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**FUELS AND MATERIALS DEVELOPMENT PROGRAM QUARTERLY PROGRESS
REPORT FOR PERIOD ENDING JUNE 30, 1971**

P. Patriarca

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METALS AND CERAMICS DIVISION

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REPORT FOR PERIOD ENDING JUNE 30, 1971

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SEPTEMBER 1971

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FOREWORD

This report is an excerpt from the Metals and Ceramics Division annual progress report and summarizes the research and development on nuclear fuels and materials in this division for the period July 1, 1970, through June 30, 1971. This work is either sponsored by or of particular interest to the Fuels and Materials Branch of the Division of Reactor Development and Technology. Not covered in this report is the "Fast-Neutron Irradiation Effects on Electrical Insulators," which is a Reactor Chemistry Division activity.

We are publishing this report in lieu of our quarterly progress report for the period ending June 30, 1971, but will resume our regular reporting for the period ending September 30, 1971.

Progress on these programs is reported for the three major divisions of the work - Fast Reactor Technology, Space Power Technology, and General Reactor Technology - under the appropriate AEC Activity titles listed below.

<u>AEC Activity Title</u>	<u>189a Number</u>	<u>AEC Activity Number</u>
FAST REACTOR TECHNOLOGY		
FBR OXIDE FUELS DEVELOPMENT	10090	04 40 02 01 1
DEVELOPMENT OF ADVANCED FBR FUEL	10092	04 40 02 01 1
FBR CLAD AND STRUCTURAL ALLOY DEVELOPMENT	10026	04 40 02 01 1
MECH PROP OF ALLOYS IN REACTOR	10097	04 40 02 03 1
FAB DEV OF FBR CLADDING	10202	04 40 02 04 1
WELDING DEV - FBR SS COMPONENTS	10219	04 40 02 04 1
PROPERTIES OF FERRITIC STEEL WELDS	10241	04 40 02 05 1
NDT TECHNIQUES FOR FBR	10106	04 40 02 04 1
SODIUM CORROSION STUDIES	10096	04 40 02 02 1
SODIUM REMOVAL AND CAUSTIC EFFECTS	10248	04 40 02 02 1
DEV OF FBR NEUTRON-ABSORBER MATERIALS	10242	04 40 02 02 1

<u>AEC Activity Title</u>	<u>189a Number</u>	<u>AEC Activity Number</u>
SPACE POWER TECHNOLOGY		
DEVELOPMENT OF NITRIDE FUELS	10213	04 40 02 01 1
CLADDING MATERIALS FOR SPACE ISOTOPIC HEAT SOURCES*	10507	04 30 05 04 1
PHYSICAL AND MECHANICAL METALLURGY OF REFRACTORY ALLOYS	10110	04 40 02 05 1
TUNGSTEN METALLURGY	10104	04 40 02 04 1
GENERAL REACTOR TECHNOLOGY		
FUEL ELEMENT FABRICATION DEVELOPMENT	10107	04 40 02 04 1
HIGH FLUX ISOTOPE REACTOR [†]	88	05 05 05 00 0
RADIATION DAMAGE [†]	103	05 06 01 03 0
JOINING RESEARCH ON NUCLEAR MATERIALS	10103	04 40 02 04 1
NONDESTRUCTIVE TESTING	10220	04 40 02 04 1
ADVANCED MATERIALS FOR STEAM GENERATORS	10217	04 40 02 02 1

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*Sponsored by Division of Space Nuclear Systems.

[†]Sponsored by Division of Research.

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*Related AEC Activity Titles are shown in parentheses.

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Summary

PART II. FAST REACTOR TECHNOLOGY

13. Fast Breeder Reactor Oxide Fuels

This program is being conducted to advance the technology of $(U,Pu)O_2$ as a fuel for the Liquid-Metal Fast Breeder Reactor. The determination of the properties and performance of sol-gel-derived oxide fuels fabricated by Sphere-Pac and pelletizing techniques has been emphasized, but comparison with materials derived from other processes such as mechanical blending is a part of our objective.

The Sphere-Pac process was used to load a variety of fuel pins for irradiation in the ETR, EBR-II, and ORR. Smear densities in the range 81 to 84% of theoretical are typical. Sol-gel-derived pellets were fabricated with controlled densities from 84 to 97% of theoretical. An equation was developed to predict the time required to reduce mixed oxide fuels to any oxygen-to-metal ratio desired. The Pu/U ratio of sol-gel-derived $(U,Pu)O_2$ fuels varied only slightly from batch to batch and not detectably from sphere to sphere within a batch. We characterized the microstructure of these fuels and assessed the effect of fission products on the structural state and therefore the properties.

The irradiation test program was continued to determine the in-reactor properties and performance of $(U,Pu)O_2$ fuel pins as functions of fabrication form, porosity distribution, stoichiometry, and irradiation conditions. We include both fast and thermal neutron irradiations at steady-state, cyclic, and transient power conditions. In our fast flux tests in EBR-II, five fuel pins containing Sphere-Pac $(U,Pu)O_2$ were irradiated to a calculated peak burnup of 6% FIMA. Two pins were removed for examination and three are being irradiated to 12% FIMA. No fuel-cladding mechanical interaction has occurred at 6% FIMA. The fission gas release rate of 80% agrees with other EBR-II-irradiated oxide fuels, and we detected no significant fuel-cladding chemical interaction, even at inner surface temperatures up to

570°C. This in contrast to the results with non-sol-gel-derived material. Microprobe analysis showed no fission products in the cladding grain boundaries. Six fuel pins containing unirradiated sol-gel $(U,Pu)O_2$ subjected to transients in the TREAT facility were examined. Both pellet and sol-gel Sphere-Pac fuel behaved the same. One capsule containing Sphere-Pac mixed oxide was irradiated in the ETR to a calculated burnup of 10% FIMA but not yet examined. Other instrumented and uninstrumented irradiations are being continued in the ETR on mechanically blended pellets, sol-gel-derived pellets, and Sphere-Pac material. Instrumented tests in the ORR with fuel having a smear density of 82% indicate that fuel-to-cladding thermal conductance in a Sphere-Pac pin is more than twice that of a pellet fuel pin with a small initial fuel-cladding gap. In ORR instrumented capsules operated at low fuel burnup, very localized cladding attack was seen in the pellet fuel pin but none in the Sphere-Pac fuel.

We initiated a series of irradiation tests to measure in-reactor axial extension of the fuel column and cladding and the internal gas pressure developed during operation under carefully controlled prototypic LMFBR power and temperature conditions.

We are developing analytical models for predicting and evaluating the performance of LMFBR fuel pins and are performing detailed examinations of irradiated fuel pins for comparison. We modified the FMØDEL fuel performance code for steady-state, power cycling, and limited transient applications. It now includes a dynamic model for fuel restructuring based on a vapor-condensation mechanism of pore migration, sub-routines for grain growth and plutonium redistribution, a fuel cracking model, and an improved cladding mechanical model to include neutron-enhanced creep. The code has been used in a variety of applications and shown excellent correspondence between calculated and measured diametral expansions, restructuring, center-line temperatures, and porosity distribution. Our work in support of the integrated fuel performance

modeling effort has included replica electron microscopy of irradiated (U,Pu)O₂ to improve our understanding of fuel restructuring, porosity distribution, fuel swelling, and fission gas release and has included an investigation of the kinetics of in-reactor and out-of-reactor (U,Pu)O₂ grain growth, actinide and oxygen redistribution in irradiated (U,Pu)O₂, and radial porosity distribution. In each case the physical observations have been used concurrently with development of mathematical description. Other activities include improvements and analysis for cladding deformation, a survey of fuel-cladding chemical interactions, and measurement of the properties of stainless steel tubing used for cladding.

