compounds. In addition, the process shortens the path from basic raw materials to the finished product and thus may lead to the development of a low-cost fuel cycle.

Improvements in fuel materials are also being sought by improved sintering techniques and development of new fabrication practices. Dispersion hardening is being pursued as a method for improving the strength of cladding materials, primarily the refractory metals.

Deposition of Refractory Uranium Compounds

R. L. Heestand C. F. Leitten, Jr.

Several systems for direct conversion of UF_6 to a refractory fuel compound have been studied. A hot-electrode cold-wall reaction chamber similar to that used for deposition of carbides was used in early survey

experiments.¹ However, the reduction always stopped with the formation of UF_4 , which condensed on the chamber walls. The only reactions attempted in the cold-wall apparatus were combinations of (1) UF_6 , H_2 , and CH_4 and (2) UF_6 , NH_3 , and CH_4 . The first combination yielded UF_4 up to 2000°C , and the second combination yielded UF_4 and an unidentified compound of uranium with carbon and nitrogen at 1300°C .

A hot-wall-tube reaction chamber was assembled for reduction-hydrolysis of UF_6 to UO_2 according to the reaction,

This reaction has been proven thermodynamically feasible when accomplished in two steps² at atmospheric pressure and at temperatures below 650°C :

However, the resulting UO_2 was of too low density and contained too much fluorine to be of commercial interest.

We are performing experiments on the single-step reduction of UF_6 at low pressures to determine the effects of proportions of UF_6 , H_2O , and H_2 on the reaction products. Currently we are limiting deposition temperatures to between 1100 and 1350°C and pressures to between 3 and 20 torr for several gas compositions. Table 1.1 indicates the chemical species obtained for the indicated temperatures, pressures, and gas compositions. Example 1 indicates that UF_4 was obtained for the combined reaction up to 1100°C . Examples 2 and 3 indicate the ranges of gas composition in which UO_2 may be obtained; however, the intermediate compounds UF_4 and UO_2F_2 were also formed if the reacting gases were allowed to premix before entering the hot zone. When the injector was placed within the hot zone at 1300°C , pure UO_2 was formed consistently using the conditions of example 4. However, if the system pressure was

¹R. L. Heestand and C. F. Leitten, Jr., Metals and Ceramics Div. Ann. Progr. Rept. May 31, 1963, ORNL-3470, pp. 75-78.

²I. E. Knudsen, H. E. Hootman, and N. M. Levitz, A Fluid-Bed Process for the Direct Conversion of Uranium Hexafluoride to Uranium Dioxide, ANL-6606 (February 1963).

Table 1.1. Typical Experimental Parameters for the Deposition of UO_2

Example	Gas Composition (%)			Temperature (°C)	Pressure (torr)	Products
	H_2	H_2O	UF_6			
1	28.1	70.26	1.64	1100	3	UF_4
2	72.4	25.8	1.8	1250	8	$\text{UO}_2\text{-UO}_2\text{F}_2\text{-UF}_4$
3	31.75	67.46	0.79	1300	6	$\text{UO}_2\text{-UO}_2\text{F}_2\text{-UF}_4$
4	78.2	21.5	0.3	1300	6	UO_2
5	68.0	30.5	1.5	1300	20	$\text{UO}_2\text{-UO}_2\text{F}_2$

increased to 20 torr, as shown in example 5, neither the high hydrogen content nor the injection of UF_6 into the 1300°C zone suppressed the formation of UO_2F_2 .

The UO_2 was obtained as a massive solid or a powder, depending on the temperature of the zone where UF_6 was introduced. The form of the deposited UO_2 depended on the temperature of the zone where UF_6 was introduced. These forms, shown in Fig. 1.1, are (a) a dendritic crystalline deposit produced at 1300°C , (b) a massive deposit (with some powder) at 1200°C , and (c) extremely fine powder (60- to 200-A diam) produced at 1100°C .

Table 1.2 gives typical UO_2 analyses obtained with various inlet gas compositions. In the case of experiment 19, small amounts of UF_4 and UO_2F_2 were detected in the system cold trap, indicating that unreacted UF_6 or UF_4 powder had passed through the hot zone. When the hydrogen content was raised, as in experiments 24, 26, and 27, UF_6 reduction was complete and no chemical species other than UO_2 was detected by chemical and x-ray diffraction analyses.

We are continuing efforts to obtain dense uniform deposits and to fully determine the effect of gas composition on deposit composition.

Fig. 1.1. Types of UO_2 Obtained by Vapor Deposition from UF_6 .
 (a) Dendritic deposit. 4.4X; (b) massive deposit; (c) electron micrograph of 60- to 200-A powder. 165,000X. Reduced 8.5%.

Table 1.2. Typical Analytical Data on Vapor-Deposited UO_2

Experiment No.	Gas Composition (%)			Temperature (°C)		Pressure (torr)	Deposit Analysis (%)		
	UF_6	H_2	H_2O	Inlet	Outlet		U	O	F
19	0.31	31.72	67.97	1100	1300	7.5	87.37	11.83	0.012
24	0.7	78.8	20.5	1100	1300	6.0	88.62	11.66	0.004
26	1.1	78.5	20.4	1050	1250	6.2	87.47	11.22	0.001
27	1.5	78.2	20.3	1250	1350	6.0	87.51	11.33	0.110

Deposition of Tungsten Alloys

J. I. Federer C. F. Leitten, Jr.

Our previous success in the fabrication of tungsten by vapor-deposition techniques¹ has led to a new program³ directed toward the study and characterization of vapor-deposited tungsten.

We have shifted our efforts to studies of the feasibility of fabricating tungsten alloys by direct thermochemical deposition techniques. The specific goal is to determine the deposition parameters that will yield homogeneous alloys of a desired composition within a particular system. Alloy constituents of interest include vanadium, niobium, tantalum, titanium, zirconium, hafnium, and rhenium. Alloys containing about 25% Re are of immediate interest; we do not expect to be concerned with the other elements in contents that exceed a few percent. We are depositing these alloys, like pure tungsten, from volatile halides.

Certain elements can disrupt the typical columnar grain structure and promote a fine-grained structure in tungsten deposits. An example of this effect is shown in Fig. 1.2. This tungsten deposit was prepared at 800°C and was previously reported as being a temperature effect. However, higher purity WF_6 produced columnar grains at all deposition temperatures. Chemical analysis revealed that the fine-grained specimen

³W. C. Thurber et al., Metals and Ceramics Div. Ann. Progr. Rept. June 30, 1964, ORNL-3670, Part II, Chap. 19 (in press).

Fig. 1.2. Fine-Grained Structure in Vapor-Deposited Tungsten. Etched in equal volumes concentrated NH_4OH and 30% H_2O_2 . 200x.

contained 80 ppm V and 40 ppm C, the vanadium arising from a contaminant in the WF_6 . We now tentatively attribute the fine-grained structure shown in Fig. 1.2 to the vanadium impurity. Vanadium, which has a high affinity for both carbon and oxygen, may have deposited as minute carbide or oxide particles and, in some manner, caused nucleation of new tungsten grains. Other reactive solutes, such as those elements previously mentioned, may behave in a similar manner.

Our main effort so far has been directed toward the deposition of tungsten-rhenium alloys. A mixture of 29% ReF_6 in WF_6 was prepared by distilling the gases into a common container. Vapor deposition was then conducted under the following conditions: 700°C, 10 torr, 70 moles H_2 per mole of combined fluorides. Good quality deposits were prepared on a tubular copper substrate. The surface texture was smooth, resembling vapor-deposited tungsten. However, the composition and thickness varied along the length of these tubular deposits. In a single deposit, the rhenium content varied from 1.7 to 35.5% over a distance of 10 in. The highest rhenium content and the thickest deposits occurred near the inlet to the reaction zone.

The grain structure of tungsten-rhenium alloy deposits depended upon the rhenium content, becoming less columnar with increasing rhenium content. Figure 1.3 compares a specimen containing 6% Re, having a mostly columnar grain structure resembling vapor-deposited tungsten, with a specimen containing about 22% Re, in which the columnar structure was not dominant, although still present. These preliminary results indicated that the grain structures of vapor-deposited tungsten-rhenium alloys will be radically different from those in pure vapor-deposited tungsten. Indeed, approximately equiaxed grain structures may possibly be obtained by control of the deposition parameters.

Fig. 1.3. Vapor-Deposited Tungsten-Rhenium Alloys.
 (a) Tungsten-6% rhenium alloy showing columnar grain structure;
 (b) W-22% Re alloy. Etched in equal volumes of concentrated NH_4OH and 30% H_2O_2 . 500 $\times$. Reduced 16.5%.

Since uniform and homogeneous tungsten-rhenium deposits would be expected in the temperature range in which the constituent elements deposit uniformly, we have started to investigate the deposition characteristics of pure rhenium. To avoid corrosion of glass and Kel-F flowmeters by ReF_6 , the fluoride was transferred from the supply cylinder directly to the reaction site in a metered stream of hydrogen. The ReF_6 concentration was controlled by its vapor pressure. In the temperature range of 500 to 800°C at a hydrogen flow rate of 3000 cm^3/min and a

pressure of 10 torr, the thickness of rhenium deposits was very non-uniform. Thick nodular deposits, shown in Fig. 1.4, occurred near the inlet to the reaction zone, indicating that ReF_6 was readily reduced under these given conditions. The deposit consisted of coarse columnar grains having considerable grown-in porosity at the grain interfaces. Further downstream, the deposits were much smoother in surface texture, although columnar in grain structure. Lowering the temperature to 400°C and decreasing the hydrogen flow to $2000\text{ cm}^3/\text{min}$ eliminated the nodular growth near the inlet of the reaction furnace and resulted in a uniform deposit.

Fig. 1.4. Nodular Rhenium Deposit. Etched in equal parts of concentrated NH_4OH and 30% H_2O_2 . 500X.

Thus, rhenium deposits of uniform thickness were obtained at 400°C , whereas uniform tungsten deposits³ were obtained at 500 to 600°C . Since nonuniform and heterogeneous tungsten-rhenium deposits were obtained at 700°C , these results indicate that better quality alloy deposits will be obtained at lower temperatures at which the two elements deposit uniformly. We are now conducting codeposition experiments at lower temperatures to confirm this hypothesis.

Thermochemical Preparation of Carbides

R. L. Heestand J. I. Federer C. F. Leitten, Jr.

Thermochemical deposition has been investigated as an approach to fabrication of high-quality metal carbides. We have studied deposition parameters of boron-carbon alloys and silicon carbide in the interest of fabricating free-standing shapes and coatings for high-temperature use.⁴ Both carbides have application in the nuclear field. Boron carbide is of interest as a neutron-absorbing material due to the high thermal-neutron absorption cross section of boron. The good high-temperature oxidation resistance of silicon carbide promotes the use of this carbide as a fuel coating or cladding material.

In general, these carbides are produced under reduced pressure (10 to 100 torr) by the reduction of the appropriate halides by hydrogen in the presence of a hydrocarbon. Optimum results for deposition of both carbides were obtained in the temperature range of 1200 to 1350°C. Due to differences in their behavior, they will be discussed separately.

We obtained boron-carbon alloys with boron contents ranging from 19 to 81%. Table 1.3 shows the composition of deposits for several different temperatures, pressures, and gas ratios. At constant temperature (1325°C), pressure (35 torr), and flow rates of BCl_3 (30 cm^3/min) and CH_4 (80 cm^3/min), the composition varied from 44 to 65% B as the hydrogen flow rate increased from 1000 to 2960 cm^3/min . Under the same conditions, except for a CH_4 flow rate of 50 cm^3/min , the composition of the deposit varied from 37 to 72% B as the hydrogen flow rate increased from 500 to 2200 cm^3/min .

Temperature also strongly influences the boron content of the deposit. Lowering the temperature from 1325 to 1275°C results in an increase from 72 to 82% B with other conditions being constant. Deposition rates were highly reproducible for any given set of deposition

⁴R. L. Heestand, J. I. Federer, and C. F. Leitten, Jr., "Thermochemical Preparation and Properties of Carbides for Nuclear Applications," paper to be presented at the AIME Symposium on Compounds of Interest in Nuclear Reactor Technology, Boulder, Colo., Aug. 3-5, 1964, and published by the AIME in a special symposium volume.

Table 1.3. Analyses and Conditions for Deposition
of Boron-Carbon Deposits

Boron (wt %)	Carbon (wt %)	Temperature (°C)	Pressure (torr)	BCl ₃ (cm ³ /min)	CH ₄ (cm ³ /min)	H ₂ (cm ³ /min)
19	81	1350	15-25	30	135	
37.2	60.6	1325	35	30	50	500
43.8	47.2	1325	35	30	80	1000
48.2	50.0	1325	100	30	80	2220
49.2	47.5	1400	35	30	80	2220
59.1	34.9	1325	35	30	80	1800
63.4	31.7	1280	35	30	80	2960
65.3	27.8	1325	35	30	80	2960
66.4	32.6	1325	45	30	80	2960
68.0	29.0	1325	35	30	80	2960
68.2	31.0	1325	40	30	60	2960
69.6	29.4	1280	35	30	80	2960
69.7	26.3	1325	35	30	50	2220
70.5	29.5	1325	40	30	80	2960
72.4	26.7	1325	35	30	50	2220
68.2	30.0	1290	35	30	50	2220
68.7	29.2	1300	35	30	70	2220
76.8	23.2	1275	40	30	50	2220
81.4	17.7	1275	20	20	50	2220
81.0	18.3	1250	20	20	50	2220
81.7	17.1	1250	10	10	50	1400
81.1	18.2	1200	10	10	50	1400
80.7	18.1	1150	10	10	50	1400

conditions, but varied between 10 and 25 mils/hr for 70 and 50% B, respectively. The lack of material balances in Table 1.3 for some of the analyses may be attributed to analytical errors.

Attempts to determine the microstructure of pyrolytic boron carbide have been unsuccessful at present due to the inert nature of the material. Figure 1.5 represents a spectrum of the as-polished structures available. This specimen demonstrates depositing a structure of composition varied by stepwise increases in temperature. The composition varied continuously from 76% B at the outer surface to 50% B at the inner surface. As anticipated, a large hardness difference accompanies the change in composition. Knoop hardnesses (1-kg load) have been measured at 2340 for 72% B and 327 for 44% B. On examination by x-ray diffraction analysis, the material appears to be crystalline with randomly oriented fine grains.

Fig. 1.5. Boron-Carbon 1/8-in.-ID Tube Deposit 0.040 in. Thick Showing Programmed Composition Change. 100x. Reduced 30%.

Larger samples were made in a resistance furnace using the same temperatures, pressures, gas ratios, and flow rates to obtain comparable deposits. Figure 1.6 is the end view of a 1/2-in.-diam, 0.030-in.-wall B₄C tube, which was deposited at 1300°C in 4 hr on the inside surface of a graphite tube. The graphite was readily removed, leaving the free-standing tube.

Fig. 1.6. Boron Carbide Tube 1/2-in. diam $\times$ 0.030-in. wall. 3 $\times$.

Silicon carbide has been deposited at a rate of approximately 10 mils/hr according to the conditions shown in Table 1.4. Clearly, variations of temperature and hydrogen ratio have little effect on composition. Stoichiometry was generally favored throughout the range of conditions under which continuous deposits were obtained. Deposits formed below 1200°C were nonuniform, while above 1350°C groups of needle-like crystals formed.

Studying the microstructures of silicon carbide was difficult. The as-polished material appeared to be single phase and was not readily etched in acids or fused sodium carbonate. The hardness of the silicon carbide deposits was 2745 Knoop with a 1-kg load. X-ray analyses also indicated that vapor-deposited silicon carbide was crystalline with randomly oriented fine grains.

Table 1.4. Analyses and Deposition Conditions
of Pyrolytic Silicon Carbide

Run No.	Si (wt %)	C (wt %)	Tempera- ture (°C)	Pres- sure (torr)	CH ₄ (cm ³ /min)	H ₂ (cm ³ /min)	SiCl ₄ (cm ³ /min)
SC-7	75.03	25.70	1300	100	80	2200	35
SC-8	68.85	29.21	1300	100	80	Varied	35
SC-11	69.62	29.38	1300	100	80	2960	35
SC-12	68.78	29.63	1250	100	80	2960	35
SC-13	70.74	26.68	1300	100	80	2220	35
SC-14	73.27	28.20	1300	100	80	2220	35
SC-24	69.75	30.48	1250	100	80	2960	35

Coatings of silicon carbide deposited on graphite, tungsten, and alumina were adherent and withstood thermal cycling; however, full evaluation has not been completed.

We have established parameters for deposition of both boron carbide and silicon carbide, and we shall conduct similar studies on other carbides of interest for high-temperature applications.

Fabrication of Aluminum-Base Irradiation Test Plates

M. M. Martin W. J. Werner

In conjunction with the Phillips Petroleum Company, we are fabricating a series of aluminum-base miniature fuel plates to be used for determining the influence of high-temperature irradiations to high burnup on the dimensional and chemical stability of U₃O₈ and UO₂ dispersions. The final design specifications and the actual rolling parameters used to achieve the core dimensions are presented in Table 1.5. The fissile materials are particles of U₃O₈ and niobium-coated UO₂-15 wt % ZrO₂ dispersed in matrices of X8001 aluminum and roll bonded at 500°C with Alclad 6061 aluminum. Both standard and instrumented plates are included in the program. The instrumented plates are identical in length and width to the standard plates but are thicker

Table 1.5. Design Specification of Miniature Fuel Plates for
High-Temperature, High-Burnup Irradiations

	Sample Plates		Instrumented Plates	
	Core A	Core B	Core A	Core B
Materials				
Cladding	Alclad 6061 Al	Alclad 6061 Al	Alclad 6061 Al	Alclad 6061 Al
Frame	Alclad 6061 Al	Alclad 6061 Al	6061 Al	6061 Al
Dispersoid				
Loading	U ₃ O ₈ (42 wt %)	63 wt % Nb-coated UO ₂ -ZrO ₂	U ₃ O ₈ (43 wt %)	64 wt % Nb-coated UO ₂ -ZrO ₂
Particle size	(-170 +325)	(-200 +230)	(-170 +325)	(-200 +230)
Matrix (-100 mesh)	X8001 Al	X8001 Al	X8001 Al	X8001 Al
Number of plates	7	6	1	1
Number of cores/plate	1	1	2	2
Loading of ²³⁵ U, g	2.205 ± 1%	2.205 ± 1%	2.205 ± 1%	2.205 ± 1%
Plate dimensions, in.				
Length	5.750 ± 0.003	5.750 ± 0.003	5.750 ± 0.003	5.750 ± 0.003
Width	1.250 ± 0.003	1.250 ± 0.003	1.250 ± 0.003	1.250 ± 0.003
Thickness	0.050 ± 0.003	0.050 ± 0.003	0.150 ± 0.003	0.150 ± 0.003
Core dimensions, in.				
Length	5.470 ± 0.061	5.470 ± 0.061	5.250 ± 0.250	5.250 ± 0.250
Width	1.000 ± 0.031	1.000 ± 0.031	1.000 ± 0.031	1.000 ± 0.031
Thickness	0.020 ± 0.003	0.020 ± 0.003	0.010 ± 0.003	0.010 ± 0.003
Rolling schedule, %				
Spread	3.90	3.30	4.0	4.3
Densification	4.30	3.10	5.0	4.5
Elongation	86.40	86.66	86.3	86.3
Total reduction in thickness	87.50	87.50	87.5	87.5

and contain two 0.010-in.-thick cores per plate with provision for inserting a thermocouple in the aluminum between the cores.

The general appearance of the various fabricated dispersions is shown in Fig. 1.7. The degree of fragmentation and stringing of the dead-burned U_3O_8 and high-fired UO_2 particles, illustrated in Figs. 1.7a and 1.7b, respectively, are characteristic of these irregularly shaped materials when roll bonded at $500^\circ C$ with a hot reduction of 84% and a cold reduction in thickness of 20%.

The quality of these dispersions of irregularly shaped U_3O_8 and UO_2 is satisfactory for operation in high-flux, high-power density test reactors. However, further improvements in particle integrity were achieved, as shown in Fig. 1.7c, by use of spherical coated particles of UO_2 - ZrO_2 solid solution. No degradation of the individual spherical particles could be observed after the dispersion had been fabricated in the same manner as those bearing irregularly shaped U_3O_8 and UO_2 . The distribution of the spherical particles, however, resulted in localized fuel concentrations in excess of those that were encountered in dispersions of equivalent uranium loading containing finer U_3O_8 particles. We are presently studying blending to minimize localized fuel concentrations.