14. Advanced Fast Breeder Reactor Fuels Development

Thermal flux irradiation of eight mixed nitride fuel pins is in progress in the ETR. The peak linear heat rate is 30 kW/ft with scheduled exposures of 30,000 and 60,000 Mwd/metric ton. Seven fuel pins were fabricated for testing in the EBR-II.

We produced and characterized (U,Pu)N fuel and UN insulator fuel for eight EBR-II pins. The sintering of UN and U_{0.8}Pu_{0.2}N depends strongly upon the nitrogen pressure. The sintering of mechanically mixed (U,Pu)N is limited by low-density regions at the original sites of the PuN particles. The nitrogen in mononitride and sesquinitride phases can be accurately determined by the Dumas method; the Kjeldahl technique with phosphoric acid dissolution is satisfactory only for mononitride. The lattice parameter of (U,Pu)N does not obey Vegard's law.

15. Cladding and Structural Materials

Irradiation of austenitic stainless steels at temperatures between 350 and about 650°C to fast neutron fluences in excess of 1×10^{21} neutrons/cm² creates voids and dislocations. This damage increases volume and also degrades the mechanical properties, particularly the ductility. We are defining the irradiation-induced property changes in standard types 304 and 316 stainless steel (cladding and structural materials for FFTF and demonstration plants) as a function of temperature and neutron fluence and attempting to decrease the property changes through control of alloy composition and microstructure. The radiation-induced

volume change in types 304, 316, and titanium-modified 316 stainless steel can be significantly reduced by cold working to introduce a high dislocation density before irradiation. Further, titanium-modified types 304 and 316 stainless steel, which were developed for resistance to radiation embrittlement above about 650°C, also exhibit higher postirradiation ductilities in the range 500 to 600°C. Thus, in the modified alloys cold work can be utilized to control the swelling without a drastic reduction in ductility.

16. Fabrication Development of Fast Breeder Reactor Cladding

We are studying various methods to produce a cheaper but higher quality of cladding. Two methods of tubing fabrication, planetary swaging and hot plug drawing were investigated. The slow planetary swaging process does not appear economic compared to the more conventional processing procedures. Methods for hot plug drawing at temperatures up to 760°C were developed. The relationship between defects and mechanical properties at elevated temperatures is being examined. Cold worked tubing is more sensitive to surface defects than annealed tubing. At high stress and short creep-rupture lives, surface notches cause a reduced lifetime and lower ductility. A procedure was developed for producing, in material for mechanical testing, artificial defects that resemble the sharp surface defects found in some lots of tubing.

17. Welding Development

We are continuing a study of the behavior of weldments in austenitic stainless steel at 370 and 650°C as a function of both welding process and variables within a process for application to LMFBR vessels and components. Submerged-arc welds exhibited lower creep-rupture strength and higher ductility in general than typical type 304 stainless steel base plate. Shielded metal-arc welds in general exhibited strength comparable with base plate. Weld-metal ductility decreased with increasing rupture life. From a study of the effect of certain minor elements including S, P, Si, B, and C, a "controlled residual element" filler metal possessing superior strength and ductility was developed for the FFTF vessel.

We have completed a state-of-the-art review of the weldability of stabilized low-alloy steels. Reports concerning the weldability of the stabilized steels have been

contradictory. We identified at least one cause of the difference of opinion. Poor weldability can be attributed to hot cracking in the heat-affected zone due to the melting of a niobium-rich eutectic.

Low-carbon 2.25% Cr-1% Mo weld metal was responsive to thermal cycling due to multipass welding techniques. This is particularly true of the low-carbon heat-affected zones, where the hardness increased from 129 to over 160 DPH. As expected, the strength of these alloys depends on the carbon level; however, the difference in as-welded strength at 565°C is reduced from a factor of 2 to about 1.4 by a 700°C postweld heat treatment.

18. Corrosion of Advanced Steam Generator Alloys

Steam generator alloys with ground surfaces and with the effects of grinding removed by electropolishing were exposed in steam for up to 14,000 hr at 650 and 595°C (1200 and 1100°F). Electropolishing substantially increased the corrosion of Incoloy 800, moderately increased it for Inconel 600, but slightly decreased it for Inconel 625 and Hastelloy X. Although the amount of corrosion on electropolished Incoloy 800 was comparatively large, the projected total attack in 20 years was still impressively low because its second-stage corrosion rate decreases significantly with time.

Stress-corrosion tests on weldments using conventional U-bend specimens in superheated steam contaminated with NaCl and oxygen failed to produce cracks. Under conditions that incorporated cycling periodically to the steam saturation temperature and introducing 25 ppm NaCl and 50 ppm O₂, many weldments with ground surfaces failed. Inconel 625 weldments did not fail under any conditions of surface treatment.

19. Sodium Corrosion in LMFBR Systems

Several vanadium alloys were tested at 600°C in static capsules to determine the effect of alloying elements on the solubility and diffusivity of oxygen in vanadium. Chromium, molybdenum, and iron lower the oxygen solubility much more than tantalum and niobium. We derived equations to determine the effect of alloying components on the oxygen diffusion coefficient; experiments designed to test the equations showed in some instances that an essential boundary condition is not met experimentally.

20. Sodium Removal and Caustic Effects

We evaluated cleaning procedures for removing sodium from metallic surfaces with respect to their corrosion effects. An apparatus was constructed to determine the effect of sodium on the oxidation of stainless steel as a function of sodium leak rate and temperature. We dissected and examined the ALCO/BLH steam generator to learn the cause of cracking in the lower tube sheet.

21. Nondestructive Testing Techniques for LMFBR

We are developing new methods, techniques, and equipment for nondestructively inspecting LMFBR cladding and structural materials, with emphasis on measuring cold work in type 316 stainless steel tubing for FFTF fuel-pin cladding.

Theoretical equations, computer programs, and calibration equipment were developed leading to new eddy-current instrumentation to identify both the size of a flaw and its depth below the surface.

We are applying ultrasonic schlieren techniques to improve our understanding of weld inspection. A transducer with multiple sensors was developed. Delta and schlieren techniques are being correlated on a stainless steel sample that scatters ultrasonic energy excessively.

We are developing magnetic permeability measurement in both flat and tubular type 316 stainless steel to determine cold work. A low-frequency eddy-current bridge was designed, constructed, and used to inspect tubing and rod with good results. A new coil system was designed to improve the sensitivity to changes in permeability.

22. Fast Breeder Neutron Absorber Materials

Characterization of and the effect of irradiation damage on neutron absorber materials are being investigated. Improved methods for indexing the x-ray diffraction powder patterns of boron carbide were developed, and patterns of the irradiated powder were interpreted. The microstructure of irradiated boron carbide powders was investigated by transmission microscopy. Damage typical of displacement damage in metals was observed, but no evidence of helium bubbles or other evidence of reaction product agglomeration was found. Free boron as a contaminant in boron carbide was shown to greatly increase the helium release rate during irradiation.