The use of coated-particle fuel in aluminum-base dispersions is being explored primarily to minimize the previously observed⁵ chemical reactions that take place under irradiation between the oxide particles and the matrix. Although these reactions apparently will not cause difficulty under conditions being proposed for present high-performance reactors, this may not be the case with future reactors intended for even higher performance. The metastable nature of the dispersions and the large gas releases that could accompany the reactions under irradiation potentially restrict their use in very high performance test reactors. We have shown that the integrity of a niobium coating on UO_2 - ZrO_2 particles can be maintained during fabrication, thus preventing

⁵A. E. Richt, C. F. Leitten, Jr., and R. J. Beaver, "Radiation Performance and Induced Transformations in Aluminum-Base Fuels," p. 469 in Research Reactor Fuel Element Conference, September 17-19, 1962, Gatlinburg, Tennessee, TID-7642, Book 2 (1963).

UNCLASSIFIED
PHOTO 66062

(a)

"DEAD-BURNED" U_3O_8

200 X

(b)

HIGH FIRED- UO_2

200 X

(c)

Nb-COATED UO_2-ZrO_2

200 X

(d)

Nb-COATED UO_2-ZrO_2

750 X

Fig. 1.7. Longitudinal Sections of Developmental Dispersions in Standard Test Plates Rolled at $500^\circ C$ to 87.5% Reduction in Thickness, Contrasting the Integrity of an Aluminum-Base Coated-Particle Dispersion to More Conventional Fuels. Reduced 44.5%.

the exposure of the oxide fuel particle to the aluminum matrix. An example of the integrity of the oxide particle coating is shown in Fig. 1.7d. We plan heat treatment and irradiation tests to evaluate the effectiveness of the coating in preventing the oxide-aluminum reactions.

Hydrogen-Absorption Studies in the Water-Vapor Aluminum System

M. M. Martin

For the past several years, the tendency for blister formation above 500°C has been unpredictable in fuel plates clad with type 6061 aluminum. We have revealed a marked change in the oxide film on this material when it is heated above 515°C in air.⁶ However, a quantitative interpretation of the results has been difficult because of the interdependency of blistering on time, temperature, humidity, initial hydrogen content, and surface oxide condition.

Recent studies have suggested that blistering is more sensitive to the water-vapor content of customary annealing atmospheres than previously thought. We are investigating hydrogen absorption by type 6061 aluminum to determine the influence of the parameters (time, 2 to 10 hr; temperature, 450 to 550°C; annealing-air dew point, 0 to 34°C; and initial surface oxide thickness, 20 to 200 μ) on the hydrogen content of the material and to interpret the results in terms of a hydrogen-absorption-blistering mechanism.

Fabrication of Uranium Carbide with UBe_{13} Sintering Aid

J. P. Hammond

The high thermal conductivity and uranium density of uranium carbide coupled with its good irradiation stability make this material a desirable fuel for advanced reactor systems. However, production of dense bodies by conventional methods requires excessively high temperatures and still fails to give an entirely satisfactory product. We previously

⁶M. M. Martin and R. L. Heestand, Metals and Ceramics Div. Ann. Progr. Rept. May 31, 1962, ORNL-3313, p. 84.

described a method using a sintering aid removable by volatilization⁷ for sintering the carbide to high density at substantially lower temperature. This method used 7 1/2 wt % UAl_2 as the additive. Because aluminum must be removed by evaporation, best results were achieved with small batch sizes and pellet diameters below 5/16 in.

In the past year, we found a method for achieving comparable sintering results without the limitation on batch or pellet size. By using powders prepared from arc-cast uranium monocarbide with approximately 3/4 wt % UBe_{13} as the sintering aid, 95% of theoretical density was achieved by vacuum sintering in a tungsten-lined tantalum crucible at 1525°C. The UBe_{13} was dissolved within the uranium carbide during sintering. Chemical analyses showed the compacts were stoichiometric in carbon and retained much of the beryllium.

Investigating the UC- UBe_{13} system, we found a quasi-binary phase diagram with a eutectic occurring at 1610°C at 32 wt % UBe. Figure 1.8 shows the UC-rich portion of this diagram (determined metallographically), with theoretical densities obtained by sintering at various temperatures with various UBe_{13} contents superimposed. We see that the best density is obtained below the eutectic platform and just to the right of the solvus. Figure 1.9 shows a typical microstructure of a compact sintered in this region. Highest density was obtained for UC charged at the 4.8% C level, with the density decreasing rapidly with increasing carbon content. High oxygen and nitrogen contents in the UC charge also impaired densification. Densities as high as those obtained in that region were also achieved for compositions within the solubility limit when a small amount of external silicon vapor was provided along with the beryllide addition.

We believe the primary factor contributing to sintering when fabricating with uranium beryllide as an aid is a scavenging effect. Beryllium vapor appears to permeate the compact during the early stage, reducing the surface oxide responsible for inhibiting the sintering of the particles.

⁷J. P. Hammond, J. D. Sease, and C. Hamby, Jr., "Uranium Monocarbide Fabrication with UAl_2 as Sintering Aid," pp. 145-153 in The Fourth Uranium Carbide Conference, East Hartford, Connecticut, May 20-21, 1963, TID-7676 (1964).

UNCLASSIFIED
ORNL-DWG 64-6114

Fig. 1.8. Sintered Density of UC-UBe₁₃ System in Relation to Solvus. Densities (percent of theoretical) are average of duplicate tests. Enclosed area indicates optimum sintering conditions.

Fig. 1.9. Microstructure of UC-1.0 wt % UBe_{13} Sintered in Vacuum 3 hr at 1550°C . Density is 95.3% of theoretical. Secondary constituent is UBe_{13} . Etched with equal parts concentrated HNO_3 , acetic acid, and H_2O . 500X.

In supplemental experiments, we introduced beryllium vapor externally to the compact as the sintering aid. Sintering for 3 hr at 1600°C aided by beryllium vapor gave densities in excess of 92% of theoretical, whereas unaided uranium carbide sintered only to 89% of theoretical. The intermediate density possibly resulted from sintering and sealing of the surface before the center had been scavenged.

Aided Sintering of Uranium Nitride

J. P. Hammond

Like uranium carbide fuel, uranium nitride has advantages of higher thermal conductivity and uranium density than UO_2 ; however, fabrication is even more of a problem than for the carbide.⁷ We have started to examine various aids for sintering UN along the lines carried out for UC.

Shown in Table 1.6 are some of the results from experiments conducted to date. These rather promising results were obtained for UN starting powder: U, 93.68 wt %; N, 5.58 wt %; C, 0.01 wt %; and

Table 1.6. Sintering Results for Uranium Nitride^a

Sintering Temperature (°C)	Sintering Aid (wt %)	Ball Milling Time ^b (days)	Sintered Density (% TD) ^c	Secondary Constituents	
				Amount	Kind
1500	2 UAl ₂	2	89.2	Very slight	Sizeable particle
1500	4 UAl ₂	2	89.8	Very slight	Sizeable particle
1600	2 UAl ₂	2	94.9	Slight	Sizeable particle
1600	4 UAl ₂	2	93.1	Very slight	Sizeable particle
1550	Al vapor ^d	6	95.0	Trace	Fine, uniformly dispersed

^aPressed as 5/16-in.-diam pellets with 2 wt % camphor binder at 25-tsi pressure and fired 3 hr in vacuum.

^bWC balls in rubber-lined drum, 4-μ starting powder.

^cAverage of two tests.

^dProvided by distillation from 10 wt % (of charge) UAl₂ powder introduced on hearth of crucible.

0, 0.102 wt %. The densification achieved for the firing listed last in Table 1.6 is attributed to a combination of the contaminant scavenging effect provided by the aluminum vapor and the extreme fineness of the UN powder. Chemical analysis indicated a 12% loss in nitrogen resulting from the fabrication. As can be seen in Fig. 1.10, the microstructure showed an unidentified constituent, but only in trace amount and finely distributed.

Dispersion Hardening of Molybdenum

K. K. Sinha⁸ M. C. McIlwain J. P. Hammond

The present trend in advanced gas-cooled reactors is toward systems that operate at temperatures in excess of 1400°C. To provide materials

⁸Visitor from India.

Fig. 1.10. Microstructure of Uranium Nitride Sintered 3 hr at 1550°C in the Presence of Aluminum Vapor. Swabbed in equal parts concentrated lactic and nitric acids and then immersed in a mixture of 30 ml lactic acid, 10 ml HNO_3 , and 2 ml HF . 1000X.

with superior strengths at this temperature level, we are trying to strengthen refractory metals, initially molybdenum, by dispersion hardening. The standard methods for effecting dispersions, such as mechanical blending of fine powders of metal and oxide, decomposition of salts to derive refractory-oxide coatings on fine metal powders, selective reduction of an oxide in an oxide mixture, and coating or codeposition of powders, were examined. These yielded coarse dispersions or failed in other ways to give desired properties. This pointed up the need for a process that would give extremely small particles of matrix and dispersoid ($<0.1 \mu$) and uniformly distribute the dispersoid. The solution to this problem was found in colloidal chemistry.

The particle size of colloidal dispersions ranges from 50 to 500 Å. The mixing of sols of matrix and dispersoid followed by collection as a cake ostensibly would yield a good dispersion. The dispersoid phases used in this program, ThO_2 and ZrO_2 , were easily prepared as sols by

conventional techniques.⁹ However, the only reference to a molybdenum sol was for a suboxide of molybdenum, which yielded insufficient concentration. Thus, we needed an improved process for preparing molybdenum sols. We discovered one that forms a colloid by supersaturation. Rapid introduction of a saturated solution of ammonium molybdate in water into 190-proof ethyl alcohol triggered the formation of a colloid of ammonium molybdate by reducing its solubility.

The sols of ammonium molybdate and ThO_2 or ZrO_2 were then mixed and centrifuged to form an ammonium molybdate-oxide powder mixture. This mixture was then selectively reduced in hydrogen to form a molybdenum-plus-oxide dispersion powder mixture. Compacts of these powders were hot pressed and extruded to full density. These alloys showed a substantially greater hot hardness than the alloys prepared by standard techniques, but examination by electron microscopy showed some segregation and growth of dispersoid particles. We are trying to reduce segregation and prevent particle growth during fabrication.

⁹H. B. Weiser, Inorganic Colloidal Chemistry, vol. II, Wiley, New York, 1935.

2. MECHANICAL PROPERTIES

J. R. Weir, Jr.

Our objective is the study of the effects produced by reactor environments on the mechanical properties of materials. These environments consist of thermal and mechanical stresses imposed on the reactor structure, chemically reactive coolants, and neutrons produced by fissioning. Our work in the past year has emphasized the study of problems associated with hydrogen and carbon dioxide as potential coolants and the problem of radiation damage to stainless steel.

Effect of Hydrogen on the Mechanical Properties of Metals¹

H. E. McCoy, Jr.

We are evaluating the high-temperature mechanical behavior of several metals in hydrogen, primarily by comparative creep-rupture testing in hydrogen and in argon. The materials studied included two heats of Inconel, Nickel 200, Nickel 270, an electron-beam zone-refined melt of nickel, high-purity copper, Armco iron, electrolytic iron, and type 304 stainless steel. All of the nickel-base materials and the copper exhibited inferior creep resistance in hydrogen, while the iron-base materials were not influenced by this environment. Hydrogen had a large effect on pure nickel and copper; the magnitude of this effect decreased with decreasing purity of the metals. This effect was characterized, in general, by these observations. (1) At the same stress and temperature, the minimum creep rate was greater in hydrogen than in argon. (2) The rupture life was less in hydrogen than in argon at an equivalent stress and temperature. (3) The rupture ductility was the same in both.

We have run several additional experiments to determine the responsible mechanism. These experiments have included measurement of permeation of hydrogen through Inconel; measurement of the surface energy

¹Condensed from the University of Tennessee Ph.D. Dissertation of H. E. McCoy, Jr., Effects of Hydrogen on the High-Temperature Flow and Fracture Characteristics of Metals, ORNL-3600 (June 1964).

of nickel in argon and in hydrogen; comparison of sintering rates of nickel powder in argon, hydrogen, and vacuum; comparison of void formation in diffusion couples of iron and nickel annealed in argon and in hydrogen; comparison of diffusion of carbon in nickel in environments of hydrogen and argon; measurements of the rate of diffusion of ^{60}Co in nickel in argon and hydrogen; and transmission electron microscopy on thin nickel creep specimens. The mechanism that we think is most consistent with the experimental observations is based on the interaction of hydrogen with dislocations. Although several details of the mechanism are lacking, it qualitatively accounts for most of the experimental observations.

Reactions of Type 304 Stainless Steel with Flowing CO_2 at Atmospheric Pressure and Elevated Temperatures²

H. E. McCoy, Jr.

We have measured the oxidation of type 304 stainless steel in CO_2 over the temperature range of 590 to 980°C. Although the oxidation rate was usually parabolic, in several cases there was a transformation from parabolic to approximately linear. These transformations were reproducible and we believe they are associated with changes in the rate-controlling step of the oxidation process. Type 304 stainless steel became carburized during exposure to CO_2 . We studied several other alloys to determine the mechanism of carburization. These included type 406 stainless steel, a British niobium-stabilized steel (20 Cr-25 Ni), Inconel, iron, Fe-1% Cr, Fe-3% Cr, and Fe-10% Cr. We found that the carburization was dependent on the chromium content; a low chromium content favored carburization and higher chromium contents inhibited carburization. We explained this effect in terms of the influence of chromium on the type of surface oxide formed.

²Condensed from an article by H. E. McCoy, "Reactions of Type 304 Stainless Steel with Flowing CO_2 at Atmospheric Pressure and Elevated Temperatures," submitted to Corrosion.

Radiation Effects on the Mechanical Properties of Stainless Steel

W. R. Martin

The influence of irradiation at elevated temperatures on the mechanical properties of structural materials is not well understood. A number of investigators have shown that the rupture life and fracture ductility of several materials are reduced by irradiation. We are evaluating the effect of irradiation on the ductility of stainless steels at elevated temperatures.

Figure 2.1 compares typical stress-strain curves for material irradiated and tensile-tested in each of two temperature ranges. Material irradiated at temperatures less than 450°C is stronger and less ductile (as measured by uniform elongation). At elevated temperatures, irradiation does not affect the strength. The ductility at temperatures above one-half of T_m , the absolute melting temperature, is reduced, and this reduction in ductility is sensitive to the strain rate.

Fig. 2.1. Effect of Irradiation on the Stress-Strain Curves of Stainless Steels.

Figure 2.2 illustrates the effect of irradiation to 7×10^{20} neutrons/cm² ($E > 1$ Mev) at 200°C as a function of deformation temperature. The magnitude of the effect of irradiation on the properties increases to a maximum and then decreases as the deformation temperature is increased to approximately $0.5 T_m$. Above $0.5 T_m$, the effect is the same as observed for material irradiated at elevated temperatures and is shown in Fig. 2.3. Thus the irradiation temperature does not significantly alter the irradiation effect observed for stainless steel tested at elevated temperatures.

The general effects we have observed may be summarized as follows:

1. Irradiation affects the stress-strain relationship of material irradiated and then tested at low temperatures; irradiation results in increased strength and reduced ductility, as measured by uniform elongation. The true tensile stress (true stress at maximum load) and the true fracture stress and strain are not altered. Thus, the deformation process and not the fracture process is affected.

2. Irradiation at elevated temperature does not affect the stress-strain relationship. Ductility, as measured by uniform and fracture strains, is reduced for deformation temperatures above $0.5 T_m$. The loss of ductility results in reductions in the true tensile and fracture stresses. The reduction in ductility is more significant at test conditions that result in intergranular failure, such as low strain rates at elevated temperature.

The loss of ductility of irradiated material deformed at elevated temperature is complex. Damage from fast neutrons has been shown³ to anneal at temperatures as low as 450°C, so one would expect that at a flux of 10^{14} neutrons cm⁻² sec⁻¹ the damage would anneal within the reactor at irradiation temperatures of 600°C and above. However, Roberts and Harries⁴ indicate that the low ductility at elevated temperatures is caused by thermal neutrons, and our results for type 304 stainless steel

³R. E. Bailey and M. A. Silliman, "Effect of Irradiation on Type 347 Stainless Steel Flow Separator in the EBR-I Core," pp. 84-102 in Symposium on Radiation Effects on Materials, Vol. 3, Am. Soc. Testing Mater. Spec. Tech. Publ. 233 (1958).

⁴A. C. Roberts and D. R. Harries, Nature 200, 773 (1963).

Fig. 2.2. Influence of Irradiation at Approximately $0.25 T_m$ on the Tensile Properties of Stainless Steel.

Fig. 2.3. Influence of Irradiation at Temperatures above $1/2 T_m$ on the Postirradiation Tensile Properties of Stainless Steel.

(Table 2.1) are in agreement. We have reported⁵ that the damage causing the low ductility at elevated temperatures does not anneal at approximately 1000°C.

Postirradiation examination of stainless steel shows that the low ductility at elevated temperature is due to grain-boundary embrittlement. Metallographic examination shows that the deformation temperature at which the irradiated alloy becomes embrittled is the temperature of transition from transgranular to intergranular mode of fracture. Grain-boundary cracks are found at smaller strains in the irradiated material than in the unirradiated alloy. In the irradiated material, these cracks propagate along the boundary rather than widen and cause complete specimen rupture at a considerably reduced strain. The dependence of the number of cracks per unit grain-boundary area on fracture strain supports these observations. Both nucleation and propagation of microcracks above $0.5 T_m$ were affected by irradiation.

The general characteristics of the effect of irradiation on the deformation of stainless steels at elevated temperatures are (1) yield stress and tensile strength are not affected; (2) ductility is reduced; (3) the reduction in ductility is more significant at test conditions that result in intergranular failure, such as low strain rates at elevated temperatures; (4) the reduction of ductility is due to grain-boundary embrittlement; (5) postirradiation heat treatments, including those that anneal the damage caused by low-temperature irradiation, do not improve the ductility at elevated temperature; and (6) the loss in ductility appears to be related to doses of thermal and epithermal neutrons and not fast neutrons.

These observations are consistent with the hypothesis that the high-temperature damage is due to helium produced by the $^{10}\text{B}(n,\alpha)$ reaction. The helium may agglomerate into grain-boundary bubbles, which act as crack nuclei at elevated temperature.

⁵W. R. Martin and J. R. Weir, Nature 202, 997 (1964).

Table 2.1. Comparison of Dose Effect on Mechanical Properties
of Type 304 Stainless Steel at Room Temperature and 842°C

Deformation Temperature (°C)	Dose neutrons/cm ²		0.2% Offset Yield Stress (psi)	True Tensile Strength (psi)	True Uniform Strain (%)	Total Elonga- tion (%)
	Fast E > 1 Mev	Thermal				
			× 10 ³	× 10 ³		
20	0	0	26.9	155.0	61.5	89.8
	3 × 10 ¹⁹	1.6 × 10 ²⁰	58.1	144.0	45.7	65.4
	3 × 10 ¹⁹	Cd covered	58.5	148.1	47.3	70.6
	5 × 10 ²⁰	7 × 10 ²⁰	91.0	140.0	40.6	50.6
842	0	0	9.3	16.1	13.5	47.4
	3 × 10 ¹⁹	Cd covered	9.0	18.4	12.8	20.0
	3 × 10 ¹⁹	1.6 × 10 ²⁰	9.0	17.9	9.2	14.0
	5 × 10 ²⁰	7 × 10 ²⁰	10.3	22.8	7.7	9.4

Influence of Preirradiation Heat Treatment on the Strength and Ductility of Irradiated Type 304 Stainless Steel

W. R. Martin

Observations of the interaction of dislocations at low temperatures with point defects generated by fast neutrons suggest that the introduction of a dislocation substructure into the material before irradiation may increase the coefficient of work hardening in irradiated material and consequently improve the ductility. Several heat treatments selected for type 304 stainless steel are given in Table 2.2. We believe that treatment 2 develops a substructure that is stable in the absence of radiation for a period greater than 2000 hr at 700°C and that treatment 3 does not develop a stable substructure. Both these treatments conclude with heating 24 hr at 482°C and 100 hr at 704°C, a treatment discussed previously by Garofalo and co-workers.⁶ This treatment stabilizes the dislocation structure by precipitation of carbides of the type $M_{23}C_6$. Treatments 4 and 5 are anneals that result in grain sizes of ASTM 5-6 and 1-2, respectively. Table 2.2 also gives the influence of these preirradiation heat treatments on the strength and ductility of type 304 stainless steel at 20°C after irradiation to a dose level of 7×10^{20} nvt ($E > 1$ Mev).

Except after treatment 2, the pre- and postirradiation strengths of the alloy are in the same sequence after the various treatments. The effect of irradiation, as measured by the ratio of post- to preirradiation strengths, decreases as the preirradiation dislocation density in the alloy increases. Similar effects of cold working have been noted earlier.⁷ However, the magnitude of the increase in yield stress of the alloy given treatment 2 is less than expected for cold-worked material. In fact, its postirradiation yield stress is less than that of the most annealed material (treatment 5).

⁶F. Garofalo, F. von Gemmingen, and W. F. Domis, Trans. Am. Soc. Metals 54, 430 (1961).

⁷T. H. Blewitt and R. R. Coltman, Phys. Rev. 82, 769 (1951).

Table 2.2. Influence of Preirradiation Heat Treatment on the Postirradiation Room-Temperature Tensile Properties of Type 304 Stainless Steel^a

Preirradiation Heat Treatment		0.2% Offset Yield Stress (psi)		Ratio of Post/Pre Yield Stress	Increase in Yield Stress (psi)	Ductility True Uniform Strain (%)		Ratio of Post/Pre Strain	Difference in Strain (%)
No.	History	Postirradiated	Preirradiated			Post-irradiated	Pre-irradiated		
		$\times 10^3$	$\times 10^3$		$\times 10^3$				
1	As received (equivalent to ~ 30% cold work)	106.0	69.2	1.5	36.8	29.0	44.0	0.66	15.0
2	Annealed 1 hr at 1038°C in H ₂ ; strained uniaxially 25% at room temperature; finally heat treated 24 hr at 482°C and 100 hr at 704°C	74.0	53.0	1.4	21.0	35.0	44.0	0.80	9.0
3	Annealed 1 hr at 1038°C in H ₂ ; strained 10% at room temperature; finally heat treated 24 hr at 482°C and 100 hr at 704°C	95.0	43.0	2.2	52.0	35.0	50.0	0.70	15.0
4	Annealed 1 hr at 1038°C in H ₂	90.0	28.0	3.2	62.0	39.0	59.0	0.66	20.0
5	Annealed 5 hr at 1260°C in H ₂	79.0	26.0	3.0	53.0	42.0	63.0	0.67	21.0

^aIrradiated to 7×10^{20} nvt (> 1 Mev). During irradiation the specimens were exposed for 2000 hr in the temperature range 120 to 170°C.

Comparing the effect of irradiation on the stress-strain curve after treatments 4 and 5, we find that the influence of grain size is the same as that found by Chow⁸ for iron at room temperature. However, the offset yield stress of the irradiated alloy does not have the grain-size independence shown by Chow for iron but is similar to that observed by Hull and Mogford⁹ for steels.

The ductility of the unirradiated alloy, as given by the true uniform elongation, is altered significantly by preirradiation heat treatment. The effect of irradiation, measured as the ratio of post- to preirradiation strain, is within the range of 0.66 to 0.70 for all treatments except treatment 2. Thus, another benefit of the development of the stable substructures appears to be a smaller loss of ductility, since the corresponding ratio is 0.8 after treatment 2. The data also suggest that treatments that improve the preirradiation ductility will also increase the postirradiation ductility of the alloy.

Neutron Flux Dosimetry

J. C. Zukas

Routine activation sampling to monitor the neutron flux has been an adjunct of all experiments operated in the ORR by the Mechanical Properties Group of the Metals and Ceramics Division. We measure the activity of dilute cobalt alloy specimens, irradiated both bare and shielded by cadmium, to obtain the necessary data for calculation of the thermal and resonance flux. We have chosen the model of Stoughton and Halperin¹⁰ for these computations, which provide values for calculating burnout of other nuclide species. We measure the fast flux with various threshold detector materials. The reaction scheme that has provided the best internal consistency to date, based on the use of ⁵⁸Ni, is shown in Fig. 2.4. In theory, we should be able to measure the flux with unshielded samples and calculate the reaction rate, making corrections

⁸J. G. V. Chow, Quart. Progr. Rept. May-July, 1962: Irradiation Effects on Reactor Structural Materials, HW-74679, pp. 5-7.

⁹D. Hull and I. L. Mogford, Phil. Mag. 8, 1213 (1958).

¹⁰R. W. Stoughton and J. Halperin, Nucl. Sci. Eng. 6, 100-118 (1959).

Fig. 2.4. Nickel-58 (n,p) ^{58}Co Reaction Scheme.

for thermal burnout of the high cross-section isomers, ^{58}Co and ^{58m}Co . However, uncertainties in cross sections, resonance integrals, and branching yields of these isomers limit the accuracy of such calculations.

The cross sections that have been reported for a single nuclide differ widely in many cases. Therefore, we are measuring thermal neutron cross sections using separated ^{58}Ni and high-purity iron along with the cobalt specimens. The ^{58m}Co is measured directly (as opposed to by difference). We are analyzing data from short irradiations while carrying out the long-time exposures.

3. NONDESTRUCTIVE TEST DEVELOPMENT

R. W. McClung

Our program is intended to develop new and improved methods of evaluating reactor materials and components. To achieve this we have studied various physical phenomena, developed instrumentation and other equipment, devised application techniques, and designed and fabricated reference standards. Among the methods being actively pursued are electromagnetics (with major emphasis on eddy currents), ultrasonics, and penetrating radiation. In addition to our programs oriented toward the development of methods, we are studying these and other methods for evaluation of problem materials and developing techniques for remote inspection.

Electromagnetic Test Methods

C. V. Dodd

We have continued research and development concerning electromagnetic phenomenon on analytical and empirical bases. As part of the program, we are studying the determination of impedance of an eddy-current probe coil as a function of coil dimensions, frequency, specimen conductivity and permeability, and coil-to-specimen spacing or "lift off." The mathematical solution has been programmed for computer operation¹ and values for several typical cases have been determined. A family of curves of coil impedance as a function of frequency (ω), conductivity (σ), permeability (μ), coil radius (R), and lift off (S) is shown in Fig. 3.1. The figure demonstrates that changes in frequency, coil radius, or conductivity can be compensated for by changes in another of these. The computer program also allows the eddy-current density and the field (vector potential) of the coil to be calculated. Figure 3.2 shows equipotential contours of the field of a coil and eddy-current densities, superimposed on a cross section of the coil that is creating

¹C. V. Dodd and W. E. Deeds, "Eddy-Current Coil Impedance Calculated by a Relaxation Method," pp. 300-314 in Symposium on Physics and Non-destructive Testing, Southwest Research Institute, San Antonio, Texas, 1964.

Fig. 3.1. Example of Calculated Normalized Impedance. The impedance components are plotted in reduced dimensionless units. The solid curves are for indicated constant values of the lift off, and the dashed curves are for constant values of the combined parameter $R\sqrt{\omega\mu\sigma}$.

Fig. 3.2. Example of Equipotential and Current Magnitude Contours. Abscissa and ordinate scales are arbitrary lattice points used for the computer calculations and related to distances. The small cross-hatched square represents the cross section of the coil, and the large cross-hatched area represents the nearby metal specimen.

them. Both the currents and the field flow around the axis of the coil. From values of these, other information such as ohmic-heating density and eddy-current-force distribution may be obtained. We are seeking more versatile calculation methods with associated computer programming.

Development has continued on the phase-sensitive eddy-current instrument.² Several new circuits have been designed and constructed for the modular instrument. These include a low-distortion high-power amplifier, video amplifiers with high gain and low distortion and noise, and stable voltage-height discriminators. These, coupled with the development of a new method for nulling the probe coils, allow more accurate metal thickness measurements since there is less error due to variations in lift off. In addition, a time-differential filter has been incorporated into the instrument to allow the detection of defects in materials in the presence of changes in wall thickness or conductivity. Included among the applications have been detection of core edge in flat fuel plates and detection of cracks in graphite spheres.

Continued studies of spacing measurements have culminated in a report³ describing in detail our method of designing and fabricating coolant-channel spacing probes. The report describes the needed compromises and provides detailed instructions for constructing an optimum spacing probe.

Ultrasonic Test Methods

K. V. Cook R. W. McClung

Our studies of ultrasonic behavior in thin sections have been directed primarily toward development of techniques to detect nonbond areas in clad structures. Studies of through transmission in flat fuel plates and sheet have continued. One- and two-crystal reflection methods have been demonstrated to be very useful for solving a number of difficult

²C. V. Dodd, Mater. Eval. 22(6), 260 (1964).

³C. V. Dodd, Design and Construction of Eddy-Current Coolant-Channel Spacing Probes, ORNL-3580 (April 1964).

inspection problems. For instance, a two-crystal system was developed to detect nonbond in brazed tube-to-header joints.^{4,5}

Many of these techniques need a reliable method of establishing the appropriate inspection angles. In order to simplify this problem, a two-crystal angle manipulator (shown in Fig. 3.3) has been designed and fabricated in cooperation with the Plant and Equipment Division. We shall use this precise mechanical system to study both reflection and Lamb-wave ultrasonic techniques. The principal advantage to this system is that each transducer can be varied through a 45° angle without changing either the distance from crystal to specimen or the point at which the ultrasound enters the specimen.

Another advance has been the design and fabrication of a two-crystal probe in which the angle of each crystal is variable. The probe, shown in Fig. 3.4, allows each crystal to be pivoted about a diameter. Hence, the probe can be used both to establish proper angles for reflection or Lamb-wave techniques and to perform the inspection. The illustrated probe has a minimum outside diameter of 0.370 in.; we feel that smaller probes are possible.

We have designed and constructed a transistorized ultrasonic dual-channel analyzer using the latest semiconductor and integrated circuitry. This instrument performs better than the old vacuum-tube model for the detection, gating, and processing of ultrasonic signals generated during nondestructive testing.

We have started to study the evaluation of fuel plate-to-side plate joints, such as those in ATR fuel assemblies, that have been pressure bonded by roll swaging. We used both sonic and ultrasonic methods on test samples of aluminum sheet that had been pinned at different roll pressures. No conclusive results were observed with the sonic method,

⁴K. V. Cook and R. W. McClung, Metals and Ceramics Div. Ann. Progr. Rept. May 31, 1963, ORNL-3470, p. 95.

⁵K. V. Cook and R. W. McClung, "An Ultrasonic Technique for the Evaluation of Heat Exchanger Brazed Joints," paper submitted for presentation at the Annual Meeting of the Society for Nondestructive Testing, Philadelphia, Pa., October 19-23, 1964, and for publication in Materials Evaluation.

Fig. 3.3. Angle Manipulator for Two Independent Ultrasonic Crystals.

Fig. 3.4. Variable-Angle Dual-Crystal Probe.

but transmission of ultrasound (although very small) was possible through the bonded joints and seemed to be increased by increasing the roll pressure. Twelve swaged joints rolled at different pressures were evaluated first ultrasonically and then destructively. Destructive results and ultrasonic data could be correlated. However, further study showed that this technique will demonstrate variation in the bond strength of joints up to a certain value above which variations in sound transmission can no longer be detected. These preliminary studies show that a technique using ultrasonics probably could be developed to evaluate the fuel plate-to-side plate pressure bonds.

Penetrating Radiation Methods

Low-Voltage Radiography and Microradiography - R. W. McClung

We have applied the low-voltage radiographic and contact micro-radiographic technique⁶ to evaluate a wide variety of specimens of thin or light-weight material. Of particular interest has been the use of the microradiographic technique on miniature samples of materials such as UC₂ and graphite that had undergone in-pile testing and were radioactive. Use of an internal dimensional standard in microradiography is described elsewhere.⁷

Gamma Scintillation Gaging - B. E. Foster and S. D. Snyder

The versatile mechanical scanner⁸ was successfully installed and modified slightly to facilitate its operation. Its successful use in developing techniques for measuring fuel inhomogeneities in fuel plates provided necessary design criteria for the fabrication of a pilot-model

⁶R. W. McClung, Mater. Res. Std. 4(2), 66-68 (1964).

⁷R. W. McClung, Metals and Ceramics Div. Ann. Progr. Rept. June 30, 1964, ORNL-3670, Part III, Chap. 25 (in press).

⁸B. E. Foster and S. D. Snyder, Metals and Ceramics Div. Ann. Progr. Rept. May 31, 1963, ORNL-3470, p. 96.

scanner and two production scanners, which will be used for homogeneity evaluation of the HFIR fuel plates. Details of this application and the application to rods are reported elsewhere.⁹

We are continuing to develop calibration standards for x- and gamma-ray attenuation measurement of fuel concentration variations, including the fabrication and use of alternate attenuation standards.⁸

We are expanding the use of the scanning system and technique toward determination of total fuel content. The results of some initial evaluations of fuel content in HFIR fuel plates have been in excellent agreement with those obtained by chemical analysis using total dissolution. Several problems are associated with this new application, but the results thus far are quite promising.

X-Ray Imaging with Closed-Circuit Television - W. H. Bridges

Several years ago we investigated the capabilities and performance of a closed-circuit television system for imaging x rays.¹⁰ At that time the only x-ray sensitive vidicons were experimental tubes with glass windows that markedly impaired their use with x-ray energies below about 90 kv constant potential. Since then, interest has increased worldwide, and a beryllium-window vidicon was developed.¹¹ This vidicon is more sensitive to x rays, particularly to low-voltage x rays. As some welds in thin-wall tubing need to be inspected in a hot cell, procuring one of the new vidicons and determining its characteristics and potential application appeared advisable.

The first task was to determine the sensitivity of the vidicon to x rays. With 100- and 150-kv constant potential x rays, the signal current from the beryllium-window vidicon was about 1.6 times that of

⁹B. E. Foster and S. D. Snyder, Metals and Ceramics Div. Ann. Progr. Rept. June 30, 1964, ORNL-3670, Part III, Chaps. 26 and 29 (in press).

¹⁰J. W. Allen and R. W. McClung, An Electronic, High-Resolution, X-Ray Imaging System, ORNL-2671 (Aug. 11, 1959).

¹¹J. P. Mitchell, M. L. Rhoten, and R. C. McMaster, X-Ray Image System for Nondestructive Testing of Solid Propellant Missile Case Walls and Weldments Final Report, WAL TR 142.5/1-5 (AD-299 987), (Aug. 1962).

the glass-window vidicon. The greatest benefit with the beryllium-window vidicon is the low attenuation of the long-wavelength low-voltage x rays. We have obtained very good images of masking tape and graphite at 12 kvp. There was every indication that much lower voltages could be used with an adequate helium environment.

The major shortcoming of the vidicon is the small size of the active area - only $3/8$ by $1/2$ in. This is ameliorated to a great extent, however, by moving the specimen that is being examined. In fact, the motion aids the observation of a defect. With a proper mechanical drive, a specimen can be scanned about as rapidly as a radiograph can be examined. Another advantage is a magnification of 10 to 30X, depending on the monitor used.

The system was tested for resolution by examination of screens of various mesh sizes, transistors and diodes, welds in tubes of different sizes and materials, and wires. A 0.0005-in. tungsten wire was plainly visible. A 200-mesh screen was clearly resolved, but resolution of 400 mesh was marginal, probably the result of the lack of response of the 8-year-old closed-circuit television system. Defects in aluminum plug welds up to $1/2$ -in. diam were clearly discernible, but with materials of greater atomic number, techniques for masking and orienting must be developed for maximum resolution.

We have recently begun a series of experiments that provide an excellent example of the potential use of an x-ray-sensitive television system. We want to measure the movement of a specimen as it is subjected to very rapid thermal excursions. The annular specimen surrounds a resistance heater and is enclosed in a metal tube that is filled with helium and water-jacketed. As the thermal excursions may proceed at a rate up to $550^{\circ}\text{C}/\text{min}$, equilibrium is not established and the use of conventional measuring devices is negated. The speed precludes the use of radiographic film techniques. By observing and photographing the monitor screen of the x-ray television system, we can continuously record the specimen motion. Incorporation of an oscilloscope permits a relatively precise (<0.002 in.) direct reading of the specimen position. The oscilloscope is triggered by the television vertical-synchronization signal and the video output is fed to the vertical-deflection amplifier. By introducing a delay between the trigger impulse and the time the oscilloscope

sweeps, the information contained in a horizontal line or group of lines from any position on the television screen may be presented on the cathode-ray tube. Now, insertion of the delayed trigger pulse of the oscilloscope sweep into the television video amplifier can put a marker on the television screen. By maintaining the marker at some distinctive specimen feature and reading the amount of delay, we may readily ascertain the movement.

Inspection Development of Problem Materials

K. V. Cook R. W. McClung

We are developing nondestructive tests for materials that are difficult to inspect, including molybdenum, tungsten, tantalum, and graphite. Ultrasonics have been of particular value in the inspection of refractory-metal rod, bar, sheet, plate, tubing, and tube shells or hollows. Some applications of our methods have been reported.¹² To avoid damaging the very expensive alloys, we have been concerned with the use of alternate materials as reference standards.

Two similar methods for ultrasonically evaluating graphite have been developed. One method is an immersion through-transmission technique that can be applied to large samples. The other method is a contact through-transmission technique that is limited to tensile specimens. Both methods were used to evaluate material from three large graphite blocks. The blocks were thinly coated with latex rubber to seal out moisture and evaluated by the immersion technique in the X, Y, and Z planes for velocity and attenuation. We selected 242 tensile specimens for all three planes to cover a good distribution of ultrasonic velocity values over a complete high-to-low range, cut them from the blocks, and evaluated them by the contact ultrasonic method, using the system shown in Fig. 3.5.

Mechanical properties will be obtained from the specimens and correlated with ultrasonic data. The Mechanical Properties Group is

¹²K. V. Cook and R. W. McClung, Metals and Ceramics Div. Ann. Progr. Rept. June 30, 1964, ORNL-3670, Part II, Chap. 14 (in press).

Fig. 3.5. System for Through-Transmission Ultrasonic Evaluation of Tensile Specimens.

determining specimen properties, such as Young's modulus, resistivity, and fracture stress and strain. These properties will be compared with the ultrasonic velocity and attenuation data to see if a usable correlation exists.

Development of Remote Inspection Techniques

R. W. McClung

We have continued to develop techniques for radiography of materials in the presence of a radioactive background.¹³ We have evaluated the

¹³R. W. McClung, K. V. Cook, and C. V. Dodd, Metals and Ceramics Div. Ann. Progr. Rept. May 31, 1963, ORNL-3470, pp. 96-97.

first sets of radiographs of the aluminum step wedge after application of the fogging background. Use of photographic chemical reduction¹⁴ increased tenfold the tolerance to background fogging radiation.

Many of our ultrasonic and eddy-current techniques and other penetrating-radiation techniques are being developed with the added criterion that they can be applied in a hot cell or other remote environment.

Third Geneva Conference Exhibits

S. D. Snyder

Five exhibit items were prepared for showing at the Third Geneva Conference to be held from August 28 through September 11, 1964. The displays are a phase-sensitive eddy-current flaw detector, a penetrating-radiation homogeneity scanner, an eddy-current gage for coolant-channel spacings, a metal identification meter, and a display of work done with contact microradiography. The four working-model items are shown in Fig. 3.6. Each of these was accompanied by a pictorial display in the form of back-lighted transparencies assembled into modules.

¹⁴R. W. McClung, "Radiography in the Presence of a Radioactive Background," paper submitted for presentation at the Annual Meeting of the Society for Nondestructive Testing, Philadelphia, Pa., October 19-23, 1964, and for publication in Materials Evaluation.

UNCLASSIFIED
PHOTO-66146

METAL IDENTIFICATION METER

PHASE-SENSITIVE EDDY-CURRENT FLAW DETECTOR

CHANNEL-SPACING MEASURING DEVICE

HOMOGENEITY SCANNER

Fig. 3.6. Nondestructive Testing Instruments Displayed at the Third Geneva Conference.

4. SOLID REACTION STUDIES

T. S. Lundy

Our purpose is to provide information concerning solid-state reactions of importance in the development of materials for high-temperature application. We are emphasizing the study of mechanisms of these reactions by measuring diffusion rates in the solid state by various methods. In particular, we have studied (1) diffusion rates in various body-centered cubic refractory metals over wide ranges of temperatures, (2) the effect of alpha-particle bombardment on the diffusion of lead in silver, and (3) the thermal diffusion of antimony and ruthenium in silver.

Diffusion in Body-Centered Cubic Metals

T. S. Lundy D. Heitkamp¹
W. K. Biermann¹ J. F. Murdock
F. R. Winslow

Our investigation of diffusion in certain body-centered cubic metals has continued. This year we emphasized measurement of diffusion coefficients in niobium and tantalum over very wide ranges of temperature. Present indications are that in both of these metals the Arrhenius-type expression $D = D_0 \exp(-Q/RT)$ with constants D_0 and Q adequately describes the temperature variation of volume diffusion coefficients. This, of course, is in direct contrast to the inadequacy of this expression in describing diffusion coefficients in β -zirconium, β -titanium, and vanadium.²

¹Visitor from Germany.

²T. S. Lundy et al., Metals and Ceramics Div. Ann. Progr. Rept. May 31, 1963, ORNL-3470, p. 67.

Diffusion of ^{44}Ti and ^{48}V in Titanium³ - J. F. Murdock, T. S. Lundy, E. E. Stansbury⁴

The diffusion of ^{44}Ti and ^{48}V in the body-centered cubic phase of iodide titanium was studied over the temperature range 900 to 1550°C. The resulting Arrhenius-type plots show curvature with the apparent activation energies and frequency factors increasing with temperature. The various possible interpretations of this behavior are considered.