PART III. SPACE POWER TECHNOLOGY

23. Materials Development for Isotopic Power Programs

A new alloy containing platinum, rhodium, and tungsten has been developed comparable to refractory alloys in strength properties but retaining the superior oxidation resistance of the noble alloys. This solid solution alloy, designated Pt-3010, is fabricable, is weldable, and melts above 2000°C. Methods for fabricating thoria-molybdenum cermets using molybdenum powders were investigated; the products were compared with cermets produced by chemical vapor deposition of the molybdenum. The cermets produced by hot pressing CVD-molybdenum-coated thoria were superior in thermal conductivity and strength. Techniques for fabricating molybdenum-thoria cermets as stand-ins for $\text{Mo-}^{244}\text{Cm}_2\text{O}_3$ and noble metals- $^{244}\text{Cm}_2\text{O}_3$ cermets are also being investigated. These cermets with controlled porosity have been fabricated to provide for helium release and at the same time maintain desirable strength. The compatibility of ^{244}Cm and ^{90}Sr compounds with candidate container materials was ascertained for times to 10,000 hr.

Plasma-arc welding was successfully applied to Hastelloy C capsules fueled with ^{90}Sr titanate. This technique overcame many of the difficulties associated with remote gas-tungsten arc welding.

24. Metallurgy of Refractory Alloys

This base-technology program for high-temperature alloys is principally concerned with tantalum-, niobium-, and molybdenum-base alloys.

Alloy T-111 was more compatible than Ta with the nitrogen partial pressure over UN in the range 1200 to 1500°C, despite its hafnium content. This behavior has tentatively been attributed to the tungsten, which permits a greater equilibrium nitrogen pressure over T-111. A simple method for calculating the solubility limit of interstitial species in solid solutions from a single lattice parameter measurement was developed. The method is used to explain previously reported but apparently quite different solubility limits in two chemically similar alloys. Oxygen contents up to 3000 ppm had little effect on the tensile properties of T-111 if the doped specimens were heat treated before testing. However, as-doped specimens were completely brittle when contaminated to only 750 ppm. Apparently the form and distribution of the oxide precipitate has a greater effect than the oxygen content. Low nitrogen

pressure moderately strengthened T-111 in creep at 1400°C but reduced the rupture strain. Several experimental observations of spinodal decomposition that cannot be explained satisfactorily by current theory were accounted for by taking into account free energy changes resulting from atomic clustering.

Hot cracking involved liquid films in Mo and TZM welds. Both oxygen and carbon were detected on the surfaces of the cracks. Grain boundary porosity in the fusion and heat-affected zones also contributed to cracking. We have fabricated T-111 and Mo thermal-convection loops. A crack in the Mo loop was successfully repaired by welding. The melting point of one brazing alloy was raised by volatilization of Cr and solution of Ta and that of another was slightly lowered by Be segregation.

High-temperature thermal conductivity of T-111 estimated from low-temperature values and high-temperature electrical resistivity data was within 3% of measured values. Electrical resistivity was also used to estimate the high-temperature thermal conductivity of ThO_2 -Mo cermets.

Creep testing of tantalum alloys showed shorter rupture lives of welded than unwelded specimens at high stresses. Alloy SU-31 had the strongest stress-rupture properties of any Nb alloy yet tested.

We began to examine the T-111 forced convection loop that was operated with lithium for 3000 hr at a 1370°C heater exit temperature. In static tantalum capsules at 600°C, increasing the oxygen concentration of the sodium led to increased dissolution of the tantalum in the sodium. When the concentration of oxygen in tantalum exceeded a threshold level, the sodium penetrated the tantalum.

25. Tungsten Metallurgy

We extended our capability for extruding tungsten alloy tubing to include W-5% Re and W-2% ThO_2 . Chemical vapor deposition of W-5% Re was optimized. We evaluated welding techniques, including gas tungsten arc and electron beam with and without filler metals, for joining tungsten and W-25% Re.

The creep strength of W-25% Re is significantly greater in low-pressure O_2 than in ultrahigh vacuum. A carbon-containing atmosphere lowers the creep strength of unalloyed tungsten. Preexisting gas bubbles in powder-metallurgy tungsten expand to form the creep cavities by the stress-directed diffusion of vacancies along the grain boundaries.

A high-temperature irradiation experiment for EBR-II was designed and constructed to find the effect of irradiation temperature and alloying on the void formation and electrical properties of tungsten.

26. Uranium Nitride Fuels

The performance of UN fuel at 1500°C was satisfactory for 5800 hr of irradiation at ~9 kW/ft. The T-111 cladding of two fuel pins developed voids and cracks, leading to failure of one fuel pin. The third fuel pin had W-25% Re cladding and performed satisfactorily. Three additional capsules were fabricated to irradiate nine fuel pins at 1000°C cladding temperature — six with UN in T-111, two with UO₂ in Nb-1% Zr, and one with UO₂ in T-111. The UO₂ fuel is for evaluation of the backup design.

PART IV. GENERAL FUELS AND MATERIALS RESEARCH

27. Fuel Element Fabrication Development

An irradiation experiment to determine the factors controlling the upper burnup limit of ATR and HFIR type fuels was completed. Manufacturing yields for the HFIR fuel element continued to increase, to a net of 97.8% for fuel plates fabricated in FY 1971. New x-ray attenuation standards for fuel homogeneity were based on more precise chemical sampling and analysis techniques. The deformation studies on dogboning were completed. Shaped cores are a solution if the cladding strength is at least half that of the core. Examination of a small failed section from an ATR fuel plate showed no evidence of foreign material within the core. Thermal conductivity of aluminum-U₃O₈ cermet was smaller for burned than high-fired U₃O₈ and consistent with expectations for aluminum containing dispersed insulator and void space.

28. Joining Research on Nuclear Materials

Experimental compositions of Inconel base metal lost ductility when tested above 500°C and did not recover it. These results corroborate those of a previous study on Incoloy 800, where ductility was not recovered for compositions that did not contain titanium.

Tensile tests at 650°C were completed on Incoloy 800 welds made with both experimental and commercially obtained filler metals. Two new alloys from International Nickel Company compared favorably with the recommended filler metal (Inconel 82).

We investigated a microfissured electron-beam weld that joined an Inconel 600 tube to an Inconel 82-clad carbon steel tube sheet. The microfissure occurred in the overlay (the heat-affected zone of the weldment) at a location in which weld bead geometry led to a stress concentration. The microfissure was attributed to liquation of a niobium-rich phase during welding.

The Schaeffler diagram, which is often employed for predicting the amount of ferrite in austenitic stainless steel welds, does not consider the large effect of heat input. Further, high manganese contents lead to erroneous ferrite predictions. Alloys with 5% Mn, which are predicted by the diagram to be fully austenitic, contained from 3 to 8% ferrite.

29. Mechanical Properties of Irradiated Metals and Alloys

Nickel 270 (99.98% nominal purity) was irradiated in EBR-II to fluences ranging from 1.0×10^{18} to 1.5×10^{22} neutrons/cm² over the range 375 to 525°C. Voids were formed over the entire range of conditions and were inhomogeneously distributed at the lower fluences. Samples of Mo, Mo-0.5% Ti, Mo-50% Re, Ta, Nb, V, and V-20% Ti were irradiated in EBR-II at various temperatures to fluences up to 3×10^{22} neutrons/cm². We characterized the microstructure using a newly developed remote thinning technique for the Ta. Tensile tests were run on the Mo-base alloys, and the DBTT was raised markedly.