Diffusion of ^{48}V in Vanadium⁵ - T. S. Lundy, C. J. McHargue

The diffusion rate of ^{48}V in single crystals of body-centered cubic vanadium was determined at temperatures from 1002 to 1888°C. The lower temperature data are enhanced on an Arrhenius-type plot relative to values expected by extrapolation of the high-temperature diffusion coefficients. Above 1600°C the equation

$$D = 58 \exp(-91,500/RT) \text{ cm}^2/\text{sec}$$

describes the data while at temperatures below about 1400°C the temperature dependence of the diffusion coefficient is

$$D = 1.1 \times 10^{-2} \exp(-61,000/RT) \text{ cm}^2/\text{sec} .$$

A Submicron Sectioning Technique for Analyzing Diffusion Specimens of Tantalum and Niobium⁶ - R. E. Pawel,⁷ T. S. Lundy

A microsectioning technique for tantalum and niobium was successfully used to remove uniform sections of metal less than 100 Å in thickness from the surface. The technique, based on the formation

³Abstract of paper accepted for publication in Acta Metallurgica and based on the University of Tennessee M. S. Thesis of J. F. Murdock, Diffusion of Titanium-44 and Vanadium-48 in Titanium, ORNL-3616 (June 1964).

⁴Consultant from the University of Tennessee.

⁵Abstract of paper accepted for publication in Transactions of the Metallurgical Society of AIME and based on part of the University of Tennessee Ph.D. Dissertation of T. S. Lundy, Diffusion in the Body-Centered Cubic Metals Zirconium, Vanadium, Niobium, and Tantalum, ORNL-3617 (June 1964).

⁶Abstract of published paper: J. Appl. Phys. 35, 435-438 (1964).

⁷Reactions at Metal Surfaces Group.

and subsequent stripping of an anodic oxide film, is presently used to study diffusion phenomena in these metals. The apparent sensitivity is sufficient for low-temperature diffusivity measurements in reasonable times. It may also be possible to describe more quantitatively previously reported "anomalous" diffusion behavior near the metal surface. The present paper considers the details of the experimental technique and presents some typical diffusivity data for the diffusion of ^{95}Nb in tantalum.

Diffusion of ^{95}Nb and ^{182}Ta in Niobium⁸ - T. S. Lundy, F. R. Winslow, C. J. McHargue

We have measured the volume diffusion coefficient of ^{95}Nb in both mono- and polycrystalline niobium over the temperature range of 1000 to 2400°C. The high-temperature specimens ($T > 1500^\circ\text{C}$) were sectioned by conventional lathe and precision-grinding techniques. The anodizing-and-stripping technique described above was used for the lower temperature specimens. The logarithm of the diffusion coefficient is a linear function of reciprocal absolute temperature down to 1200°C but deviates from linearity below this temperature. Over a diffusivity range of almost 10^7 , the diffusion coefficient D is well described by the equation

$$D = 1.66 \exp(-97,600/RT) \text{ cm}^2/\text{sec} .$$

The low-temperature enhancement is probably due to short-circuit diffusion along lattice defects.

In a limited number of measurements, we found the diffusivity of ^{182}Ta in niobium to be about half that of ^{95}Nb in niobium, and the activation energies to be approximately the same for the two cases.

Effect of Alpha Bombardment on the Diffusion of Lead in Silver

D. Heitkamp¹ W. Biermann¹ T. S. Lundy

We measured the diffusion of ^{212}Pb in silver single crystals in the temperature range of 360 to 480°C by using the recoil method of Hevesy

⁸T. S. Lundy, Diffusion in the Body-Centered Cubic Metals Zirconium, Vanadium, Niobium, and Tantalum, ORNL-3617 (June 1964).

and Seith,⁹ a surface-counting technique. Experiments were performed both with and without alpha-particle bombardment from a ten-curie source of ^{210}Po . In the absence of such bombardment, the temperature dependence of the diffusion coefficient in the near-surface region may be described by

$$D = 600 \exp(-61,700/RT) \text{ cm}^2/\text{sec}.$$

Bombardment with 10^{11} 2.2-Mev alpha particles per square centimeters per second produces approximately 9.6×10^8 defects per second in silver and increased the diffusion coefficient by $6 \times 10^{-18} \text{ cm}^2/\text{sec}$ at all temperatures. Such an enhancement agrees satisfactorily with theoretical predictions based on analyses by Lomer¹⁰ and Dienes and Damask.¹¹

Thermal Diffusion of Antimony and Ruthenium in Silver¹²

W. Biermann¹ D. Heitkamp¹ T. S. Lundy

The thermal-gradient redistribution of antimony and ruthenium in very dilute solid solutions in silver was investigated by radioactive tracer techniques. The concentration of antimony increased considerably at the hot side of the specimens and decreased at the cold side. The steady-state concentration was given by a straight line on a plot of the logarithm of the antimony concentration vs the reciprocal absolute temperature. The redistribution can be described by an unusually large negative heat of transport $Q = (-29 \pm 3) \text{ kcal/mole}$. The kinetic treatment of Wirtz can explain the data if it is assumed that most of the activation energy for migration of antimony atoms is necessary to open up the vacancy into which the atom jumps. This treatment, however,

⁹G. v. Hevesy and W. Seith, Z. Physik. 56, 790 (1929).

¹⁰W. M. Lomer, "Defects in Pure Metals," p. 255 in Progress in Metal Physics vol. 8, Pergamon Press, New York, 1959.

¹¹G. J. Dienes and A. C. Damask, Proc. U. N. Intern. Conf. Peaceful Uses At. Energy, 2nd. Geneva, 1958 29, 340 (1959); J. Appl. Phys. 29, 1713 (1958).

¹²Abstract of paper submitted to Acta Metallurgica.

allows a very wide variation in the predicted heat of transport. The concentration profile for ruthenium in silver annealed under a temperature gradient was quite different from any redistribution that could be explained by thermal diffusion alone. No heat of transport could be calculated from the ruthenium distribution.

5. ZIRCONIUM METALLURGY

M. L. Picklesimer

We are conducting research along several lines on zirconium-base alloys of potential use as structural materials in several water-cooled and/or -moderated reactor systems. The principal projects presently under way are: (1) studies of the physical metallurgy, consisting of transformation kinetics and morphologies, mechanical properties, phase diagrams where necessary, and heat-treatment response; (2) the development, evaluation, and utilization of preferred orientation and strain anisotropy in α -zirconium alloys during fabrication, and the utilization of the yield-stress anisotropy in increasing maximum permissible design stresses in structures; (3) the determination of the effects of composition, temperature, and environment on the oxidation-corrosion rates in the thin film stages of oxide growth; (4) a study of the effects of alloy composition and oxidation environment on the structural properties of thin oxide films in situ; and (5) investigation of stress reorientation of precipitated hydrides in Zircaloy-2.

Zirconium Alloys

P. L. Rittenhouse M. L. Picklesimer

We have followed the transformation kinetics of zirconium alloys containing from 1 to 7.5 wt % Mo by electrical resistivity measurements and also obtained some information on the phase boundaries. The resistivity results obtained were similar to our previous results¹ for zirconium-niobium alloys rich in zirconium. At low alloy content (less than 3 wt % Mo or 10 wt % Nb), we can establish an $\alpha + \beta \rightarrow \beta$ transformation temperature consistent with metallographic results. At no level of alloy content can a eutectoid temperature be unambiguously observed by changes in electrical resistivity.

The transformation of a Zr-0.9 wt % Fe alloy was also studied by measurement of electrical resistivity and by metallography. Resistivity

¹P. L. Rittenhouse and M. L. Picklesimer, Metals and Ceramics Div. Ann. Progr. Rept. May 31, 1963, ORNL-3470, p. 55.

changes near the eutectoid temperature indicated that at least three phases were present in the specimen over appreciable temperature ranges during both heating and cooling cycles. Rates of heating and cooling were from 2 to 8°C/min, and Fig. 5.1a shows the typical variation of resistivity with temperature. Zirconium-copper alloys containing less than 2 wt % Cu show similar behavior on cooling but not on heating. Zirconium alloys containing Ni, Cr, or Pd do not show such behavior on either heating or cooling, giving curves shaped as shown in Fig. 5.1b, which is typical of a binary alloy system that transforms rapidly. The temperature designated T_1 in Fig. 5.1a was 780°C, which is slightly below the presently accepted eutectoid temperature of 790 to 800°C. The temperature T_2 , the start of the "bump" that indicates the presence of three phases, was 795°C; and the temperature T_3 for the solvus line was 845 to 850°C, in agreement with the presently accepted phase diagram.² Isothermal anneals for 3 hr during both heating and cooling cycles did not appreciably change the resistivity at any temperature above 780°C. Either the alloy has a remarkable metastability in comparison to the Ni, Cr, and Pd alloys, or the oxygen present (about 150 ppm) caused the Zr-Fe alloy to behave as a ternary alloy. This amount of oxygen is apparently insufficient to cause such behavior in the alloys containing Ni, Cr, and Pd.

To determine if three phases exist in the Zr-Fe alloy at temperatures near 800°C, specimens were heat treated for 30 min at temperatures from 750 to 860°C, water quenched, and metallographically examined. Those held at 860°C were all beta phase at temperature, those at 810 and 840°C showed the normal $\alpha + \beta$ structure, and those held at 750 and 770°C showed fine recrystallized α -zirconium plus a large amount of a precipitate difficult to resolve at 1000X. In those specimens held at 780 and 795°C, the same alpha matrix was observed, the precipitate particles were appreciably larger, and anodizing showed conclusively that three

²F. N. Rhines and R. W. Gould, "The Zr-Fe System," pp. 62-73 in Advances in X-Ray Analysis, vol. 6, ed. by W. M. Mueller and Marie Fay (Proceedings of the Eleventh Annual Conference on Application of X-Ray Analysis, Aug. 8-10, 1962) Plenum Press, New York, 1963.

Fig. 5.1. Schematic Electrical Resistivity Curves for
(a) Zr-0.9 wt % Fe, (b) Lean Zr-Ni, Zr-Cr, and Zr-Pd Alloys.

phases were present. According to the presently accepted phase diagram,² the two minor phases should be β -zirconium and Zr_4Fe . Our data are in agreement with this phase diagram except that we find a lower eutectoid temperature.

The Effect of Preferred Orientation and Stress on the Directional Precipitation of Hydrides in Zircaloy-2

P. L. Rittenhouse

Hydrogen pickup associated with the corrosion of α -zirconium alloys is a major deterrent to their use as reactor materials, since the modest concentrations of hydrogen soluble in these alloys are sufficient to precipitate zirconium hydride platelets when the alloys are cooled from operating temperature. The effect of these platelets on ductility depends on their orientation relative to the applied stress and is nearly zero in Zircaloy-2 of relatively low hydrogen content when the

stress axis is parallel to the platelets.³ That stress can reorient the hydrides has been shown;⁴ and this reorientation can either enhance or lower ductility, depending on the distribution of the hydrides relative to the stress axis before and after reorientation.

We tested specimens of three lots of Zircaloy-2 of known preferred orientation to determine the effect of stress direction and preferred orientation on the directional precipitation of the hydrides.⁵ Controlled amounts of hydrogen were added to all the materials. We heated some specimens to a temperature above the solvus, loaded them elastically in tension to a maximum stress of 20,000 psi, and slowly cooled them to room temperature under stress. A second group of specimens was plastically deformed by bending at room temperature, heated above the solvus, and cooled without load. The angles between a reference direction and the traces of several hundred hydride platelets were measured on three surfaces. These were plotted as histograms such as shown in Fig. 5.2 for one lot of Zircaloy-2 stressed in the transverse direction. A chart of pole distribution of the hydrides, Fig. 5.3, was constructed from the data on three orthogonal planes. This construction presently requires a trial and error synthesis, but a computer program is being written which will give the pole distribution directly from the trace data.

Although hydride study is still in progress, at least three conclusions may be drawn now. First, the preferred orientation has little if any influence on the orientation of hydride platelets in as-received sheet material, the hydride texture being similar to the orientation of slag inclusions in rolled steels. Second, the hydrides precipitated after plastic deformation tend to align themselves parallel to the tensile strain component and perpendicular to the compressive strain

³R. P. Marshall and M. R. Louthan, Jr., Trans. Am. Soc. Metals 56, 693-700 (1963).

⁴R. P. Marshall, Hydride Orientation and Mechanical Properties of Thin-Walled Zircaloy Tubing, DPST 63-74-8 (Oct. 1963).

⁵P. L. Rittenhouse and M. L. Picklesimer, The Effect of Preferred Orientation and Stress on the Directional Precipitation of Hydrides in Zircaloy-2, ORNL-TM-844 (June 1964).

Fig. 5.2. Histograms Showing Hydride Traces on the Three Surfaces of Schedule 18 Zircaloy-2 for Three Stress Levels.

Fig. 5.3. Hydride Pole Figures for Three Stress Levels in Schedule 18 Zircaloy-2.

component. Finally, hydrides precipitated under an elastic stress redistribute appreciably only when the stress axis is perpendicular to a high concentration of basal planes.

Texture Determination by Hardness Anisotropy in α -Zirconium Alloys

P. L. Rittenhouse M. L. Picklesimer

The engineering design of structural members of α -zirconium alloys requires consideration of the anisotropy of mechanical properties resulting from preferred orientation. Rapid and semiquantitative methods of evaluating anisotropy and determining preferred orientation are needed for examining large numbers of test specimens. A method was developed that uses Knoop microhardness measurements to provide an approximation of the (0001) pole figure, the figure of most importance.

Last year,⁶ we reported studying by Knoop microhardness the anisotropy of five schedules of polycrystalline Zircaloy-2 and the $\{10\bar{1}0\}$, $\{11\bar{2}0\}$, and (0001) planes of a single crystal of Zircaloy-2. We have now collected data on additional polycrystalline material, on four more planes of Zircaloy-2 single crystals, and on ten crystallographic planes of iodide-zirconium single crystals. The hardness results for both the Zircaloy-2 and zirconium single crystals are shown in Fig. 5.4 in terms of the coordinate angles α and β . We define angle β as the angle between the basal plane and the plane of examination and angle α as the angle between the long diagonal of the Knoop indenter and the projection of the basal pole on the plane of examination. The hardness was a function of both crystallographic plane and direction, and for any plane was a minimum when the long diagonal of the indenter was parallel to the projection of the basal pole on that plane (i.e., at $\alpha = 0$). The deformation systems of zirconium and Zircaloy-2 differed significantly on planes within 40° of the basal plane ($0 \leq \beta \leq 40^\circ$). This difference is shown by the decrease in hardness in zirconium but the continued increase in hardness in Zircaloy-2 as the basal plane is approached.

We have developed an empirical method for determining the texture of polycrystalline Zircaloy-2, using the hardness data obtained from the single crystals and from a specific pattern of hardness measurements on the unknown material. Three metallographic specimens of the polycrystalline unknown are prepared with their planes of examination perpendicular to the rolling direction ($\bar{R}$ plane specimens), the transverse direction ($\bar{T}$ plane), and the normal direction ($\bar{N}$ plane) of the fabricated plate. Twelve Knoop microhardness measurements are made on each specimen, three each at successive 45° intervals from one of the fabrication directions (defined in Fig. 5.2) in the surface of the specimen. As in Fig. 5.5, the Knoop hardness number is plotted against the angle θ , which is defined as the angle between the long diagonal of the Knoop indenter and a reference fabrication direction. Then a second angular coordinate, ψ , of the hardness anisotropy is determined

⁶P. L. Rittenhouse, Metals and Ceramics Div. Ann. Progr. Rept. May 31, 1963, ORNL-3470, pp. 56-58.

Fig. 5.4. Microhardness Anisotropy in Single Crystals of Zirconium and Zircaloy-2. See text for definition of direction angles.

Fig. 5.5. Knoop Hardness as a Function of Direction in Zircaloy-2 Fabricated by Two Selected Schedules. The planes of measurement are $\bar{N}$, normal to the normal direction; $\bar{R}$, normal to the rolling direction; and $\bar{T}$, normal to the transverse direction. Angle θ is between the long diagonal of the Knoop indenter and a reference direction.

with the use of a hardness contour map, such as Fig. 5.6, constructed from the single-crystal data. In this figure, hardness contours are plotted against the directional coordinate angles α and β . From a plot of the polycrystalline hardness data, such as Fig. 5.5, the angle θ for the minimum hardness in a plane is located and designated θ_1 . The corresponding ψ_1 is read from the β scale for $\alpha = 0$ at the hardness corresponding to θ_1 . Similarly, ψ_2 , corresponding to $\theta_2 = \theta_1 + 10^\circ$, is read from the hardness at θ_2 and $\alpha = 10^\circ$. This process is repeated for successive 10° intervals, recognizing that θ and $180^\circ - \theta$ are the same. Finally the values of ψ for the different angles are averaged to give $\bar{\psi}$ for the plane.

Fig. 5.6. Hardness Map for a Single Crystal of Zircaloy-2.

The procedure is repeated for each of the three specimens, designating each $\bar{\psi}$ by the appropriate symbol for the plane of examination. The values for $\bar{\psi}_R$, $\bar{\psi}_T$, and $\bar{\psi}_N$ are plotted on a Wulff net, as shown in Fig. 5.7, to define two areas that contain equal numbers of basal poles. The line separating these two areas defines an "average" basal pole figure for the material. Figure 5.8 shows typical results for such measurements for two schedules⁷ of Zircaloy-2 together with x-ray-diffraction pole-figure data, indicating the satisfactory approximation of the method.

An x-ray diffraction value for $\bar{\psi}$ can be determined using quantitative inverse pole-figure data. The values determined by x-ray and the hardness techniques are compared in Table 5.1.

Table 5.1. The Angle $\bar{\psi}$ Determined by X-Ray Diffraction and Knoop Hardness

Schedule ^a	$\bar{\psi}_R$ (deg)		$\bar{\psi}_T$ (deg)		$\bar{\psi}_N$ (deg)	
	X-ray	KHN	X-ray	KHN	X-ray	KHN
9	77	77	73	76	16	15
J	77	73	22	32	48	51
1	71	67	43	46	29	26
8	76	70	70	71	17	17
62	72	70	40	44	26	34

^aSchedules as defined in reference 7.

⁷P. L. Rittenhouse and M. L. Picklesimer, Metallurgy of Zircaloy-2: Part I - The Effects of Fabrication Variables on the Anisotropy of Mechanical Properties, ORNL-2944 (Oct. 13, 1960); Part II - The Effects of Fabrication Variables on the Preferred Orientation and Anisotropy of Strain Behavior, ORNL-2948 (Jan. 11, 1961).

UNCLASSIFIED
ORNL-DWG 64-6111

Fig. 5.7. Plotting the Values of $\bar{\psi}_R$, $\bar{\psi}_T$, and $\bar{\psi}_N$ for Determining the Pole Figure.

UNCLASSIFIED
ORNL-DWG 64-6110

Fig. 5.8. Comparison of Hardness and X-Ray Data Pole Figures for Two Schedules of Zircaloy-2.

The smallest number of hardness measurements consistent with satisfactory texture data is 36; these must be made on a specific pattern on three orthogonal planes.

Determination of Pole Figures by Quantitative Metallography

M. L. Picklesimer P. L. Rittenhouse

The study of preferred orientation and strain anisotropy in α -zirconium alloys as functions of fabrication variables requires pole figures for many of the specimens studied. The effects of stress on the reorientation of embrittling hydrides in Zircaloy-2 can be effectively evaluated only if the pole figures of the hydride plates can be determined. The preferred orientation of grains can be determined by x-ray diffraction, but specimen preparation is quite difficult and expensive in many cases and the procedure is time consuming. The preferred orientation of hydride plates cannot be determined by x-ray diffraction; some other technique must be used.

We have developed a suitable technique for determining approximately both types of pole figures using a polarizing metallurgical microscope and quantitative metallography. The determinations are rapidly and easily performed, requiring metallographic preparation of only three specimens. In many cases, the total required time is 2 to 3 hr.

Two observations led to the development of the technique. First, the hydride platelets generally grouped into sheets or "cornflakes" in the grain boundaries of well-annealed Zircaloy-2 and as thin long plates within the grains of cold-worked Zircaloy-2. Thus, they can be considered, for the present purposes, as thin flat sheets distributed in some pattern in the three-dimensional body of the specimen. Second, the basal plane trace of individual grain of zirconium or Zircaloy-2 can be located in a polarized-light microscope by use of a sensitive tint plate between the specimen and the analyzer disk, since the trace is parallel to the north-south cross hair of the eyepiece just as the color of the grain changes from blue to red on clockwise rotation of the stage.⁸ The angles

⁸S. L. Couling and G. W. Pearsall, Trans. AIME 209, 939 (1957).

between hydride sheet traces (or the basal plane trace) and selected reference directions can be measured by an eyepiece goniometer or the rotating stage. If a preferred orientation of either kind exists in the material, the measurement of several hundred trace angles on each of the three orthogonal surfaces of the specimen material should indicate an angular preference, which in turn should reveal the three-dimensional texture.