The types of damage that occur in 1100, 8001, and 6061 aluminum-base alloys have been characterized. Alloy 6061 shows considerably less swelling than the other alloys. This is attributed to the fine Mg₂Si precipitate in the 6061 alloy, whereas the others are basically solid solution alloys.

30. Nondestructive Test Development

We continued analytical studies of eddy-current phenomena with emphasis on development and use of computer programs to solve specific problems. Phase-sensitive eddy-current instrumentation was stabilized at high frequencies.

Improved models and experimental techniques for flaw characterization by ultrasonic frequency analysis were developed and confirmed on test specimens containing artificial flaws. The acousto-optic equipment was modified and stabilized to allow studies of schlieren, Bragg diffraction, and holographic techniques with less concern about loss of optical alignment.

Several combinations of cladding and base materials were studied by scattering and fluorescence generated by ^{147}Pm radiation. To increase accuracy and inspection speed, work was initiated with an x-ray unit and a mechanical scanner. Preliminary calibration

curves and resolution studies show promise for using closed-circuit television for interpretation of radiographs. We completed a conceptual design for a laboratory facility for neutron attenuation studies using ^{252}Cf .

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Part II. Fast Reactor Technology

13. Fast Breeder Reactor Oxide Fuels

A. L. Lotts   C. M. Cox

This program is being conducted to advance the technology of (U,Pu)O₂ as an LMFBR fuel. Determination of the properties and performance of sol-gel-derived oxide fuels fabricated by Sphere-Pac and pelletizing techniques is emphasized, but these fuels are also compared with other fuels, such as pellets from mechanically blended or coprecipitated oxide. The main objectives of our program are:

1. to establish the performance characteristics and limitations of (U,Pu)O₂ fuels fabricated by different processes,
2. to obtain a fundamental understanding of the mechanisms involved in the irradiation behavior of fuel elements incorporating these fuels,
3. to develop fabrication techniques that provide both economy and a product with optimized performance, and
4. to develop analytical models sufficiently accurate to optimize experimental design and to predict fuel element response to LMFBR conditions.

These objectives are being met through a program that includes fabrication of fuel with different structures, characterization of these by out-of-reactor methods, and irradiation under a variety of conditions. The emphasis is on irradiation testing, postirradiation examination of the various fuel structures, and evaluation in terms of performance models. We are utilizing such facilities as the Oak Ridge Research Reactor, the Transient Reactor Test Facility, the Experimental Breeder Reactor II, and the Engineering Test Reactor. The program includes instrumented and noninstrumented tests under steady-state, power cycling, and transient conditions. The interpretation of the results depends heavily upon the preirradiation character-

ization and quality assurance program on the fuels and upon correlations with the theoretical fuel modeling work.

This program also provides technology that applies to the Gas-Cooled Breeder Reactor, development for which is reported in Chap. 31. This is a joint program with the Chemical Technology Division, which prepares the sol-gel-derived fuel, and the Reactor Division, which conducts the irradiation tests in the ORR.

DEVELOPMENT OF FABRICATION PROCESSES

J. D. Sease

The objective of our (U,Pu)O₂ fabrication program is to develop processes by which mixed oxide fuel of controlled density and stoichiometry can be fabricated for irradiation tests. A large portion of this program has been the development of Sphere-Pac and sol-gel pellet fabrication techniques. The Sphere-Pac process was used to load approximately 175 in. of fuel for irradiation tests. Sol-gel-derived pellets with controlled densities from 84 to 97% of theoretical were fabricated for irradiation tests in EBR-II.

Sphere-Pac Development

R. A. Bradley   W. J. Lackey   J. D. Sease

The Sphere-Pac process uses low-energy vibration to infiltrate a close-packed bed of coarse microspheres (420–600 μ m) with fine microspheres (<44 μ m) to achieve packed bed densities 85% of theoretical.¹

1. R. B. Fitts, A. R. Olsen, and J. Komatsu, "Sphere-Pac Fabrication of Sol-Gel Nuclear Fuels," *Amer. Ceram. Soc. Bull.* 47(9), 844 (1968).

The density of fuel pins loaded by the Sphere-Pac process is a linear function of the coarse bed density,² which varies as much as 5% between pins.³ We conducted a statistically designed experiment to determine the source and magnitude of the variation in coarse bed densities.² The experiment covered a coarse bed density range from 57.6 to 61.3% of theoretical. An analysis of variance on the data led to the following conclusions:

- 1 we were more than 99% sure that there was a variation between batches,
- 2 there was not sufficient evidence to indicate a difference between operators nor between two samples from a particular batch, and
- 3 the standard deviation describing a single operator's ability to reproduce his work with the same sample of microspheres was 0.40.

We believe that most of the observed variation in coarse bed densities was caused by differences in the densities of the microspheres in different batches. This experiment showed that the density of the coarse bed from a given batch of microspheres can be reproduced within 1% if the loading conditions are properly controlled. Later we found that the feed rate and the time and amplitude of vibration had no significant effect on the density of the coarse bed.

Since the density of the microspheres has the greatest effect on the density of the coarse bed and thus on the final smear density, we conclude that altering the density of the microspheres is the most practical way of controlling the density of Sphere-Pac fuel pins. This conclusion was substantiated when we loaded 13 Sphere-Pac pins for the EBR-II, Series II irradiation

experiment. Even though we attempted to vary the smear density from 80 to 85% of theoretical, all 13 fuel pins had smear densities between 81.6 and 83.8% of theoretical.⁴

An alternate Sphere-Pac method, which incorporates all of the plutonium in the coarse fraction, has been proposed.^{5,6} This process offers several significant advantages over the conventional Sphere-Pac process, including a reduction in the number of steps required to load a fuel rod and decreased alpha contamination.

Pellet Development and Fabrication

R. A. Bradley

The objectives of this work are to develop methods of fabricating sol-gel (U,Pu)O₂ pellets and to produce pellets of controlled density and stoichiometry for irradiation tests. In addition to fabricating sol-gel (U,Pu)O₂ pellets we have procured mechanically mixed (U,Pu)O₂ pellets from WADCO and heat treated them to reduce sorbed gas to the specified limit.

The sol-gel process for making (U,Pu)O₂ pellets and methods of density control have been described.⁷ This process was used for fabricating 84 to 97%-dense pellets for the EBR-II, Series II irradiation experiment and 88 to 92%-dense pellets for the GCBR F-1 irradiation experiment replacement pins. The pellets fabricated during the past year are summarized in Table 13.1.

4 R. A. Bradley, W. J. Leonard, T. B. Lindemer, and W. H. Pechin, *Fuels and Materials Development Program Quart. Progr. Rept. Sept. 30, 1970*, ORNL-4630, pp. 13-15.

5 J. D. Sease, R. A. Bradley, C. R. Reese, W. H. Pechin, and A. L. Lotts, "Sphere-Pac and Pelletization of (U,Pu)O₂," pp. 323-41 in *Symposium on Sol Gel Processes and Reactor Fuel Cycles*, Gatlinburg, Tennessee, May 4-7, 1970, CONF-700502.

6 J. D. Sease and F. E. Harrington, "U-Fines - A New Concept in Microsphere Fuels," *Amer. Ceram. Soc. Bull.* **50**, 423 (1971).

7 R. A. Bradley, *Metals and Ceramics Div. Annu. Progr. Rept. June 30, 1970*, ORNL-4570, pp. 48-49.

2 R. A. Bradley and W. J. Lackey, *Fuels and Materials Development Program Quart. Progr. Rept. June 30, 1970*, ORNL-4600, pp. 5-7.

3 R. A. Bradley, *Fuels and Materials Development Program Quart. Progr. Rept. March 31, 1970*, ORNL-4560, pp. 6-7.

Table 13.1. (U,Pu)O₂ pellets fabricated for irradiation experiments

Irradiation experiment	Pellet configuration	Density (% of theoretical)	Oxygen-to-metal ratio
EBR-II, series II	Solid	84	1.96
	Solid	89.5	1.955, 1.98
	Solid	97	1.97
GCBR F-1 replacement pins	Annular ^a	92.3	1.94
	Annular ^a	92.3	1.98
	Solid ^a	88.6	1.98

^aDished end

Stoichiometry Control

R. A. Bradley T. B. Lindemer

Uranium-plutonium dioxide fuel for LMFBR applications is required to have an oxygen-to-metal ratio near 1.97. For some of our irradiation experiments ratios as low as 1.94 are required. It is not always easy to achieve these oxygen-to-metal ratios; therefore, we investigated the reduction of mixed oxide to the hypostoichiometric state.

We theoretically analyzed the reduction of $(U,Pu)O_2$ in flowing hydrogen. The reduction process is kinetically controlled and limited by the rate at which water vapor can be removed from the furnace. Using Markin's⁸ thermodynamic data, the following equation was developed to predict the time required for reduction to any oxygen-to-metal ratio.

$$t = \frac{11.208Nx}{f} \int_4^{V_{Pu}} H dV_{Pu},$$

where

t = time required to reduce $U_{1-x}Pu_xO_2$ to desired V_{Pu} ,

V_{Pu} = valence of plutonium,

N = moles of mixed oxide,

f = flow rate of H_2 in liters per unit time at STP, and

H = the average H_2/H_2O during an increment of reduction.

The integral $\int_4^{V_{Pu}} H dV_{Pu}$ has been evaluated as a function of V_{Pu} and reduction temperature and is given in Fig. 2 of ref. 9. The details of the kinetic analysis are described elsewhere.^{9,10} Using the knowledge gained in this study we have consistently obtained the oxygen-to-metal ratio required for various irradiation experiments.

We also investigated the reduction of $(U,Pu)O_2$ by the C-CO-CO₂ system. In this system it is important that the carbon be in close proximity to the mixed oxides; for example, less than 0.025 in. The reduction is then controlled by the rate of the reaction $C + CO_2 \rightleftharpoons 2 CO$.

The kinetic analysis and experimental data show that reduction by the C-CO-CO₂ system is much quicker than by flowing hydrogen.^{9,10} Also, much lower oxygen-to-metal ratios can be achieved than is practical by hydrogen reduction.

Fuel Pin Fabrication

R. A. Bradley J. H. Erwin
W. J. Leonard M. K. Preston¹¹

Fuel pins for irradiation testing in the ORR, ETR, and EBR-II were fabricated this year. We completed 19 unencapsulated fuel pins for a 37-pin EBR-II sub-assembly shared with Babcock and Wilcox Company.¹² We fabricated 12 fuel pins for irradiation in the ETR to provide fuel for the Chemical Technology Division's fuel reprocessing studies.¹³ We also loaded one fuel pin for irradiation in the ORR to study mechanical interaction between fuel and cladding during power cycling.¹⁴

Construction of Fuel Cycle Alpha Facility

R. A. Bradley

Our capability for working with plutonium and other alpha emitting materials was significantly improved by the construction of the Fuel Cycle Alpha Facility (FCAF). The FCAF, which replaces the Building 3019 Interim Alpha Facility, consists of two 24 X 48 ft and one 24 X 24 ft laboratories in Building 4508, Room 265. The FCAF is equipped with its own room ventilation and exhaust system and a separate glove box exhaust system which permits operation of glove boxes in a once-through purge mode or in conjunction with a gas purifier and recirculating system. A layout of the FCAF, showing the location of presently installed glove boxes, is shown in Fig. 13.1.

A 5-in. prototype coater for pyrolytic carbon coating microspheres for HTGR recycle is in laboratory 1. Operations there will not involve highly alpha-active materials. Principal operations in the two alpha laboratories will be:

Laboratory 2

1. preparation of uranium-plutonium oxide powder,

8. T. L. Markin, *Chem. Eng. Progr. Symp. Ser.* **80**, 43 (1967).
9. T. B. Lindemer and R. A. Bradley, *Kinetic Models for the Synthesis of $(U,Pu)O_{2-y}$ by Hydrogen-Reduction and Carbothermic Techniques*, ORNL-TM-3358 (April 1971).
10. T. B. Lindemer and R. A. Bradley, "Kinetic Models for the Synthesis of $(U,Pu)O_{2-y}$ by Hydrogen-Reduction and Carbothermic Techniques," accepted for publication in *Journal of Nuclear Materials*.

11. On loan from General Engineering Division.
12. R. A. Bradley, W. J. Leonard, and M. K. Preston, *Fuels and Materials Development Program Quart. Progr. Rept. Dec. 31, 1970*, ORNL-TM-3300, pp. 3-4.
13. R. A. Bradley, *ibid.*, pp. 4-6.
14. R. B. Fitts, R. L. Senn, and R. A. Bradley, *Fuels and Materials Development Program Quart. Progr. Rept. March 31, 1971*, ORNL-TM-3416, pp. 25-26.

Fig. 13.1. Fuel cycle alpha facility.

2. fabrication of uranium-plutonium oxide pellets,
3. heat treatment of plutonium-bearing oxide, carbides, or nitrides,
4. centerless grinding of ceramic fuel bodies,
5. loading of fuel rods,
6. fabrication of carbon-bonded HTGR fuel rods,
7. storage of fissile material.

Laboratory 3

1. metallography of alpha-active materials,
2. welding of fuel rods,
3. decontamination of fuel rods,

4. sodium and NaK bonding of fuels,
5. storage of fissile materials.

CHARACTERIZATION OF (U,Pu)O₂ FUELS

J. D. Sease J. M. Leitnaker

The preirradiation characterization of a fuel material is necessary for understanding the fabrication processes and for interpreting irradiation test results. Characterization includes both the examination of the fuel material as produced and the determination of basic properties of the fuel.

Analytical Chemistry

W. H. Pechin   R. A. Bradley   W. J. Lackey

The analytical techniques for determining water content and metallic impurities in (U,Pu)O₂ have been given considerable attention because of the highly variable results that have been obtained.

The specifications for (U,Pu)O₂ fuel require that the average moisture content be less than 30 ppm. It is determined by passing dry nitrogen over the specimen as it is heated to 900°C and measuring the amount of water released with a P₂O₅ electrolytic cell.