Consider the traces a plane cuts on three mutually orthogonal surfaces formed by the three orthogonal reference directions. If the angles between the traces and the reference directions are defined so that different reference directions are used for the three trace angles, the trace angles α , β , and γ are related by the trigonometric relationship

$$\tan \alpha \tan \beta \tan \gamma = 1 \quad .$$

Thus, the selection of values for any two of the trace angles fixes the value for the third.

Since the sheets of hydride platelets are so small that almost none of the sheets cut any two of the specimen surfaces, a statistical approach to the analysis is required. Consider that sheets of precipitate are formed in a specimen such that the individual sheets are small relative to the size of the specimen, but let them have a preferred distribution of orientation in space rather than a random one. Then the measurement of a sufficient number of traces on each of three orthogonal surfaces of the specimen should show a preferred distribution that should enable an approximation of the preferred orientation in space.

Typical results of such measurements are shown in Fig. 5.2, where the histogram-type data have been smoothed into curves. The smoothed histograms represent intensity curves, each point of which is a normalized sum of the poles along a zone of all planes that could form that particular trace on that surface. The pole figure is determined by a trial and error solution by the same method of approximation that is used for the determination of the inverse pole figure from x-ray

diffraction data.⁹ Of course, only an approximate (0001) pole figure is given by the basal plane trace method, but this figure is the important one in evaluating strain anisotropy. Typical pole figures for hydride plates are shown in Fig. 5.3.

The associated equipment required (besides the polarized-light microscope) is an eyepiece goniometer and a rotating stage on the microscope, each coupled to a potentiometer to permit electrical measurement of the angle measured, an x-y recorder, and a stepping potentiometer. The electrical angle signal is fed to the x-axis of the recorder and the stepping potentiometer is used to advance the recorder pen along the y-axis so that several points at the same trace angle do not print on each other. With this equipment, the operator can measure between 600 and 800 trace angles per hour in comparison to less than 200 per day by the more conventional manual technique.

Oxide Film Studies

J. C. Banter

We are determining the optical properties of oxide films formed on zirconium in various corrosion environments to gain information on the oxidation-corrosion mechanisms. Initial experiments have been performed with zirconium foil specimens bearing anodically formed oxide films.

To determine the refractive indices and thicknesses of these films, we developed a new method based on the interference patterns exhibited on transmission of light through the films. The metal was dissolved from the film over a selected area of the specimen, leaving a clear window of the oxide supported by a frame of the remaining metal. The transmission of each film was measured over the spectral range of 2000 to 28,000 Å with a double-beam recording spectrophotometer. The transmitted light exhibits interference maxima at those wavelengths where

$$nT \cos r = m\lambda/2$$

⁹L. K. Jetter, C. J. McHargue, and R. O. Williams, J. Appl. Phys. 27, 368-374 (1956).

and interference minima where

$$nT \cos r = (2m + 1)\lambda/4$$

with n = refractive index of the oxide film at wavelength λ , T = oxide film thickness, r = the angle of refraction into the film, and m = the order of the interference peak. For normally incident light, $\cos r = 1$.

As the angle of incidence of the light is increased, the wavelength of the peak for any given order of interference shifts toward shorter wavelengths. At some angle of incidence, this shift is sufficient to cause the minimum for a given order to coincide in wavelength with the maximum for that same order at normal incidence. Since the order of interference is known, values for nT and $nT \cos r$ can be calculated. Then, both n and T can be calculated using these values and Snell's law,

$$n = \sin i / \sin r \quad ,$$

where i = the angle of incidence of the light. Dividing values of nT determined at other wavelengths by T determined as above, the values of n at the other wavelengths can be determined. Figure 5.9 shows results in the visible and ultraviolet regions of the spectrum for two different oxide films approximately 5500 Å thick.

As an internal check on the method, we calculated the film thicknesses from the values of $nT \cos r$ at the various wavelengths using values of n taken from curves such as those in Fig. 5.9. In all cases, the individual values agreed to within 2%. Thus, the method also provides an accurate measure of the film thickness.

Attempts to apply the same technique to films formed by oxidation of zirconium foil in air and in high-temperature water were not successful due to an intrinsic absorption of visible and ultraviolet light by these films. No interference patterns were exhibited, even for films only 1500 Å thick. Similar measurements in the infrared region of the spectrum should prove more fruitful, as the thermally formed films do not show the intrinsic absorption there. However, this region can be used only for films several tens of thousands of angstroms thick, as thinner films cannot exhibit interference patterns at these wavelengths.

Fig. 5.9. Refractive Index as a Function of Wavelength for Anodized Films on Zirconium Foil.

Preparation of Single Crystals of Zirconium and Zirconium Alloys

J. C. Wilson

A new, rapid, solid-state method for growing single crystals of zirconium and Zircaloy-2 in thin strips was described last year.¹⁰ This year the process has been studied in detail in order to extend the method to thicker sections and reduce the effects of composition variations among different lots of zirconium. In addition, crystals up to 13 mm in diameter and 10 cm long have been produced by zone melting. A paper

¹⁰J. C. Wilson, Metals and Ceramics Div. Ann. Progr. Rept. May 31, 1963, ORNL-3470, pp. 59-60.

summarizing much of the work is to be published soon.¹¹ The following paragraphs describe some of the more important points.

The solid-state-growth method consists of forming a narrow, beta-phase zone (by electron-beam heating) and traversing the zone along the length of the specimen. There are at least three steps in the process: (1) production of a few large beta grains across the width and thickness of the specimen in or near the starting zone; (2) growth of each large beta grain so formed, in the direction of zone travel, by consuming all the alpha grains in its path at the leading alpha-beta interface; and (3) transformation of each large beta grain to a single alpha grain at the trailing alpha-beta interface. Once growth is well started, the moving beta zone consists of a few elongated grains whose boundaries extend the length of the zone (in the general direction of zone travel). Steps 2 and 3 are rather insensitive to experimental parameters or to which lot of a material is used.

Step 1, the production of grains sufficiently large to grow with the moving beta zone, is the most difficult and variable step in the process. The morphology and growth rates of the grains in the original beta zone differ visibly among the six lots of zirconium metal used. The characteristic behavior of each material is altered by zone refining but not by working or heat-treating processes that might affect the texture. Therefore the differences in behavior are probably due to variations in composition. These variations must be small, because the composition of all materials used was well within the limits for reactor-grade-I crystal bar. In general, the initial beta zone must be heated to a temperature (from 1100 to 1500°C) at which grains larger than twice the specimen thickness are formed.

¹¹J. C. Wilson and M. L. Picklesimer, "Variable-Gradient, Electron-Beam Heating Methods for Growing Single Crystals of Zirconium," paper presented at 1964 International Conference on Electron and Ion Beam Science and Technology, Toronto, Canada, May 6-8, 1964, under joint auspices of the Electrochemical Society and AIME (proceedings to be published by John Wiley & Sons, Inc., New York).

Figure 5.10 illustrates the different behavior of three lots of zirconium under identical conditions. In material (c), no elongated grains grew until the specimen was cooled and reheated to a higher temperature (1300°C) and traversed at a slower rate (0.5 cm/hr).

The growth process apparently requires steep temperature gradients; if the surface-to-volume ratio is decreased (as by using a thicker strip), the gradients are made less steep and producing large grains is more difficult. Using higher temperatures, decreasing the zone travel rate, and sometimes cycling through the alpha-beta transformation temperature will often help initiate grain growth. In some material better growth occurs if lateral temperature gradients are superimposed on the predominantly longitudinal gradients normally employed. Multiple, individually controlled electron guns have proved useful for producing arbitrary heating patterns on the specimens. One material has proved particularly sensitive to the direction of temperature gradients; each beta grain elongated in the direction of the maximum local temperature gradient, so by manipulation of the heating pattern, we could cause periodic changes in direction of the boundary between adjacent beta grains. This behavior is tentatively attributed to the "temperature gradient zone melting process" postulated by Pfann.¹²

Two observations suggest that growing large crystals in the alpha phase in zirconium may be practical. Alpha annealing following localized plastic deformation of the temperature-stable structure, material (b), illustrated in Fig. 5.10, produced a grain 5 mm wide in a few hours. Also, during annealing of zone-refined crystals at 830°C, boundary migration rates of the order of 1 mm/hr have been observed.

During zone-refining operations, cylindrical single crystals up to 13 mm in diameter and as long as 10 cm have been produced at rates of 2 cm/hr on the first- or second-zone pass. The yield of large crystals may decrease on subsequent passes, because thin elongated surface grains often form. The crystals that grow from the melt are frequently nucleated

¹²W. G. Pfann, Zone Melting, John Wiley & Sons, New York, 1958.

Fig. 5.10. Solid-State Crystal Growth in Three Different Lots of 1×25 mm Zirconium Strip at a Maximum Temperature of 1200°C and a Zone Travel Rate of 4 cm/hr. "S" and "F" show extent of beta zones at start and finish, respectively. Unetched.

back in the solid starting section of the bar. This suggests that seeding may be possible. The composition of the material used apparently has little effect on crystal growth by zone melting.

Crystals produced by both the solid-state and zone-melting methods generally show diffuse or streaked Laue diffraction spots. Annealing at 830°C for periods of 10 to 100 hr usually produces sharp spots. Apparently, crystals with the basal plane parallel to the rod axis (or the basal plane parallel to the face of strip specimens) tend to show a higher degree of as-grown perfection than do other orientations.

Zone Refining of Zirconium

J. C. Wilson

We purified several pounds of crystal-bar zirconium by floating-zone refining with an electron-beam heat source. Although a crude apparatus designed for 6-mm rods was used, stable zones were produced in rods as large as 13 mm in diameter. The vacuum system blanks off below 10^{-8} torr, but there are signs of occasional contamination with carbon and possibly oxygen. A bakeable ion-pumped system is being assembled to reduce contamination during future refining.

Purification achieved in 4 passes (at 3 cm/hr) of a 7-mm bar 20 cm long may be judged from the analyses in Table 5.2 and the fact that, of the 18 elements sought in the region 3 cm from the head of the bar, all were below either 10 ppm or a detection limit of 20 ppm. In later batches, more careful operation of the system reduced the pickup of carbon so it was not discernible at the 20-ppm level.

Resistivity ratios ($\rho_{300^\circ\text{K}}/\rho_{4.2^\circ\text{K}}$) as high as 450 have been measured. After a few passes the ratio is usually above 300 over one-third to one-half the bar. The measurements were made on an unannealed specimen by D. S. Easton of the Theory of Alloying Group. The highest resistivity ratios were invariably found toward the tail of the bars, as has been observed by others.¹³ This fact, the oxygen distribution from analyses,

¹³J. P. Langeron, Compt. Rend. 256, 5570 (1963).

Table 5.2. Composition of Zirconium Bar Before and After Zone Refining

Impurity	Position in Bar	Initial Concentration (ppm)	After Zone Refining (ppm)
Oxygen	Head	5	32
Oxygen	Tail	5	10
Hafnium	Tail	95	80
Nitrogen	Total		< 1
Hydrogen	Total		< 1
Carbon	Total	20	60

and the observation that vacuum annealing invariably lowers the resistivity ratio in zirconium¹⁴ suggest that oxygen is primarily responsible for the low ratios observed in the past.

One difficulty in zone refining zirconium stems from the anisotropy of thermal expansion in the alpha phase and perhaps from some kinking at the trailing alpha-beta interface. Under certain conditions the bar becomes skewed with respect to its original axis. The electron gun has a large central aperture, so that a large amount of misalignment can be tolerated. The electron beam is focused to a width much less than a millimeter at the specimen in order to maximize the superheat for volatilization of impurities. Others who have zone refined zirconium with induction heating^{15,16} have usually found some collection of iron and nickel in the tail. Since the iron and nickel contents in the tails of our ingots are about the same as in the original bar, the intense heating is apparently effective. Also, increased stirring of the melt probably results from the superheat.

¹⁴D. S. Easton, ORNL, personal communication.

¹⁵G. D. Kneip, Jr. and J. O. Betterton, Jr., J. Electrochem. Soc. 103, 684 (1956).

¹⁶J. P. Langeron et al., Compt. Rend. 248, 35 (1959).

The gun configuration has allowed crystal-bar material to be zone melted directly. Figure 5.11 shows that as-deposited zirconium and titanium can be zone melted without difficulty in spite of variations in diameter and shape. Direct melting without the usual prior machining or mechanical working to a cylinder is much more economical of material and time. The large grains produced in the titanium bar suggest that single crystals can be grown as easily as in zirconium.

UNCLASSIFIED
Y-55696

Fig. 5.11. Tails of Zone-Refined As-Deposited Crystal-Bar Zirconium and Titanium. (a) Zirconium after nine passes showing typical offsetting that occurs in multipass specimens. (b) Titanium bar after one and two passes; the right section is the as-deposited crystal bar; the center sections received one zone pass, and the left section received two passes.

PART II.

SOLID STATE DIVISION

6. IRRADIATION EFFECTS ON ALLOYS AND STRUCTURAL MATERIALS

M. S. Wechsler

The research of the Radiation Metallurgy Section of the Solid State Division at ORNL is directed toward the problem of the radiation embrittlement of metals and alloys. The mechanical properties of structural alloys depend in large measure on the relative atomic arrangement of the various alloying constituents. One aspect of the change in properties upon irradiation involves a rearrangement of the positions of the alloying atoms, thus forming structures not found at the same temperatures in unirradiated alloys. A practical case where such atomic rearrangements may be particularly important is that of austenitic stainless steels. Here the alloy is in a metastable state before irradiation. Upon irradiation, this metastability may be eliminated with an accompanying deterioration of mechanical properties.

The effect of irradiation on diffusion-controlled processes is being studied theoretically and experimentally. A discussion is given below of recent developments in the theory of the kinetics of radiation-enhanced diffusion. The theory is applied to radiation-enhanced ordering in Cu-Al alloys. In addition, the results of recent irradiation experiments on Cu-15 at. % Al are described. It has been found that the rate of radiation-enhanced ordering in this alloy is decreased by prior cold working. This is interpreted to indicate that the cold working introduces sinks for radiation-produced defects, thus decreasing the effectiveness of each defect in facilitating the ordering reaction.

Another type of diffusion-controlled process is the segregation or clustering of solute atoms in alloys. Segregation in alloys is exemplified by the Cu-Ni system and the effect of irradiation in accelerating segregation has been investigated. In this case, the experiments were performed by the isochronal annealing of samples that were given prior irradiation or quenching treatments.

It is of interest to extend the experiments on the face-centered cubic copper-base alloys to alloy systems that exhibit the body-centered cubic structure. This will serve to test the generality of the earlier observations. Furthermore, the results on body-centered cubic alloys

will have a greater bearing on the important problem of radiation-embrittlement in low-carbon pressure vessel steels. For these reasons, an investigation of Fe-Si alloys has been initiated and some preliminary resistivity measurements are described below.

Still another type of diffusion-controlled process of considerable significance in connection with mechanical properties is the precipitation reaction. For steels, the precipitation of nitrogen is particularly important. This is being studied by means of low-frequency internal friction and a special device has been developed that enables measurements to be made during reactor irradiation. It is found that the loss of nitrogen from solid solution in alpha-iron is accelerated by irradiation.

In addition to the work on radiation-induced atomic rearrangements, research is under way on the direct effect of radiation on flow and fracture properties. From the more basic point of view, the techniques of etch pitting and electron microscopy are being used to study dislocation arrangements and mobility in iron and iron alloys. This is a relatively new effort and no observations have been made as yet on irradiated samples.

The effect of neutron irradiation on the tensile properties of iron and steel is also being investigated. The long-range objective of this phase of the work is a determination of the specific influence of the dose rate. This has a bearing on the use of structural materials in reactor environments because of the fact that the materials-testing irradiations are conducted at high fluxes for relatively short periods of time, whereas structural materials in service are expected to receive comparable doses at low fluxes over much longer periods of time. A careful study of this aspect of radiation effects is laborious and lengthy, but the first in a series of irradiations in the ORR directed toward this problem is under way.

Finally, there are the investigations of the impact properties of commercial steels. This work is closely coordinated with that dealing with tensile properties because of the close connection between plastic deformation and fracture in metals. The present series of irradiations is devoted largely to synthetic heat-affected-zone samples. Earlier experiments have indicated that, despite the higher initial ductile-brittle

transition temperature in the heat-affected zone material, the increase in transition temperature upon irradiation at about 50°C (120°F) is roughly the same as for the baseplate material. These experiments are now being extended to elevated-temperature irradiations.

It should be mentioned in conclusion that new facilities are being designed for conducting irradiations in the BSR. These include a neutron converter for fission-spectrum irradiations and a cryostat for performing irradiations at liquid nitrogen temperature.

Kinetics of Radiation-Enhanced Diffusion in Cu-Al

J. H. Barrett

Because interstitials and vacancies are produced in equal numbers during irradiation, either one might produce radiation enhancement of diffusion. Experimental results for the temperature dependence of radiation-enhanced diffusion effects in the Cu-15 at. % Al alloy have been analyzed^{1,2} on the basis of diffusion enhancement due to vacancy motion and on the basis of diffusion enhancement due to interstitial motion. This analysis did not yield a clear-cut decision as to which defect is active in enhancing diffusion though it did suggest that the active defect is the interstitial. In order to develop other means for distinguishing which defect is the active one, the kinetics of some of the experiments have been analyzed. To perform this analysis, it was assumed that the electrical resistivity is some function of the short-range order of the alloy and that the short-range order is some function of J , the number of defect jumps per lattice site in the alloy. These two assumptions lead to the form $\rho = \rho(J)$ for the resistivity. The time dependence of J can be computed for various assumed experimental conditions. Using these expressions for $J(t)$, the relative kinetics of different experimental runs can be compared.

¹M. S. Wechsler et al., Solid State Div. Ann. Progr. Rept. Aug. 31, 1962, ORNL-3364, pp. 127-134; J. M. Williams et al., Solid State Div. Ann. Progr. Rept. May 31, 1963, ORNL-3480, pp. 135-142

²J. H. Barrett and E. J. Lee, Solid State Div. Ann. Progr. Rept. May 31, 1964, ORNL-3676 (in press).

By using methods reported previously,¹ it is possible to deduce the form of $J(t)$ in certain cases. If vacancies are the diffusion-enhancing defects, J varies as $t^{3/2}$ for first runs and J varies as t for second runs. First runs are experiments on previously unirradiated samples; second runs are experiments on samples irradiated for a week or more with a subsequent anneal at 210°C. If interstitials are the diffusion enhancing defects, J varies as t for both first and second runs. Figure 6.1 shows experimental first- and second-run curves³ for a sample. The second run curve is also shown translated to the left along the $\log t$ scale until it coincides with the first-run curve at $f = 0.5$; this corresponds to the assumption that J is proportional to the same power of t for both runs. In addition, the second-run curve is shown translated on the $\log t$ scale to coincide with the first-run curve at $f = 0.5$ followed by a compression of the $\log t$ scale by a factor of $2/3$; this corresponds to the assumption that J varies as $t^{3/2}$ for the first run and J varies as t for the second run. The curves in Fig. 6.1 strongly indicate that the first and second runs have the same dependence of J on t . This result points to the conclusion that the interstitial is the diffusion-enhancing defect during irradiation of Cu-Al.

Another experiment for which an analysis of the kinetics was found to be informative was an interrupted irradiation.⁴ Figure 6.2 shows the results of this experiment. The curve up to the time of withdrawal from the reactor and after reinsertion in the reactor was drawn through the experimental points. The method used to estimate the behavior of the resistivity during the interruption of the irradiation required knowledge of the behavior that would have occurred if the irradiation had not been interrupted. The experimental curve suggested that the decrease of resistivity after the specimen was reinserted in the reactor was a resumption of the decrease that was occurring when the irradiation

³Curves 1 and 2 of Fig. 6.1 are the same as runs 4-I and 4-II of Fig. 18.5 of the first report cited in Ref. 1.

⁴M. S. Wechsler et al., Solid State Div. Ann. Progr. Rept. Aug. 31, 1959, ORNL-2829, pp. 110-118, Fig. 72.

Fig. 6.1. Fractional Departure from Completion of the Decrease in Electrical Resistivity of Cu-15 at. % Al vs Time of Irradiation at 100°C for First and Second Runs at Position 4, Hole C, of the ORNL Graphite Reactor. Experimental points have been left off the curves.

Fig. 6.2. Change of Electrical Resistivity of Cu-15 at. % Al vs Time for Interrupted Irradiation at 45°C in Hole 52 of the ORNL Graphite Reactor.

was interrupted. It was estimated from the experimental curve that the decrease which occurred during the period of interruption was equal to the decrease that would have occurred during an uninterrupted 180-min irradiation. An "uninterrupted" time scale was constructed by treating the total time of the interruption as the equivalent of 180 min. In Fig. 6.2 the experimental values obtained after resumption of irradiation are replotted on this uninterrupted time scale. By ignoring the transient behavior, curve 1 was drawn through the experimental points on the uninterrupted time scale.