Moisture contents ranging from 7 to 60 ppm have been obtained for a single batch of mixed oxide. To determine the source of this variation, a statistically designed experiment was performed.¹⁵ We concluded that most of the variability was due to moisture-laden air introduced into the apparatus as the sample was loaded. The addition of an air lock for loading samples without introducing air into the analyzer reduced the variability to acceptable values.¹⁶

Metallic impurities in (U,Pu)O₂ have been determined by emission spectroscopy, spark source mass spectroscopy, and wet chemical analysis. The results have been highly variable, particularly for Fe, Cr, and Ni. Metallographic examination of the mixed oxide revealed metallic inclusions scattered throughout the samples. We believe that analysis of very small samples (<0.050 g) of the material containing impurities as a second phase leads to variable results. We now analyze for impurities using solutions obtained by dissolving an entire pellet; the results are considerably more reproducible.

Homogeneity of (U,Pu)O₂

R. A. Bradley   W. J. Lackey   W. H. Pechin

We reported previously the use of gamma-ray spectroscopy to determine quantitatively the ratio of plutonium to uranium in a batch of microspheres that had been found to be inhomogeneous by alpha autoradiography.¹⁷ We used gamma spectroscopy to analyze 11 additional batches that appeared by alpha

autoradiography to be uniform. These analyses showed that there was a slight variation in ratio from batch to batch, but within the limits of detection (about 0.5%), there was no variation from sphere to sphere within a batch.¹⁸

Microstructure of Sol-Gel (U,Pu)O₂ Pellets

R. A. Bradley   W. J. Lackey

The microstructure of the 84, 89, and 97%-dense sol-gel (U,Pu)O₂ pellets prepared¹⁹ for the EBR-II, Series II fuel pins is shown in Fig. 13.2. The microstructure of the 84%-dense pellets consisted of a very porous matrix with open, surface-connected porosity, regions of almost theoretically dense material dispersed throughout the matrix, and regions with an intermediate amount of closed porosity. This structure is typical of low-density pellets produced from sol-gel (U,Pu)O₂. The average grain size of these pellets was about 3 μm.

The 89 and 97%-dense pellets, which were made from powder whose properties had been altered by an oxidation-reduction treatment, contained a more uniform distribution of porosity. The 89%-dense pellets contained considerable closed porosity trapped inside grains in addition to porosity on the grain boundaries. The trapped porosity was a result of rapid grain growth during sintering in an oxidizing atmosphere. The 97%-dense pellets, which were made from the same powder as the 89%-dense ones but sintered in a reducing atmosphere, had very fine porosity on the grain boundaries and a relatively small number of larger pores scattered uniformly throughout the pellet. The small grain size, about 4 μm, and lack of trapped porosity are attributed to the reducing atmosphere.

Fission Product Behavior in Oxide Fuels

J. M. Leitnaker   L. A. Harris   J. P. DeLuca

Fission products in mixed oxides may cause several important effects. One of these is that they may interact directly with the cladding material. A second effect is that these fission products will affect the oxygen potential of the fuel, and, as a secondary result, the oxygen may react with the cladding material. A third effect is that the fission products differ in volume

15. R. A. Bradley and W. H. Pechin, *Fuels and Materials Development Program Quart. Progr. Rept. Dec. 31, 1970*, ORNL-TM-3300, pp. 8-10.

16. R. A. Bradley and W. H. Pechin, *Fuels and Materials Development Program Quart. Progr. Rept. March 31, 1971*, ORNL-TM-3416, pp. 3-5.

17. W. J. Lackey, R. A. Bradley, and W. H. Pechin, *Metals and Ceramics Div. Annu. Progr. Rept. June 30, 1970*, ORNL-4570, pp. 50-51.

18. R. A. Bradley, W. J. Lackey, and W. H. Pechin, *Fuels and Materials Development Program Quart. Progr. Rept. June 30, 1970*, ORNL-4600, pp. 11-12.

19. R. A. Bradley, *Metals and Ceramics Div. Annu. Progr. Rept. June 30, 1970*, ORNL-4570, p. 48.

Fig. 13.2. Microstructure of sol-gel $(U,Pu)O_2$ pellets for EBR-II series II irradiation experiment. (a) 84% dense, calcined in argon and sintered in $Ar-4\% H_2$, 3 μm grain size (b) 89.5% dense, calcined by oxidation-reduction and sintered in $Ar-10\% CO_2$, 16 μm grain size (c) 97% dense, calcined by oxidation-reduction, sintered in $Ar-4\% H_2$, 4 μm grain size Upper photos 200X, lower 1000X

from the parent fuel. This change in volume may cause increased fuel-cladding interaction. Our goal has been to define or measure these effects as accurately as possible.

Dissolution of rare-earth oxides in oxide fuels. Rare earths and yttrium use up to 60% of the oxygen released when mixed oxide fuel undergoes fissioning. The bound state of the oxygen is uncertain. For example, Johnson et al.²⁰ assumed that the rare earths dissolve largely as the sesquioxide. We have shown by two methods that $\text{EuO}_{1.5}$, which may be considered typical of the trivalent rare earths, dissolves in the fluorite lattice with consequent oxidation of the solid solution.

The first method used was direct measurement of sample weight gain. UO_2 and Eu_2O_3 , equilibrated at an oxygen potential defined by a CO -to- CO_2 ratio of 10 at 1000°C , were subsequently mixed, pressed into pellets, and reequilibrated in the same atmosphere. Substantial weight gains indicated that solution was accompanied by oxidation, approaching a composition $(\text{U,Eu})\text{O}_{2.00}$.

The second method was less direct but equally conclusive. We measured x-ray lattice parameters of coprecipitated urania-europia samples that varied in europium-to-uranium ratio and had been equilibrated at a CO -to- CO_2 ratio of 10. The parameters deviated from the line predicted²¹ for solution of Eu_2O_3 in fluorite lattices but agreed with the line predicted for $(\text{U,Eu})\text{O}_{2.00}$.

We constructed an apparatus to measure the weight change of $(\text{U,Eu})\text{O}_{2\pm x}$ samples in controlled gas atmospheres. Preliminary measurements indicate variations in oxygen-to-metal ratios of less than 0.04 over oxygen pressure from 10^{-22} to 10^{-7} atm at 1000°C . Improvement of the apparatus has made it possible to define the composition to ± 0.002 in oxygen-to-metal ratio and extend the temperature range of measurements to 1300°C . Calibration is currently under way.

Thermal expansion of $(\text{U,Eu})\text{O}_2$ – implication to $(\text{U,Pu})\text{O}_2$. Thermal expansion measurements of $(\text{U,Ce})\text{O}_{2.00}$ by Markin et al.²² showed a remarkable nonlinearity over a range of cerium-to-uranium ratios. Using techniques described in Chap. 12, we found this same nonlinearity by high-temperature x-ray diffraction for $(\text{U,Eu})\text{O}_2$ solid solutions at oxygen potentials

Fig. 13.3. Oxygen potentials of systems of interest in oxide fuel pins.

defined by CO_2 -to- CO ratios of 100 and 10. At the lower oxygen potentials the lattice size varied linearly with temperature.

The similarity between $(\text{U,Ce})\text{O}_2$ solid solutions and $(\text{U,Pu})\text{O}_2$ solid solutions²³ leads to questions about the thermal expansion of the fuel itself. Previous measurements on $(\text{U,Pu})\text{O}_2$ were made on samples prepared in hydrogen-nitrogen mixtures,²⁴ and thus undoubtedly substantial nitrogen was combined in the lattice.²⁵

The $(\text{U,Eu})\text{O}_2$ measurements thus assume a much larger importance in indicating a differing behavior of the metal ions at different oxygen potentials. The $(\text{U,Eu})\text{O}_2$ measurements also suggest that the fuel $(\text{U,Pu})\text{O}_2$ will have a linear rather than nonlinear expansion as suggested by the $(\text{U,Ce})\text{O}_2$ measurements.