The variation with time of the defect concentration after withdrawal of the sample to the edge of the reactor can be predicted by methods reported previously.¹ The accumulated number of jumps J for each type of defect was computed from the concentration of that defect. From such a computed value of $J(t)$, the equivalent time that would have produced the same $J(t)$ during an uninterrupted irradiation was calculated. From this equivalent time value and the uninterrupted irradiation curve, the value of the resistivity was obtained. In this way curves were constructed to describe the behavior of $\rho(t)$ following withdrawal of the sample to the edge of the reactor. Four curves are drawn; two assume the diffusion-enhancing defect to be the interstitial and two assume it to be the vacancy.

If the interstitial is the active defect, the kinetics may be described by simple interstitial-vacancy recombination, for which the concentration of interstitials is $(K/\gamma\nu_i)^{1/2}$ before interruption of the irradiation. After interruption, the interstitial concentration decays with second-order kinetics, so that the concentration is given by

$$i = \frac{(K/\gamma\nu_i)^{1/2}}{1 + (t - t_I)/\tau_1} \quad ,$$

where t_I is the time of interruption, $\tau_1 = (K\gamma\nu_i)^{-1/2}$, K is the displacement production rate per atomic site, γ is a dimensionless constant that is a measure of the capture radius for the annihilation of an interstitial at a vacancy, and $\nu_i = \nu_{oi} \exp(-M_i/kT)$ is the interstitial jump rate. Curve 2 of Fig. 6.2 was constructed for $\tau_1 = 50$ min;

it is seen to give a good fit to the experimental points. However, from the parameters already determined by analysis² of the temperature dependence of the enhanced diffusion effects ($K = 10^{-10} \text{ sec}^{-1}$, $\gamma = 25$, $\nu_{oi} = 10^{14} \text{ sec}^{-1}$, and $M_i = 0.82 \text{ ev}$), the value calculated for τ_1 is 105 min. Curve 3 was constructed using this value. The various parameters that are inserted into the theory² can be adjusted so as to give a value of 50 min for τ_1 and still retain good agreement with the experiments on the temperature dependence. For instance, this could be done by changing ν_{oi} from 10^{14} to $4.4 \times 10^{14} \text{ sec}^{-1}$ with appropriate changes in other parameters involved in the theory of the temperature dependence. The fit of the theory to the experimental temperature dependence would be affected only slightly. Since the parameters put into the theory were somewhat arbitrarily chosen in the first place, such alterations are not out of the question.

If the vacancy is the active defect, its concentration is $(2K\beta t)^{1/2}$ before interruption of the irradiation and is $(2K\beta t_I)^{1/2} \exp(-t/\tau_2)$ after the interruption, where $\tau_2 = (\beta\nu_v)^{-1}$, β is approximately the concentration of fixed sinks, and $\nu_v = \nu_{ov} \exp(-M_v/kT)$. From the parameters determined by analysis² of the temperature dependence of enhanced diffusion ($K = 10^{-10} \text{ sec}^{-1}$, $\beta = 2 \times 10^{-7}$, $\nu_{ov} = 10^{14} \text{ sec}^{-1}$, and $M_v = 0.78 \text{ ev}$), a value of 1920 min was calculated for τ_2 . Curve 4 was constructed using this value. Curve 5 was constructed using $\tau_2 = \infty$. Up to times reaching a considerable fraction of τ_2 , the behavior of the curves is independent of τ_2 . In order to obtain agreement with the experimental points, τ_2 should have a value of approximately 100 min. This value could be achieved by changing ν_{ov} from 10^{14} to $2 \times 10^{15} \text{ sec}^{-1}$ and readjusting some of the other parameters. However, the resulting agreement between theory and experiment for the temperature dependence probably would not be so good as that previously obtained,² particularly for the second runs.

It is to be concluded that the transient behavior shown in Fig. 6.2 following interruption of the irradiation can be better described by theory if the interstitial, rather than the vacancy, is assumed to be the active defect. This is in accord with the conclusion reached by comparison of the relative kinetics of the curves in Fig. 6.1. This is also in accord with the better agreement² of experiment and theory for the temperature dependence when the interstitial is assumed as the active defect.

Effect of Deformation upon Neutron Radiation-Enhanced
Diffusion in Cu-Al Alloys

J. M. Williams M. S. Wechsler B. C. Kelley

Neutron irradiation of alpha-Cu-Al alloys at temperatures of 0 to 210°C produces a decrease in the electrical resistivity which is attributable to an increase in short-range order.⁵⁻⁸ The radiation-produced point defects enhance diffusion with the result that the alloy can achieve its equilibrium degree of order at lower temperatures than would otherwise be possible. The resistivity decrease saturates as the equilibrium ordered state is approached. The magnitude of the resistivity decrease depends on the initial preparation of the samples and the irradiation temperature. For slow-cooled single crystals irradiated at 100°C, the magnitude of the change is 0.16 $\mu\text{ohm-cm}$.

The rate of the ordering reaction is a measure of the radiation-enhanced diffusivity, which in general depends upon the temperature and the neutron flux. The analysis of the temperature and flux dependence of the radiation-enhanced ordering rate in terms of the theory of radiation-enhanced diffusion gives information as to the mechanism of annihilation of the point defects.^{9,10} In well-annealed single crystals, the vacancies and interstitials disappear predominantly by mutual annihilation. However, the introduction of large numbers of point defect

⁵M. S. Wechsler and R. H. Kernohan, "The Effect of Radiation on Diffusion-Controlled Reactions in Copper Base Alloys," p. 81 in Radiation Damage in Solids, Vol. II, International Atomic Energy Agency, Vienna, 1962.

⁶M. S. Wechsler, "Fundamental Aspects of Radiation Effects on Diffusion-Controlled Reactions in Alloys," p. 86 in Radiation Effects on Metals and Neutron Dosimetry, American Society for Testing and Materials, Philadelphia, 1962.

⁷C. R. Houska and B. L. Averbach, J. Appl. Phys. **30**, 1525 (1959).

⁸B. S. Borie and C. J. Sparks, Metals and Ceramics Div. Ann. Progr. Rept. May 31, 1962, ORNL-3313, pp. 204-206; "The Short-Range Structure of the Alloy Cu-16 at. % Al," submitted to Acta Crystallographica.

⁹J. H. Barrett, Jr., Bull. Am. Phys. Soc. **9**, 284 (1964).

¹⁰J. M. Williams et al., Solid State Div. Ann. Progr. Rept. May 31, 1963, ORNL-3480, pp. 135-142.

sinks, such as dislocations, would be expected to change the removal mechanism to fixed sink annihilation, concomitantly reducing the number of jumps necessary for removal of each radiation-produced defect. Thus, the rate of radiation-enhanced ordering should be reduced in samples subjected to deformation prior to irradiation.

The experimental plan for this investigation was based on the following prospective behavior of the deformed samples. The cold work was expected to produce dislocations and point defects and to disturb the state of short-range order. It has been stated in previous reports^{10,11} that a heat treatment of 2 hr at 750°C followed by cooling at 15°C/hr to room temperature results in a state of short-range order characteristic of 210°C. Therefore, aging of the cold-worked samples at 210°C should restore them to about the same state of order as that for annealed, slow-cooled samples. This temperature is high enough to allow annealing of point defects also, but too low to permit removal of dislocations.

Single-crystal rods about 6 in. long and 0.049, 0.057, 0.060, 0.064, and 0.074 in. in diameter were grown from the melt. The specimens were annealed 2 hr at 750°C and cooled at 15°C/hr to room temperature. Their resistivities were measured at liquid nitrogen temperature (-196°C) with the sample in a knife-edge sample holder. Then the four samples of diameters 0.057, 0.060, 0.064, and 0.074 in. were cold worked to a common diameter of 0.050 in. by drawing them through a succession of dies, each die 0.003 in. smaller than the previous one. The samples were drawn at room temperature at a speed of 2 in./min. The 0.049-in.-diam sample was not cold worked at all. This procedure resulted in the preparation of five samples of about 0.050-in. diam, each with a different amount of cold work. The degree of cold work ranged from 0 to 54% reduction in area (RA) for the five samples. Following the cold working, the resistivities were again measured at -196°C by use of the knife-edge sample holder. A 2 1/2-in. length of each of the specimens was then mounted in a reactor irradiation capsule and was suitably wired for measurement of the resistivity. The capsule was immersed in liquid

¹¹J. M. Williams et al., Solid State Div. Ann. Progr. Rept. Aug. 31, 1962, ORNL-3364, pp. 129-134.

nitrogen, and the resistivities of the specimens were again determined. The results, shown in Fig. 6.3, agreed within 1% with the measurements made in the knife-edge sample holder. This is within the accuracy of the gage length determination for the samples mounted in the capsule. Figure 6.3 shows that the highest degree of cold working caused an increase in the resistivity from 8 to 10 $\mu\text{ohm-cm}$ or about 25%.

Fig. 6.3. Resistivity vs Percent Reduction in Area at Room Temperature for Cu-15 at. % Al, Before and After Aging at 210°C.

In order to restore the degree of order characteristic of 210°C, as discussed above, the capsule was then placed in a furnace and the samples were aged 25 hr at 210°C. The results of the measurements following this aging treatment are also shown in Fig. 6.3. It is seen that the resistivity remaining after aging at 210°C was only 10% greater than the annealed value for the most heavily deformed sample.

For the irradiation, a heater was placed in the capsule, and the entire assembly was placed in hole C of the ORNL Graphite Reactor. The resistivities were measured as a function of irradiation time at 100°C. Figure 6.4 shows the change in resistivity plotted vs the logarithm of the irradiation time for the five specimens. The undeformed single crystal exhibits the rather rapid approach to equilibrium that we previously observed at this temperature and flux level.⁵ The rate of the decrease for the deformed specimens, however, is markedly reduced. The time for a given amount of resistivity change for the sample of 23% RA is greater than that for the undeformed specimen by a factor of about

Fig. 6.4. Change in Resistivity vs Irradiation Time at 100°C for Cu-15 at. % Al Cold Worked to Various Reductions in Area and Aged at 210°C; Irradiated in Hole C of the ORNL Graphite Reactor.

400; for the sample of 31% RA, as compared to the undeformed sample, this factor is about 2000. The two specimens that were most severely deformed (40, 54% RA) showed essentially no changes in resistivity.

The large reduction in the rate of the resistivity decrease for the cold-worked specimens results from the annihilation of defects at the dislocations produced by the cold working. The dislocation density for the 23% RA specimen may be calculated under the assumption that the fixed sink mechanism predominates. For this mechanism at steady state the concentration of either vacancies or interstitials is¹⁰

$$c = \frac{K}{\alpha \lambda^2 \nu},$$

where K is the defect production rate, α is the dislocation density, λ is the defect jump distance, and ν is the defect jump rate. The cumulative number of defect jumps after irradiation time t is then given by

$$J(t) = c \nu t = \frac{K}{\alpha \lambda^2} t. \quad (1)$$

For the reactor location used, the value of K has been determined as $10^{-10} \text{ sec}^{-1}$ in previous reports,^{6,11} and the value of λ^2 is about 10^{-15} cm^2 . Unfortunately, due to the permanent shutdown of the ORNL Graphite Reactor, it was not possible to obtain the saturation values of the resistivity decreases for the cold-worked samples. However, let us assume that the saturation resistivity decrease would have been the same as that for the undeformed sample. Then from Fig. 6.4, the time for half completion for the 23% RA sample is $t = 2 \times 10^4 \text{ min} = 1 \times 10^6 \text{ sec}$. Then, letting $J = 1$ for the number of defect jumps per atom for half completion,¹⁰ we deduce from Eq. (1) a dislocation density of 10^{11} cm^{-2} . This would appear to be a reasonable value for a fairly heavily cold-worked sample.

Annealing of Cu-Ni Alloys Following Neutron Irradiation,
Quenching, and Deformation

W. Schüle¹² M. S. Wechsler
B. C. Kelley J. M. Williams

It has been shown by means of magnetic susceptibility measurements that neutron irradiation of Cu-Ni alloys stimulates segregation of the components.¹³ Furthermore, the segregation is accompanied by a decrease in the electrical resistivity.¹⁴ In order to better understand the mechanism for this effect, it was decided to investigate the annealing behavior of some Cu-Ni alloys after irradiation, quenching, and deformation treatments. The changes in resistivity upon isochronal annealing were measured for several samples, each of which had been subjected to one of the following treatments: (1) neutron irradiation at -180°C , (2) quenching from 600, 850, and 1050°C , (3) quenching from 600°C and irradiation at -180°C , and (4) deformation at below -100°C .

¹²Present address: CCR - Euratom, Ispra (Varese), Italy.

¹³F. M. Ryan, E. W. Pugh, and R. Smoluchowski, Phys. Rev. **116**, 1106 (1959).

¹⁴A. Ascoli, "Neutron-Bombardment-Enhanced Segregation in Cu-Ni Alloys," p. 105 in Radiation Damage in Solids, Vol. II, International Atomic Energy Agency, Vienna, 1962.

A number of foil resistivity specimens were prepared from Cu-Ni alloys ranging in composition from 25 to 65 wt % Cu. They were annealed 3 hr at 850°C in vacuo and slow cooled at 22°C/hr to room temperature. One of the specimens was selected as a standard specimen and its resistance was determined at liquid nitrogen temperature (-196°C) with a Rubicon six-dial microvolt potentiometer. Thereafter, the resistances of the other specimens were measured at liquid nitrogen temperature by comparison with this standard sample by use of a Kelvin bridge.

Part of the samples were placed in the hole 50 cryostat of the ORNL Graphite Reactor and irradiated three weeks at -180°C. The samples were then removed and held at -196°C until the radioactivity had decayed to such a low level that the isochronal annealing could be carried out in the laboratory.

Figure 6.5 shows the isochronal annealing curves for increasing temperatures for the four alloy compositions studied. The change in resistivity is taken with respect to the slow-cooled or preirradiation value. The points for -196°C in Fig. 6.5 indicate that little change in resistivity was produced as a result of the irradiation at -180°C. However, we see that upon isochronal annealing a decrease in resistivity occurs which starts gradually at -50°C and reaches a minimum at 250 to 300°C. Thereupon, the resistivity increases again and eventually exceeds the preirradiation value. For unirradiated samples given the same annealing treatment, no decrease in resistivity was observed for the Ni-55 wt % Cu and Ni-65 wt % Cu samples, and only a slight decrease was observed for the Ni-40 wt % Cu sample (Fig. 6.6). The decrease in resistivity upon isochronal annealing following irradiation at -180°C (Fig. 6.5) is believed to be due to enhanced segregation of the nickel and copper which takes place when the radiation-produced defects become mobile.

Since the largest decrease in resistivity was observed for Ni-40 wt % Cu alloy (Fig. 6.5), this composition was selected for further study. Figure 6.7 shows the isochronal annealing curve for Ni-40 wt % Cu upon increasing the temperature to 580°C and then decreasing to 250°C.

Fig. 6.5. Change in Resistivity of Cu-Ni Alloys upon Isochronal Annealing after 3 Weeks Irradiation at -180°C . Measurements at -196°C .

Fig. 6.6. Change in Resistivity upon Isochronal Annealing of Slowly Cooled Cu-Ni Alloys. Measurements at -196°C .

Fig. 6.7. Change in Resistivity upon Isochronal Annealing of Ni-40 wt % Cu Alloys Previously Irradiated 3 Weeks at -180°C . Measurements at -196°C .

We note that upon decreasing the temperature the original resistivity is recovered at about 350°C. This indicates that the freezing-in temperature, below which no change in the state of segregation takes place upon cooling in the unirradiated alloy, is about 350°C. At temperatures above 350°C the vacancies in thermal equilibrium are in sufficient concentration to produce the equilibrium state of segregation in reasonable times.

For the quenching experiments, a sample was suspended in a vertical vacuum furnace at the desired quenching temperature and then dropped into a vessel of diffusion pump oil contained at room temperature within the vacuum system. Figure 6.8 shows the isochronal annealing curves for Ni-40 wt % Cu samples quenched from 600, 850, and 1050°C. The curves for a slow-cooled sample and a sample irradiated at -180°C are also shown for comparison. The excess resistivity (about 2 $\mu\text{ohm-cm}$) retained upon quenching is attributed to the quenching-in of the more random state characteristic of the higher temperatures. As can be seen in Fig. 6.8, an increase in the quenching temperature in the range 600 to 1050°C produces a decrease in the quenched-in resistivity. This behavior has been noted previously for Cu-Al alloys¹⁵ and is presumably due to greater defect mobility during the quench for the higher quenching temperatures. In the isochronal annealing curves, the decrease in resistivity for the quenched samples in Fig. 6.8 starts at a higher temperature (about 150°C) than for the irradiated sample (about -100°C). This is an indication that the defect whose motion produces the segregation after quenching is not the same one responsible for the segregation after low-temperature irradiation.

In another experiment on Ni-40 wt % Cu, the combined effects of quenching and irradiation were studied. A sample was quenched from 600°C and then irradiated for 3 weeks at -180°C. The resulting isochronal annealing curve is shown in Fig. 6.9, where the curves from previous figures are also shown for comparison. The annealing behavior in the lower range of temperatures (-100 to 200°C) is very similar to that for

¹⁵M. S. Wechsler and R. H. Kernohan, Acta Met. 7, 599 (1959).

Fig. 6.8. Change in Resistivity upon Isochronal Annealing of Ni-40 wt % Cu Following Quenching from 600, 850, and 1060 $^{\circ}\text{C}$. Curves for a sample irradiated at -180°C and a slow-cooled sample are also shown for comparison. Measurements at -196°C .

Fig. 6.9. Change in Resistivity upon Isochronal Annealing of Ni-40 wt % Cu Following Quenching from 600 $^{\circ}\text{C}$ plus Irradiation at -180°C . Curves following other treatments are shown for comparison. Measurements at -196°C .

the sample that was only irradiated. This suggests that segregation occurs in the quenched-plus-irradiated sample in this temperature range by the same mechanism as in the sample that was only irradiated. If this mechanism were interstitialcy diffusion due to radiation-produced interstitials, it is difficult to understand why the interstitials in the quenched-plus-irradiated sample did not recombine with the vacancies quenched from 600°C and thereby cause a different annealing behavior than for the irradiated-only sample. It may be that the segregation in irradiated samples is due to enhanced nucleation of the segregation process at damage clusters produced by the irradiation. In this case, quenched vacancies would have little effect. This idea will be tested by doing low-temperature electron irradiations, where no damage clusters are created.

Finally, in Fig. 6.10 the isochronal annealing curve for a sample cold worked below -100°C is compared with the previous curves. For the deformation, a 0.016-in. foil of Ni-40 wt % Cu was cooled in liquid nitrogen, passed through a rolling mill whose rolls had been cooled with dry ice, and immediately immersed again in liquid nitrogen. Several such passes were made until the final thickness was 0.008 in. Then a resistivity sample was cut from the foil while it was immersed in liquid nitrogen. The resulting isochronal annealing curve (Fig. 6.10) is quite broad and complicated, and no analysis of it is attempted at this time.

Resistivity Measurements in Fe-3.7 wt % Si Alloys

J. M. Williams M. S. Wechsler

The common feature of the Cu-Al and Cu-Ni work described above is that the irradiation accelerates the rate at which the alloys can be equilibrated at lower temperatures. It is a matter of both fundamental and practical interest to determine whether or not such effects take place in body-centered cubic metals, particularly iron and its alloys. Accordingly, a study of dilute Fe-Si alloys has been undertaken. The studies made thus far consist of laboratory resistivity measurements in preparation for irradiation experiments. Measurements of the resistivity as a function of temperature from -196 to 1050°C have been made for an

Fig. 6.10. Change in Resistivity upon Isochronal Annealing Following Various Cold-Working, Quenching, and Irradiation Treatments for Ni-40 wt % Cu. Measurements at -196°C .

Fe-3.7 wt % Si alloy. Also, the change in resistivity upon quenching from temperatures up to 850°C has been investigated.

A number of resistivity samples with 1-in.-gage lengths were cut from a 0.008-in.-thick foil of Fe-3.7 wt % Si. The samples were annealed 2 hr at 1000°C and cooled at 50°C/hr to 400°C followed by a 25°C/hr cool to room temperature.

For the at-temperature measurements, a sample was mounted in a Lavite holder with thermocouples spot-welded to the ends of the sample just outside the potential probes. The resistance was first measured at liquid nitrogen temperature. Then the sample was placed in a vacuum furnace, and the resistivity was measured as a function of temperature up to 850°C (run A, Fig. 6.11). At this point, the temperature controller failed, and the sample was cooled to room temperature. After the controller was repaired, a new curve was obtained, which extended to 1050°C (run B, Fig. 6.11). The two curves showed roughly the same behavior, but

Fig. 6.11. Resistivity as a Function of Temperature for Iron and Fe-3.7 wt % Si.

they did not superimpose. Some earlier results for iron^{16,17} are also shown in Fig. 6.11.