Oxygen potentials determined by molybdenum in $(\text{U,Pu})\text{O}_2$ fuels. Fission product molybdenum, seen in metallic inclusions in irradiated fuel, can indicate the oxygen potential under reactor operating conditions. The oxygen potential is indicated by the extent of the reaction $\text{Mo}(\text{S, in inclusion}) + 2 [\text{O}] (\text{in fuel}) \rightleftharpoons \text{MoO}_2 (\text{S, in fuel})$. Figure 13.3 illustrates the relationship between oxygen potentials fixed by various CO -to- CO_2 ratios to that by the Mo/MoO_2 couple with molybdenum at unit activity and with MoO_2 at unit activity and at an activity of 3.4×10^{-3} . The variation of

20. C. E. Johnson, I. Johnson, and C. E. Crouthamel, "Fuel-Clad Chemical Interactions in Mixed Oxide UO_2 -20 w/o PuO_2 Stainless steel Clad Fast Reactor Fuel," paper presented at American Nuclear Society New Orleans Meeting, April 1971.

21. G. Brauer and H. Gradinger, *Z. Anorg. Allgem. Chem.* **276**, 209–26 (1954).

22. T. L. Markin, R. S. Street, and E. C. Crouch, *J. Inorg. Nucl. Chem.* **32**, 59–75 (1970).

23. T. L. Markin and E. C. Crouch, *ibid.*, 77–82.

24. T. B. Lindemer and R. A. Bradley, Oak Ridge National Laboratory, unpublished work.

25. J. Roth et al., *Trans. Amer. Nucl. Soc.* **10**, 457–58 (1967).

activity of molybdenum is reflected by variation of the molybdenum-to-ruthenium ratio in the fission product inclusions. Published results^{26,27} show this ratio to vary with location in the fuel pin and even more with different fuel samples, presumably because of their different initial oxygen potential. We have calculated the ratio for different fuel compositions and irradiation histories given by Olsen, Fitts, and Cox²⁸ and found wide variations. The calculation illustrates that shifts in fission product yields can affect the calculated oxygen potential dramatically. We conclude from these calculations that molybdenum can be used as a marker to measure the fuel's oxygen potential and that careful calculation of the fission product composition using the actual fuel pin history is necessary.

IRRADIATION BEHAVIOR

C. M. Cox   T. N. Washburn

We are determining the in-reactor properties and performance of (U,Pu)O₂ fuel pins as functions of fabrication form, porosity distribution, stoichiometry, and irradiation conditions. This program includes both fast and thermal flux irradiations and steady-state, cyclic, and transient power conditions. To obtain a fundamental understanding of the irradiation behavior of these fuels, we concentrate on well-characterized operating conditions, detailed postirradiation examinations, and analysis in terms of fuel performance models.

Fast Flux Irradiation Tests

A. R. Olsen

The ORNL oxide fuels irradiations in the EBR-II currently involve two series of tests. All five pins in the encapsulated Series I group containing Sphere-Pac (²³⁵U-20% Pu)O₂ were irradiated initially to a calculated peak burnup of 6% FIMA. Two pins were examined, and the other three are being irradiated toward a target peak burnup level of 11.8% FIMA. A revised safety analysis for this extended testing has been issued.²⁹ Unencapsulated pins are being irradiated in

the Series II tests.³⁰ We fabricated 19 of the pins in the 37-pin subassembly, while the other 18 were fabricated by the Babcock & Wilcox Company (B&W). During the past year we assumed responsibility for the irradiation test and postirradiation examination of the entire series. Details of the testing program and the individual pin operating conditions are reported in the data package for these tests. All fuels are (²³⁵U-20% Pu)O₂. The ORNL pins contain sol-gel-derived fuel, while the B&W pellets and Vi-Pac shards were processed from coprecipitated powder. The tests have been coordinated to provide data for

1. the evaluation of particulate fuels (Sphere-Pac and Vi-Pac) for LMFBF use, and
2. the comparison of performance characteristics of pellets fabricated from coprecipitated or sol-gel-derived powders.

The emphasis in these tests is on the effects of fuel form and void distribution on the release of fission gas, fission product redistribution, and mechanical and chemical interactions of fuel and cladding. A linear heat rate of 14 kW/ft, cladding temperatures of 550 to 650°C, and burnup levels to 100,000 MWd/metric ton are planned.

The postirradiation examination is continuing for the two Series I pins that have completed their scheduled irradiation. The details of the examination are reported as they are obtained.³¹⁻³³ The operating conditions and available performance data are summarized in Table 13.2. The significant results to date follow.

1. We found no fuel-cladding mechanical interaction, since the diametral changes are essentially those predicted³⁴ for fast-flux-induced void swelling in the stainless steel cladding. The annealed type 304 cladding swelled almost twice as much as the annealed type 316 cladding.

2. The fission gas release rate of 80% agrees with other EBR-II oxide fuel tests but is higher than that

30. A. R. Olsen et al., *Preirradiation Data for ORNL Series II and B & W Oxide Fuel Tests in EBR-II*, ORNL-TM-3446, in preparation.

31. A. R. Olsen, *Fuels and Materials Development Program Quart Progr Rept Sept 30, 1970*, ORNL-4630, pp 27-29.

32. A. R. Olsen, *Fuels and Materials Development Program Quart Progr Rept Dec 31, 1970*, ORNL-TM-3300, pp 15-19.

33. A. R. Olsen, J. L. Miller, and D. R. Cuneo, "Fast Flux Irradiation Tests," *Fuels and Materials Development Program Quart Progr Rept March 31, 1971*, ORNL-TM-3416, pp. 15-20.

34. T. T. Claudson, R. W. Barker, and R. L. Fish, *Nucl Appl Technol* 9, 10-23 (1970).

26. D. R. O'Boyle, F. L. Brown, and J. E. Saneck, *J Nucl Mater* 29, 27-42 (1969).

27. J. I. Bramman et al., *J Nucl Mater* 25, 201-15 (1968).

28. A. R. Olsen, R. B. Fitts, and C. M. Cox, *Analysis of the Validity of Fast Reactor Fuel Tests in Existing Test Reactors*, ORNL-TM-2716 (October 1969).

29. A. R. Olsen and F. J. Homan, *Experiment Description and Hazards Evaluation for the Series I ORNL Oxide Fuels Irradiation in EBR-II*, ORNL-TM-2635 supplement (June 1970).

Table 13.2. Fabrication and operating data for pins with irradiation completed in EBR-II series I oxide fuel tests

Conditions and results	Pin S-1-A	Pin S-1-E
Cladding, type of stainless steel	304	316
Fuel smear density, % of theoretical	83	82
Linear heat rate, kW/ft at 193 MeV/fission		
Peak	13.7	13.5
Average	12.2	12.0
End-of-life peak	12.7	12.5
Peak cladding temperatures, °C		
Inner surface	570	570
Outer surface	540	540
Equivalent days at full power	234.1	234.1
Peak cladding fluence, neutrons/cm ²		
Total	4.2×10^{22}	4.2×10^{22}
>0.1 MeV	3.6×10^{22}	3.6×10^{22}
Fuel burnup, % FIMA by ¹⁴⁸ Nd analysis		
Peak	5.87 ^a	5.74
Average	5.24 ^a	5.12
Fission gas release, %		80
Peak cladding diametral change, %	0.71 ± 0.16	0.40 ± 0.08
Peak capsule diametral change, %	0.29	0.32

^aPredicted from EBR-II fission rates, analysis not yet available.

found for similar fuel irradiated in a thermal flux.³⁵ This difference was expected since a higher percentage of the fuel in the fast flux tests operated above 1700°C, where essentially all of the gas is released, and self-shielding causes more fissions in the cooler regions in the thermal flux tests.