For the quenching experiments, the samples were suspended in a vertical vacuum furnace for 1 hr at the quenching temperature. Two quenching media were used - iced brine and diffusion pump oil. For the quenches into iced brine, the vacuum chamber was filled with helium, the bottom of the vacuum tube was opened, and the sample was dropped into a container filled with iced brine. For the quenches into diffusion pump oil, the oil was contained within the vacuum chamber and the sample was quenched without interrupting the vacuum.

The results of the quenching experiments are shown in Fig. 6.12. The results of the iced-brine quenches were less reproducible than those for the oil quenches, as can be seen by the erratic behavior near 800°C and the lack of reversibility upon reducing the quenching temperature. The higher resistivity values upon decreasing the temperature are attributed

¹⁶P. R. Pallister, J. Iron Steel Inst. (London) 161, 87 (1949).

¹⁷N. G. Bäcklund, J. Phys. Chem. Solids 20, 1 (1961).

Fig. 6.12. Change in Resistivity vs Quenching Temperature for Fe-3.7 wt % Si. Measurements at -196°C .

to a coating of oxide, which was more severe for the iced-brine quenches than for the oil quenches. However, for both types of quenches there is a decided decrease in the resistivity upon quenching from above 400°C , which suggests a rearrangement of the iron and silicon atoms. Experiments will be performed to see if this rearrangement is enhanced by irradiation.

In-Reactor Internal Friction Measurements of Interstitial Rearrangements in Body-Centered Cubic Metals

J. T. Stanley W. E. Brundage

Recent research has stressed the critical importance of interstitial impurities in the body-centered cubic metals. In particular, the concentration and distribution of nitrogen in pressure vessel steels are thought to have a significant effect on the mechanical properties of these alloys. For example, it has been pointed out^{18,19} that the creep resistance of steels is markedly affected by the concentration of nitrogen in solid solution; the higher the nitrogen concentration in

¹⁸J. M. Robertson and R. W. Nichols, "High-Temperature Mechanical Properties of Steels Used in Gas-Cooled Reactor Pressure Vessels," p. 14 in Steels for Reactor Pressure Circuits, Special Report No. 69, The Iron and Steel Institute, London, 1961.

¹⁹J. Glen and J. D. Murray, "Metallurgical Aspects of Creep in Carbon- and Low-Alloy Steels," p. 40 in Steels for Reactor Pressure Circuits, Special Report No. 69, The Iron and Steel Institute, London, 1961.

solid solution, the better the creep resistance. Furthermore, the poorer creep resistance of aluminum-killed steels as compared to silicon-killed steels may be associated with the reduction in the nitrogen in solid solution due to the formation of aluminum nitride. In certain reactor applications, this factor may be important in connection with reactor pressure vessels, since the better notch ductility of the aluminum-killed steels is offset by the poorer creep resistance. The nitrogen in steel may also be responsible for the different effects of irradiation on the aluminum- and silicon-killed steels. For example, Nichols and Harries²⁰ have found that the increase in yield stress upon irradiation reaches a peak as a function of irradiation temperature for the aluminum-killed but not for the silicon-killed steels. It has been suggested²¹ that the dependence on irradiation temperature is possibly due to free vacancies produced by the irradiation. More free vacancies are perhaps present in the aluminum-killed steels because the nitrogen is tied to aluminum as aluminum nitride and therefore is not available for trapping vacancies.

The study of the effect of neutron irradiation on the precipitation of carbon in alpha-iron²² has indicated that the loss of carbon from solid solution after solution annealing and quenching is accelerated by the irradiation. Two mechanisms are suggested for the enhanced loss of carbon from solid solution. Upon warm-up after low-temperature irradiation, during which the radiation-produced defects do not anneal out, the carbon atoms are thought to be trapped by the vacancies produced by the radiation. However, when the irradiation is carried out at ambient temperature (about 60°C), the accelerated loss of carbon is believed to occur as a result of nucleation sites for precipitation provided by the radiation-produced damage clusters.

²⁰R. W. Nichols and D. R. Harries, "Brittle Fracture in Irradiation Effects in Ferritic Pressure Vessel Steels," p. 162 in Radiation Effects on Metals and Neutron Dosimetry, ASTM-STP-341, American Society for Testing and Materials, Philadelphia, 1962.

²¹S. F. Pugh, "Radiation Damage in Alloys," paper presented at the International Summer School on Solid State Physics, Mol, Belgium, Aug. 1963, to be published in the proceedings.

²²H. Wagenblast and A. C. Damask, J. Phys. Chem. Solids 23, 221 (1962).

The above discussion emphasizes the importance of studying the effect of radiation on the arrangement of nitrogen in iron and steel. Perhaps one of the most effective ways to study the rearrangement of interstitial impurities in body-centered metals is by internal friction measurements of the Snoek anelastic relaxation peak, which yield information concerning the amount of the interstitial impurity in solid solution and its mobility. For this reason, a flexure pendulum apparatus was developed (described in a previous report)²³ that enables such measurements to be made during reactor irradiation. The present report presents some results of irradiation of Fe-N alloys that were obtained with the use of the in-pile flexure pendulum. In addition, torsion pendulum measurements on V-N-O alloys made in the laboratory following irradiation are reported.

Aging of the Nitrogen Peak in Fe-N Alloy

Specimens were cut from 0.005-in.-thick Ferrovac E foil which had been cold rolled from 1 1/2-in.-diam bar. The specimens were decarburized by heating in moist hydrogen at 720°C for 72 hr. The decarburized specimens were then heated to 950°C for 1 hr in a dry hydrogen atmosphere and slow cooled (100°C/hr) to 590°C to obtain a large grain size. The specimens were nitrided at 590°C in an atmosphere of ammonia and hydrogen gas. The gas mixture was adjusted to produce a nitrogen content of about 0.015 wt % N₂. The nitrided specimens were quenched in water from 590°C to retain the nitrogen in solid solution.

The apparatus used for these experiments was designed to fit into the low-temperature irradiation facility in hole 50 of the Oak Ridge Graphite Reactor. The method of measuring internal friction was the same as the one previously described,¹⁷ but the apparatus was more compact, allowing rapid heating and cooling. The size of the apparatus can be judged from Fig. 6.13 which is approximately to scale. The diameter of the tube which carries the heater and solenoid winding is 5/16 in.

²³J. T. Stanley, Quart. Progr. Rept.: Irradiation Effects on Reactor Structural Materials, HW-76635, p. 10.1 (Feb. 15, 1963).

Fig. 6.13. In-Reactor Flexure Pendulum Apparatus.

The drawing shows only half of the apparatus which holds two specimens back to back. The capsule was about 8 in. long.

With this apparatus the specimen could be cooled rapidly enough to retain nitrogen in solution after it had been annealed at 400°C. This treatment will be referred to as a re-solution anneal, as it restores the original nitrogen internal friction peak after an aging treatment at some lower temperature. The re-solution anneal is carried out by heating the specimen to 400°C in vacuo and then cooling rapidly by simultaneously turning off the heater current and admitting helium gas into the chamber.

Out-of-reactor experiments in a mockup of the reactor facility showed that essentially all of the nitrogen could be retained in solution if the specimen cooled from 400 to 50°C in about 6 min. To achieve this cooling rate in the mockup, it was necessary to cool the chamber walls with dry ice. In the low-temperature irradiation facility, the chamber walls were kept cool by the flow of cold helium gas through the heat exchanger.

Even though the specimen is cooled fast enough to retain all of the nitrogen in solution as detected by the internal friction peak, it

is still possible for there to be differences in the number of nucleation sites for precipitation for different rates of cooling. However, studies of the aging of the nitrogen peak at 65°C showed little difference between the specimen water quenched from 590°C and gas quenched from 400°C, as described above. These two sets of data are shown in Fig. 6.14 along with data for the specimen after various amounts of irradiation at low temperature.

Fig. 6.14. Fractional Change in the Nitrogen Peak Height vs Aging Time at 65°C for Fe-0.015 wt % N.

The results presented in Fig. 6.14 represent measurements made on two specimens of about the same nitrogen content. The aging run after the 23-day irradiation was made on one specimen (specimen A) and the rest of the aging runs were for another specimen (specimen B).

The measurements for specimen B were made in the order listed in the caption, and, except for the initial water quench, each aging run was preceded by a 400°C re-solution anneal as described above. The

results in Fig. 6.14 show that irradiation does increase the rate of nitrogen precipitation and that the 400°C re-solution anneal removes most of the effect of the irradiation.

A comparison of the aging runs made after the 23-day irradiation and the 3-day irradiation shows that the time for half completion of the reaction is about the same in both cases but that aging is somewhat faster in the early stages of precipitation for the 23-day irradiation and slower in the later stages. A possible explanation of this effect might be based on trapping of nitrogen atoms at irradiation-produced defects, as proposed by Wagenblast and Damask²² for Fe-C alloys. Thus, after the 23-day irradiation, there would be enough defects produced to remove about one-third of the nitrogen atoms by trapping. This process occurs very rapidly and accounts for the more rapid loss of nitrogen from solid solution in the early stages. The slower precipitation in the later stages would be explained by assuming that, since the nitrogen content is lowered rapidly by trapping, the number of precipitates that grow to the critical size is reduced. However, at the present time, such reasoning must be regarded as speculative since in such a complicated system there are many other possible explanations.

Breakup of Precipitates by Irradiation

The present concepts of neutron damage in metals indicate that each primary collision of a fast neutron with a metal atom produces a region of intense damage approximately 100 Å in diameter. If this damaged region encompasses a precipitate particle, it is likely that the particle will be redissolved in the lattice and may then reprecipitate as a number of smaller particles. Such a redistribution of precipitate would have a marked effect on the mechanical properties of the material. Experimentally, it is difficult to separate such effects from others that occur during irradiation. However, Piercy²⁴ has shown that precipitate particles in Cu-Co alloys are broken up by neutron irradiation and are then reprecipitated as smaller particles. In the Cu-Co alloys a measure of the size of

²⁴G. R. Piercy, J. Phys. Chem. Solids 23, 463 (1962).

the precipitate particles can be obtained from magnetic susceptibility measurements. Such techniques are applicable to only a few alloys. It would be possible to obtain some information about the breakup of nitride precipitates in iron if an increase in the nitrogen in solution were detected during irradiation. The in-reactor internal friction apparatus is particularly well suited for such an experiment. However, rough calculations, based on our present ideas about the size of the damaged region produced by a primary displacement event and a guess about the rate of precipitation of the nitrogen in the damaged region, show that the level of nitrogen solubility produced by this mechanism will probably be too small to be observed. Nevertheless, breakup of precipitate was put forth as a possible explanation for some effects observed in an earlier experiment.²³

An experiment has been carried out on an Fe-N specimen to see if breakup of precipitates can be observed as a change in the amount of nitrogen in solution during irradiation. The specimen contained about 0.03 wt % N and was aged out of the reactor at 65°C for about 120 hr. Figure 6.15 shows that the nitrogen internal friction peak decreased to about 0.0015 after 20 hr and remained constant thereafter. Irradiation did not change the height of the internal friction peak, and therefore it is concluded that the amount of nitrogen in solution remained constant. This experiment shows that breakup of precipitate particles by irradiation did not occur at a rate great enough to explain the results of an earlier experiment and, therefore, those results are probably due to a particle size effect.

Irradiation of Vanadium

The trapping of interstitial impurity atoms in body-centered cubic metals by vacancies may be an important factor in the response of these metals to irradiation. Some examples have been mentioned above. As we have seen, the study of this process in iron is complicated by the low solubility of the interstitials at low temperatures. In contrast, the solubility of the interstitial impurities, nitrogen and oxygen, in vanadium is high; and large Snoek-type internal friction peaks occur in vanadium. An investigation has been made of the effect of irradiation on the oxygen and nitrogen peaks in vanadium in an effort to observe the trapping of these interstitials by vacancies.

Fig. 6.15. The Effect of Irradiation on a Fully Aged Sample. Out-of-reactor aging followed by in-reactor aging at 70°C of a sample of Fe-0.03 wt % N. Vibration frequency is 48 cps.

The internal friction of a vanadium specimen²⁵ was measured in a torsion pendulum from room temperature to 320°C. The results are shown in Fig. 6.16. The two internal friction peaks were identified as due to oxygen and nitrogen according to the work of Powers and Doyle.²⁶ Since the oxygen and nitrogen contents are below their respective solubility limits, there is no precipitation of oxides or nitrides. The specimen was removed from the torsion pendulum and irradiated at the face of the BSR for 12 1/2 hr. The fast neutron flux in this position is 3×10^{12} neutrons $\text{cm}^{-2} \text{sec}^{-1}$ (> 1 Mev), and the dose in this irradiation was 1×10^{17} neutrons/ cm^2 . During the irradiation, the pool water temperature rose from 18 to 33°C. The specimen was held at room temperature for 10 days and was then placed in the torsion pendulum for measurement. The results of the internal friction measurements after the irradiation are shown in Fig. 6.16. No change in either the oxygen or nitrogen peak was observed. The same specimen was again irradiated in the BSR for 51 hr, receiving an additional dose of 0.5×10^{18} neutrons/ cm^2 .

²⁵Purchased from A. D. Mackay, Inc.

²⁶R. W. Powers and M. V. Doyle, J. Appl. Phys. 30, 514 (1959).

Fig. 6.16. Internal Friction of Vanadium Tested in a Torsion Pendulum after Irradiation in the Bulk Shielding Reactor. Neutron doses for neutrons with energy above 1 Mev.

The internal friction measurements were repeated and are shown in Fig. 6.16. After this irradiation, the oxygen peak had decreased by about 5%, and the nitrogen peak had decreased about 10%.

A rough calculation of the vacancy concentration produced by a 51-hr irradiation at the face of the BSR gives 0.2 at. %, assuming no annihilation of vacancies during irradiation. If the 10% decrease in the height of the nitrogen peak were due to trapping of nitrogen by radiation-produced vacancies, it would be possible to estimate the binding energy between the nitrogen atom and the vacancy. On the basis of the law of mass action, the atomic concentration of the nitrogen vacancy pairs is given by

$$N_{NV} = N_N N_V \exp(E_b/kT) \quad ,$$

where N_{NV} , N_N , and N_V are the concentrations of the nitrogen-vacancy pairs, free nitrogen atoms, and free vacancies, respectively, and E_b is the nitrogen-vacancy binding energy. Then substituting $N_{NV}/N_N = 0.1$, $N_V = 0.002$, and $T = 535^\circ\text{K}$ (262°C), we find that $E_b = 4000$ cal/mole. This value of the binding energy is less than half of the binding energy of carbon atoms to vacancies in iron, 9200 cal/mole, as determined by

Arndt and Damask.²⁷ In the above, no account has been taken of vacancy binding to oxygen atoms. Also, the calculation of the vacancy concentration is quite approximate. However, we may conclude that the binding energy between vacancies and interstitial impurities may not be insignificantly small in vanadium.

Fission-Spectrum Irradiation Facility for the BSR

W. E. Brundage

Accurate evaluations of the results of radiation experiments often require that the intensity and the energy distribution of the incident neutrons be well known. Experiments needing relatively high flux of high-energy neutrons generally must be performed in a reactor where the flux level and spectrum are subject to variations due to such factors as reactor control-rod motion and changes in core loading or adjacent experiments. Unless these factors can be adequately controlled, a continual flux monitoring program must be carried out.

One method of overcoming these difficulties is to irradiate in a region surrounded by a source of fission neutrons since the fission spectrum is well known. A design study demonstrating the feasibility of such a facility for use in the BSR has been completed. Once preliminary flux calibration is performed, it is expected that the neutron spectrum will not change with time. Also, over long periods of time, the intensity will be proportional to the flux of thermal neutrons at the outer surface of the fission source, which may be measured with relative ease and accuracy.

The facility, shown schematically in Fig. 6.17, is similar in geometry to a lower power (500 w) converter also proposed²⁸ for the BSR. Neutrons from one face of the reactor will thermalize by passage through D₂O and will be absorbed in a tubular "neutron-converter" element containing ²³⁵U. Samples, placed inside the tube, will be irradiated with the high-energy neutrons from the fissioning ²³⁵U.

²⁷R. A. Arndt and A. C. Damask, Acta Met. 12, 341 (1964).

²⁸R. R. Coltman et al., Solid State Div. Ann. Progr. Rept. May 31, 1963, ORNL-3480, p. 57.

UNCLASSIFIED
ORNL-DWG 64-6242

Fig. 6.17. Fission-Spectrum Irradiation Facility.

The proportion of partially moderated neutrons reflected back into the sample chamber will be reduced by having a minimum amount of moderating material in the vicinity of the converter.

The converter tube, 3 in. in inside diameter and 12 in. long, will contain about 300 g of 93% enriched ^{235}U in the form of an aluminum-uranium alloy. This alloy will be clad with aluminum and the inside of the tube will be lined with cadmium.

In order to achieve sufficiently high fission flux, 15 kw of heat will be generated in the converter tube. No satisfactory system for removing this power could be found without introducing some moderator into the "unmoderated region." By optimizing flow conditions,²⁹ it was found that the heat could be removed with water flowing through small square channels outside the converter tube. Figure 6.18 represents a horizontal section through the facility. It can be seen that only one-half of the circumference of the tube is used for the coolant. The remaining portion acts as an alternate path for heat removal in case the coolant flow fails. In that event, the heat would be conducted to the outer surface of the coolant tube. The radial fins serve as a conducting path to the outer surface of the facility where the heat can be

²⁹The heat flow calculations were performed by G. H. Llewellyn of the ORNL Design Engineering Department.

UNCLASSIFIED
ORNL-DWG 64-5451

Fig. 6.18. Section Through Converter Tube.

dissipated to the surrounding D₂O and water. This safety path will prevent the converter tube from exceeding a safe temperature without coolant flow, even with a power generation rate over double that of the design value.

The possible hazards associated with operation of the facility are being evaluated, and it appears that the system is inherently safe for any credible accident involving criticality, coolant failure, or a reactor excursion.

It is expected that the facility will provide a region for sample irradiation 3 in. in diameter and 6 in. long with a uniform flux of $8 \times 10^{11} \text{ cm}^{-2} \text{ sec}^{-1}$ in the fission spectrum. The temperature of the wall of the sample chamber will be below 60°C if the pool water is used for heat removal; the addition of a chilling system would permit this temperature to be reduced to 25°C.

Some neutrons reflected back from the moderator (moderated feedback) will also be present. Computer calculations,³⁰ which were based on an infinite-length cylinder with the same cross section as the facility, show that the increase in atomic displacements in the irradiated samples caused by the moderated feedback will be less than 7%.

³⁰The flux calculations were performed by J. R. Knight, Oak Ridge Central Data Processing Division.

Crystallography of Dislocations and Dislocation Loops
in Deformed Iron³¹

S. M. Ohr D. N. Beshers³²

Crystallographic analyses of dislocations and dislocation loops in deformed body-centered cubic iron observed in the electron microscope have been carried out by applying the electron diffraction theory of contrast at dislocations. Dislocations in deformed iron are in the form of tangles, with interspersed clusters of dislocation loops, from the very first stage of deformation. Crystallographic analyses show that the tangles consist of dislocations of two distinct Burgers' vectors in the ratio of approximately 2:1. The dislocations of the primary system are composed of segments of both signs in roughly equal proportion. The Burgers' vector of a majority of dislocation loops is identical to that of the primary dislocations, and the rest of the loops belong to the secondary system. The loops are found to be pure edge prismatic dislocations lying in $\{111\}$ planes and are identified as being of the vacancy type. From a consideration of the elastic theory of defect interaction, it is concluded that the interactions of dislocations with dislocations of dissimilar Burgers' vectors and the formation of a cluster of small loops around the dislocations and junctions are responsible for formation of dislocation tangles.

Plastic Deformation of Iron and Its Alloys

S. M. Ohr

With the development of direct methods of observing lattice defects with the light and electron microscopes, the plastic properties of metals and alloys have been successfully studied in terms of the behavior of these lattice defects. The purpose of this program is to apply these direct methods to the study of the effect of irradiation on the mechanism of plastic deformation in iron and its alloys.

³¹Abstract of a paper to be published in Philosophical Magazine.

³²Columbia University, New York, New York.

We have initiated with both vacuum-melted high-purity iron and Fe-Si alloy samples: (1) observation of the distribution of dislocations at the surface following plastic deformation and the measurement of dislocation mobility by etch-pit techniques, (2) direct observation and crystallographic analysis of dislocations and dislocation loops in thin foils by transmission electron microscopy and electron diffraction, and (3) mechanical tests performed at various temperatures and strain rates.

Figure 6.19a shows an optical micrograph of etch pits at dislocations in Ferrovac E iron, while Fig. 6.19b shows the same specimen observed by transmission electron microscopy. The sample, 5 mils thick, was deformed 2% in tension and was polished and etched for the observation of etch pits. The sample was then thinned electrolytically to approximately 1000 Å for observation by transmission electron microscopy. Figure 6.19a reveals low-angle dislocation boundaries, as well as dislocations introduced by deformation. Figure 6.19b exhibits the same features but at higher magnification; a grain boundary, low-angle boundaries consisting of parallel rows of dislocations, and complex tangles of dislocations and dislocation loops are shown.

The observations of plastic properties will be repeated on irradiated samples, and any changes in structure and in parameters that characterize yielding and deformation will be investigated. The nature of dislocation interactions at low temperatures is to be correlated with the low temperature brittleness of these body-centered cubic metals.

Irradiation Effects on the Mechanical Properties of Iron and Iron Alloys

N. E. Hinkle

A program is under way³³ to study the effect of irradiation on the tensile properties of iron and iron-base alloys of various grain sizes. The tensile properties are to be measured as a function of dose, dose rate, and irradiation temperature. Also, the separate effects of thermal- and fast-neutron fluxes are being investigated.

³³N. E. Hinkle, Solid State Div. Ann. Progr. Rept. May 31, 1963, ORNL-3480, pp. 128-131.

Fig. 6.19. (a) Optical Micrograph of Etch Pits at Dislocations, and (b) Transmission Electron Micrograph from the Same Specimen of Ferrovac E Iron.

The dependence of yield stress on grain size has been measured for samples of Ferrovac E (a vacuum-melted high-purity iron) and Ferrovac 1020 steel (vacuum-melted iron alloy containing 0.2% C and 0.5% Mn). The various grain sizes are obtained by varying the times and temperatures of the prior heat treatments. The heat treatments employed and the dependence of lower yield stress on grain size are shown in Fig. 6.20 for Ferrovac E. The yield stress, σ_{YS} , is plotted vs the reciprocal square root of the grain radius, d , in accordance with the Cottrell-Petch relation^{34,35}

$$\sigma_{YS} = \sigma_0 + K_Y d^{-1/2} \quad (1)$$

where it is thought that σ_0 represents the lattice friction stress and K_Y is proportional to the stress necessary to unpin a dislocation from its locking atmosphere. The data in Fig. 6.20 indicate agreement with Eq. (1) for Ferrovac E for samples heat treated in the α phase ($T < 910^\circ\text{C}$) and in the γ phase ($T > 910^\circ\text{C}$). A typical photomicrograph showing the grain structure of a sample heat treated in the α phase is given in Fig. 6.21. This is to be compared with the photomicrograph in Fig. 6.22 of a sample heat treated in the γ phase. The gamma-treated sample exhibits considerable subcell formation within the grains. However, the values of yield stress as a function of grain size for the gamma-treated samples are consistent with those for the alpha-treated samples, as is seen in Fig. 6.20. It will be of interest to compare the effects of irradiation on samples given the two types of heat treatments.

For the vacuum-melted 1020 steel, subcritical heat treatments ($T < 723^\circ\text{C}$) produce a very fine grain structure containing spheroidized carbide particles. The yield-stress-grain-size relationship coincided with that for the Ferrovac E, indicating that the carbides have little or no effect on the yield stress as far as Eq. (1) is concerned. However,

³⁴N. J. Petch, J. Iron Steel Inst. (London) 173, 25 (1953).

³⁵A. H. Cottrell, Trans. Met. Soc., AIME 212, 192 (1958).

UNCLASSIFIED
ORNL-DWG 64-6307

Fig. 6.20. Yield Stress vs Reciprocal Square Root Grain Radius for Ferrovac E with Various Heat Treatments. Strain rate: 0.02 min^{-1} .

Fig. 6.21. Microstructure of Ferrovac E Heat Treated in the α Phase. The sample was cold worked about 95% reduction in area, annealed 2 hr in vacuum at 815°C, and furnace cooled. 100x.

Fig. 6.22. Microstructure of Ferrovac E Heat Treated in the γ Phase. The sample was cold worked about 95% reduction in area, annealed 4 hr in vacuum at 950°C, and furnace cooled. Note the subcell structure within the grains. 100x.

efforts to establish the yield-stress-grain-size relationship for the Ferrovac 1020 steel previously given supercritical heat treatments ($T > 840^{\circ}\text{C}$) have thus far been unsuccessful.

The first of a series of irradiation assemblies containing iron and steel tensile specimens has been irradiated in a piggyback position of the ORR poolside facility. The tensile specimens in this assembly (ORR-56) were fabricated from Ferrovac E, Ferrovac 1020 steel, and an ASTM A-212, grade B, pressure vessel steel, each of various grain sizes. In addition, a few samples of an EGCR pressure vessel heat of A-212B and an ASTM reference heat of A-212B were included for purposes of comparison with data of other investigations. The specimens were irradiated at 40 to 50°C and at 260°C.

As is shown in Fig. 6.23 for the low-temperature irradiation, the samples were spring-loaded against a series of water-cooled tubes. For the elevated-temperature irradiations, the samples with sheathed thermocouples attached were placed in aluminum capsules filled with aluminum powder. The capsules were wrapped with sheathed heating elements and strapped together in a stringer arrangement as shown in Fig. 6.24. The completed irradiation assembly prior to enclosure in a welded aluminum can is shown in Fig. 6.25.

UNCLASSIFIED
PHOTO 63987

Fig. 6.23. Partial Assembly of ORR-56 Showing the Tensile Samples Spring Mounted Against the Water-Cooled Tubes.

UNCLASSIFIED
PHOTO 63988

Fig. 6.24. Elevated-Temperature Capsules and Stringer Prior to Placing in ORR-56 Assembly.

Fig. 6.25. Completed Assembly of ORR-56 Prior to Enclosure. The column of samples adjacent to the scale at the left was positioned toward the reactor face.

The in-reactor operation proved that the experiment design was satisfactory; thus future piggyback irradiation assemblies will use the same basic design. Hot-cell disassembly of the experiment has been completed, and testing of the tensile specimens will start soon.

A major objective of this work is to determine the specific influence of dose rate in addition to the total dose. For this reason, it is especially important that careful measurements of the neutron flux be made. Experiment ORR-56 contained flux monitors of nickel, iron, and cobalt. The nickel flux monitors, cadmium-shielded, are used to determine the neutron flux greater than 2.9 Mev, assuming an effective threshold cross section of 0.39 barn for the reaction $^{58}\text{Ni}(n,p)^{58}\text{Co}$, which corresponds to a mean fission-spectrum cross section (averaged over the entire fission spectrum) of 0.10 barn.³⁶ The cadmium shielding is needed to minimize the thermal neutron burnup of the ^{58}Co isotope. Unshielded iron monitors are used to determine the neutron flux greater than 4.0 Mev, assuming an effective threshold cross section of 0.60 barn for the reaction $^{54}\text{Fe}(n,p)^{54}\text{Mn}$. This value corresponds to 0.060 barn³⁶ for the mean fission-spectrum cross section. The calculations are made using the relationship

$$\phi = \frac{A}{N_0 \sigma (1 - e^{-\lambda t_i})(e^{-\lambda t_d})}, \quad (2)$$

where

A = activity, in disintegrations per second, of radioactive isotope per gram of monitor,

N_0 = number of atoms of reacting isotope per gram of monitor,

σ = effective threshold cross section for fast neutron monitors or capture cross section for cobalt,

$\lambda = 0.693/T_{1/2}$ where $T_{1/2}$ is the half-life of the radioactive isotope,

t_i = irradiation time, and

t_d = decay time after reactor shutdown.

³⁶T. O. Passell, "The Use of Nickel-58 and Iron-54 as Integrators of Fast-Neutron Flux," p. 501 in Neutron Dosimetry, vol. I, International Atomic Energy Agency, Vienna, 1963.

The cobalt monitors are used to determine the thermal neutron flux by the reaction $^{59}\text{Co}(n_{\text{th}}, \gamma)^{60}\text{Co}$. The activity of unshielded cobalt monitors is due to both thermal and epithermal neutrons. Therefore, cadmium-shielded cobalt monitors are also included in order to determine the amount of activity due to epithermal neutrons. The disintegration rate of the cadmium-shielded cobalt monitors in experiment ORR-56 was less than 5% of the disintegration rate of the bare cobalt monitors. Therefore, the thermal neutron flux, with errors of less than a few per cent, is calculated by Eq. (2) using the the disintegration rates of the bare cobalt monitors. The neutron flux for experiment ORR-56, calculated as outlined above, is shown in Fig. 6.26.

Fig. 6.26. Neutron Flux vs Horizontal Distance from ORR Poolside Tank Face for Experiment ORR-56. The curves shown refer to the maximum and minimum fluxes along the vertical section occupied by a column of samples.

Reactor Pressure Vessel Materials³⁷

M. S. Wechsler R. G. Berggren

The characteristics of nuclear reactor pressure vessels are described, and a discussion is given of the use of prestressed concrete, stainless steel, ferritic steel, and low-alloy high-strength steel as materials of construction.

Impact Tests on Irradiated Pressure Vessel Steels

R. G. Berggren W. J. Stelzman T. N. Jones

It is recognized that in large welded steel structures the metallurgical condition and mechanical properties of the weld metal and the heat-affected zone adjacent to the weld may be of critical importance. The heat-affected zone may be especially important since the ductile-brittle transition temperature tends to be higher for the heat-affected zones than for the weld metal or the baseplate material. This may be seen in Table 6.1, where values of the transition temperature corresponding to the 20-ft-lb level in Charpy V-notch tests are shown for the steel used in the EGCR pressure vessel.³⁸ The impact curves for baseplate, weld metal, and heat-affected zone material from the EGCR steel are shown in Figs. 6.27 and 6.28.

In actual weldments, the heat-affected region is usually quite localized, and it is difficult to machine notch-impact samples from weldments whose properties will be indicative of the metallurgical condition of the heat-affected zone. For this reason, the heat-affected zone samples used in this study are prepared synthetically (under subcontract at Rensselaer Polytechnic Institute). The microstructures characteristic of the heat-affected zones corresponding to particular welding parameters are introduced by subjecting the samples to special thermal cycling treatments. For the results shown in Table 6.1, the thermal cycling treatment was designed to produce microstructures corresponding to peak temperatures of 2400°F (1316°C), preheat temperatures

³⁷Abstract of paper submitted to Nuclear Safety.

³⁸R. G. Berggren, W. J. Stelzman, and T. N. Jones, Solid State Div. Ann. Progr. Rept. May 30, 1964, ORNL-3676 (in press).

Table 6.1. Mechanical Properties of EGCR Pressure Vessel Steels:
ASTM A-212, Grade B, and E-7016 Weld Metal

Heat Number	Material Condition	Charpy V-Notch 20-ft-lb	
		Transition Temperature (°F)	Transition Temperature (°C)
<u>Normalized Baseplate</u>			
A-2056	a	36	2
A-2110	a	12	-11
A-2061	b	-10	-23
A-2106	b	-15	-26
A-19216	b	-42	-41
A-21822	b	-40	-40
A-21829	b	-10	-23
A-22193	b	-20	-29
A-23965	b	-36	-38
<u>Deposited Weld Metal</u>			
Girth weld (stress relieved)	c	-62	-52
Longitudinal weld (stress relieved)	c	-112	-80
<u>Synthetic Heat-Affected Zones</u>			
A-2056	d	110	43
A-2056	e	80 to 100	27 to 38
A-2056	f	100	38
A-2056	g	82 to 106	28 to 41
A-2110	d	48	9
A-2110	e	28	-2
A-2110	f	65	18
A-2110	g	25 to 50	-4 to 10

^aNormalized at 1650°F (899°C) for 1 hr/in. of thickness and cooled in air.

^bFabrication scrap from EGCR pressure vessel.

^cStress relieved at 1150°F (621°C) for 4 hr.

^dHeat-affected zone synthetically prepared for a weld energy input of 95,800 joules/in. with a peak temperature of 2400°F (1316°C) and a cooling rate of 18°F/sec (10°C/sec) at 1000°F (538°C).

^ePrepared as in footnote "d" and stress relieved for 4 hr at 1150°F (621°C).

^fSame as "d" except with energy input of 145,500 joules/in. and cooling rate of 9°F/sec (5°C/sec) at 1000°F (538°C).

^gPrepared as in footnote "f" and stress relieved 4 hr at 1150°F (621°C).

Fig. 6.27. Impact Energy Absorbed in Fracture vs Test Temperature for Baseplate and Weld Metal Charpy V-Notch Impact Samples of EGCR Steel.

Fig. 6.28. Impact Energy Absorbed in Fracture vs Test Temperature for Baseplate and Synthetic Heat-Affected Zone Samples of EGCR Steel. Curves are shown for the synthetic heat-affected zone samples as thermal cycled to produce a microstructure characteristic of a heat input of 95,800 joules/in. and for similar samples stress relieved at 1150°F (621°C).

of 210°F (99°C) and 275°F (135°C), and energy inputs of 95,800 and 145,500 joules/in. Table 6.1 and Fig. 6.28 also indicate the benefit to be derived from a stress-relief anneal.

In the application of low-carbon steels to reactor pressure vessels, attention must be given to the increase in transition temperature upon irradiation. In an earlier study³⁹ of the effect of irradiation on baseplate and simulated heat-affected zone samples, it was found that

³⁹R. G. Berggren, M. S. Wechsler, and T. N. Jones, Solid State Div. Ann. Progr. Rept. Aug. 31, 1961, ORNL-3213, pp. 39-42.

the increase in transition temperature upon irradiation at about 120°F (49°C) was roughly the same for the baseplate and heat-affected zone material, despite the higher initial transition temperature for the heat-affected zones. For a neutron exposure of about 9×10^{18} neutrons/cm² ($E > 1$ Mev), the increase in transition temperature was somewhat greater than 200°F (110°C).

To extend the study of irradiation effects on the notch-impact transition temperature of heat-affected zone materials to elevated exposure temperatures, three irradiation experiments were installed in the poolside facility of the ORR during the past year. The experiments contained Charpy V-notch impact samples of both baseplate and synthetic heat-affected zone materials. The design of the irradiation capsule is shown in Fig. 6.29. For the first two experiments, the desired irradiation temperature of 550°F (288°C) was exceeded. In the first experiment, the stainless steel leaf springs relaxed during the elevated-temperature exposure changing the heat flow characteristics of the experiment and premature heater failures were experienced. In the second experiment, leaf springs of Inconel X and ceramic-fiber thermal insulation were used. In this case, the thermal barrier presented by the ceramic-fiber paper was greater than expected and the operating temperature of the experiment was about 900°F (482°C). Again, premature heater failures were experienced. The third irradiation capsule contained swaged-wire heating elements, which are sheathed with stainless steel and insulated with MgO. This capsule has now been operating satisfactorily in the ORR for a period of about seven weeks.

Charpy Impact Machine Calibration

R. G. Berggren W. J. Stelzman T. N. Jones

Efforts to meet the stringent Charpy test calibration standards of this program have met with only partial success. The Charpy impact testers used in this program satisfy the ASTM standards. However, attempts to calibrate the machines using calibration specimens provided by the Army Materials Research Agency (AMRA) have revealed errors arising from the dynamic characteristics of the machines. These errors have been

UNCLASSIFIED
ORNL-DWG 63-6848AR

Fig. 6.29. Capsule for Elevated-Temperature Irradiations of Charpy V-Notch Impact Samples.

reduced but not yet to AMRA requirements. The testing machine vendor is presently modifying one of our machines to meet AMRA calibration standards, and acceptance tests are scheduled. If successful, our second machine will be similarly modified and calibrated.

To determine the probable error of previously reported results, impact specimens of an ASTM A-212, grade B steel of a type previously tested in our two machines were tested in calibrated impact testing machines at AMRA and at Rensselaer Polytechnic Institute. The fracture energies obtained on these calibrated machines were in good agreement with energies obtained on our machines. Thus it appears that the AMRA calibration specimens of heat-treated SAE-4340 steel are more sensitive to testing machine variables than is the ASTM A-212, grade B steel. This apparent anomaly, of differing results for calibration specimens and agreement of results for the mild steel, is probably a consequence of the very different microstructures and fracture behavior of the two steels. Therefore, the data obtained for mild steels tested in our

machines are considered quite reliable. In addition, reported radiation-induced shifts of impact transition temperature are considered valid since machine errors will tend to cancel out when comparing unirradiated with irradiated specimens.

INTERNAL DISTRIBUTION

1-3. Central Research Library	63. T. S. Lundy
4-5. ORNL - Y-12 Technical Library	64. R. N. Lyon
Document Reference Section	65. H. G. MacPherson
6-15. Laboratory Records	66. R. E. MacPherson
16. Laboratory Records, RC	67. M. M. Martin
17. ORNL Patent Office	68. W. R. Martin
18. G. M. Adamson, Jr.	69. R. W. McClung
19. J. C. Banter	70. H. E. McCoy, Jr.
20. J. H. Barrett	71. H. C. McCurdy
21. S. E. Beall	72. R. E. McDonald
22. M. Bender	73. D. L. McElroy
23. R. G. Berggren	74. C. J. McHargue
24. J. O. Betterton, Jr.	75. M. C. McIlwain
25. D. S. Billington	76. F. R. McQuilkin
26. A. L. Boch	77. A. J. Miller
27. B. S. Borie	78. E. C. Miller
28. W. H. Bridges	79. F. H. Neill
29. R. B. Briggs	80. S. M. Ohr
30. W. E. Brundage	81. P. Patriarca
31. J. V. Cathcart	82. A. M. Perry
32. G. W. Clark	83. M. L. Picklesimer
33. K. V. Cook	84. P. L. Rittenhouse
34. J. H. Crawford	85. M. W. Rosenthal
35. J. E. Cunningham	86. G. Samuels
36. J. H. DeVan	87. H. W. Savage
37. C. V. Dodd	88. W. Schüle
38. D. A. Douglas, Jr.	89. J. L. Scott
39. J. I. Federer	90. O. Sisman
40. B. E. Foster	91. G. M. Slaughter
41. A. P. Fraas	92. G. P. Smith, Jr.
42. J. H. Frye, Jr.	93. S. D. Snyder
43. R. J. Gray	94. I. Spiewak
44. B. L. Greenstreet	95. J. T. Stanley
45. W. R. Grimes	96. W. J. Stelzman
46. J. P. Hammond	97. J. O. Stiegler
47. W. O. Harms	98. J. A. Swartout
48. R. L. Heestand	99. A. Taboada
49-53. M. R. Hill	100. W. C. Thurber
54. N. E. Hinkle	101. D. B. Trauger
55. H. W. Hoffman	102. G. M. Watson
56. H. Inouye	103. M. S. Wechsler
57. T. N. Jones	104. A. M. Weinberg
58. G. W. Keilholtz	105. J. R. Weir
59. B. C. Kelley	106. W. J. Werner
60. J. A. Lane	107. G. D. Whitman
61. C. F. Leitten, Jr.	108. J. M. Williams
62. A. L. Lotts	109. R. O. Williams

110. J. C. Wilson
 111. F. R. Winslow
 112. H. L. Yakel, Jr.

113. F. W. Young, Jr.
 114. C. S. Yust
 115. J. C. Zukas

EXTERNAL DISTRIBUTION

116. A. J. Alexander, AEC, CANEL
 117. R. D. Baker, Los Alamos Scientific Laboratory
 118. L. Brewer, University of California, Berkeley
 119. V. P. Calkins, GE, NMPO
 120. W. Cashin, Knolls Atomic Power Laboratory
 121. R. M. Cilimberg, Division of Reactor Development,
 AEC, Washington
 122-123. D. F. Cope, AEC, ORO
 124. G. K. Dicker, Division of Reactor Development,
 AEC, Washington
 125. E. A. Evans, GE, Hanford
 126. W. C. Francis, Phillips Petroleum Company
 127. R. G. Grove, Mound Laboratory
 128. D. H. Gurinsky, BNL
 129. S. Hasko, NBS
 130. A. N. Holden, GE, APED
 131. J. S. Kane, University of California, Livermore
 132. J. H. Kittel, ANL
 133. E. J. Kreih, Westinghouse, Bettis Atomic Power
 Laboratory
 134. W. L. Larsen, Iowa State University, Ames Laboratory
 135. R. E. Pahler, Division of Reactor Development,
 AEC, Washington
 136. S. Paprocki, BMI
 137. D. Ragone, GA
 138. L. M. Raring, Pratt & Whitney, CANEL
 139. Research and Development, AEC, ORO
 140. A. H. Roberson, U. S. Department of the Interior,
 Bureau of Mines
 141. W. Rostokev, Illinois Institute of Technology
 Research Institute
 142. F. C. Schwenk, Division of Reactor Development,
 AEC, Washington
 143-144. J. M. Simmons, Division of Reactor Development,
 AEC, Washington
 145. L. E. Steele, Naval Research Laboratory
 146. R. H. Steele, Division of Reactor Development,
 AEC, Washington
 147. W. F. Sheely, Division of Research,
 AEC, Washington
 148. A. Strasser, United Nuclear Corporation
 149. W. R. Voigt, Division of Reactor Development,
 AEC, Washington

- 150. C. E. Weber, Atomics International
- 151. G. W. Wensch, Division of Reactor Development,
AEC, Washington
- 152. M. J. Whitman, Division of Reactor Development,
AEC, Washington
- 153-167. Division of Technical Information Extension