3. There was no evidence of significant fuel-cladding chemical interaction even at cladding inner surface temperatures up to 570°C. Figure 13.4 shows typical transverse cross sections from the peak heat rate region in both pins, together with higher magnification views of the interfaces. We have seen only minor uniform reactions and no intergranular penetration of the cladding in these tests or in thermal flux tests with Sphere-Pac fuels. This lack of penetration has been confirmed by microprobe analysis, which shows no fission products in the cladding grain boundaries. This result is compared with those of other irradiation tests in "Fuel-Cladding Chemical Interaction" later in this chapter.

35. A. R. Olsen, *Trans. Amer. Nucl. Soc.* 13, 32–33 (1970).

Transient Irradiation Tests

C. M. Cox   D. R. Cuneo³⁶   E. J. Manthos

Destructive examinations and final evaluations were completed for the transient irradiation tests previously reported.³⁷ Six fuel pins containing unirradiated sol-gel (U,Pu)O₂ were subjected to power transients, as described in Fig. 13.5, at the Transient Reactor Test Facility (TREAT). No failure occurred, even though 50 vol % of the fuel melted in the peak power regions of two Sphere-Pac pins. Figure 13.6 shows the as-polished microstructures at the fuel column midplanes after the tests. The large circular voids are believed to be bubbles formed by coalescence of adsorbed gases present from fabrication. While appreciable restructuring in four pins is evident, examination of etched microstructures indicated that fuel melted only in pins TR-2A and TR-2B. Flux peaking caused localized melting at the ends of the fuel columns of pins TR-1A and Tr-1B.

Operating and examination data are summarized in Table 13.3. Note that appreciable grain growth was observed in all pins except TR-1C. Although the fuel pins showed no significant dimensional changes, neutron radiographic and destructive examinations showed extensive fuel relocation within the cladding. This included fuel column separations, densification during cooling from the molten state, axial migration, and the previously noted large bubbles.

A gap formed between the Sphere-Pac fuel and cladding by a combination of sintering and shrinkage during cooling from the melt. The influence of fuel column separations on length changes tended to be offset by sintering and shrinkage. Pellet fuel pins showed occasional separations at pellet interfaces, apparently due to ratcheting. The melt volume corresponds to a fuel-to-cladding heat transfer coefficient of 3.4 W cm⁻² °C⁻¹ or greater for the Sphere-Pac fuel pins, at least double the steady-state value reported by Fitts in a later section of this chapter.

Comparison with data reported by other investigators indicates that for the types of transients considered in this work, Sphere-Pac fuel of the same smear density and sol-gel and coprecipitated pellets behave equivalently.³⁸

36. On loan from the Reactor Chemistry Division.

37. C. M. Cox, D. R. Cuneo, E. J. Manthos, and R. E. Adams, *Metals and Ceramics Div. Annu. Progr. Rept. June 30, 1970*, ORNL-4570, pp. 58–59.

38. C. M. Cox, D. R. Cuneo, and E. J. Manthos, *Performance of Sphere-Pac and Pelletized (U,Pu)O₂ During Severe Overpower Transients*, ORNL-TM-3384 (July 1971).

Fig. 13.4. Transverse metallographic sections from the peak heat rate section of EBR-II series I pins containing $(^{235}\text{U}-20\% \text{Pu})\text{O}_2$ fuel.

Uninstrumented Thermal Flux Irradiation Tests

A R Olsen D R Cuneo³⁶

The purpose, scope, conditions, and some results have been given³⁹ with detailed descriptions of the 11 numbered capsules of this series. The results of the tests irradiated to low and intermediate burnup levels have been presented^{40,41}

Capsule 43-113 was removed from the reactor at a calculated burnup of 10% FIMA and awaits examination

Capsules 43-117, 43-118, and 43-119 are the first capsules that we have irradiated with mechanically mixed $(\text{U,Pu})\text{O}_2$ pellet fuel. Although the tests are primarily for head-end chemical processing studies, we removed one metallographic section each from three of the four pins in capsule 43-117. This capsule was

39 A R Olsen and D R Cuneo, *Metals and Ceramics Div Annu Progr Rept June 30 1970* ORNL-4570 pp 53-55

40 A R Olsen, C M Cox, and R B Fitts, *Trans Amer Nucl Soc* 12, 605-6 (1969)

41 A R Olsen, *Trans Amer Nucl Soc* 13, 32-33 (1970)

Fig. 13.5. Time variation of heat rate at fuel column midplane in transient experiments.

irradiated at a peak linear heat rate of 13 kW/ft to calculated burnup of 1.3% FIMA. Neutron radiographs of these pins showed: (1) interrupted central void formation in the top and bottom pins, which operated at linear heat rates of 8 to 10 kW/ft, (2) evidence that the "central" void is wandering off the fuel axis, and (3) a separation between the $^{238}\text{UO}_2$ insulator pellet and the top fuel pellet in the cooler outer regions of the pellet. This separation is not evident near the central

void. The metallographic examination is scheduled for next year.

We have continued the examination of all tests in this series, with emphasis on electron microscopy and microprobe analysis. The data have been used to improve our understanding of in-reactor fuel performance and to develop mathematical models to predict such performance. This is discussed in subsequent sections.

Fig. 13.6. Transverse sections taken from the midlengths of fuel pins irradiated in TREAT.

Table 13.3. Summary of operating and examination data for ORNL TREAT capsules^a

Fuel pin	TR-1A	TR-1B	TR-1C	TR-2A	TR-2B	TR-2C
Operating data ^b						
Fuel pin temperature before transient, °C	410	449	414	400	436	410
Peak instantaneous linear power, kW/ft	175	155	118	178	164	103
Energy release, cal/g	390	380	292	525	491	313
Postirradiation examination						
Overall fuel column length change, ^c mils	90	-20	-30	-60	-30	40
Radius of fuel central void, ^b mils	0	0	0	17	28	0
Volume of fuel melting, ^b %	0	0	0	50 ^{±2}	51 ^{±2}	0
Radius of equiaxed grain growth, ^b mils	94	111	0	111	111	78
Fuel-cladding radial gap, ^b mils	2.4 ^{±1.2}	3 ^{±3}	1.5 ^{±1}	4.4 ^{±2.6}	3.7 ^{±3}	1.2 ^{±1.2}

^aFabrication data and preliminary results are given in Table 15.7, p. 58, ORNL-4570.^bAt fuel column midplane.^cBased on neutron radiographs; estimated accuracy, ±20 mils.

ETR Instrumented Tests

T. N. Washburn   R. A. Buhl

The ETR instrumented tests are designed to determine the performance of mixed oxide fuel under simulated LMFBR design operating conditions. The first two capsules (43-120 and 43-121) are being irradiated to investigate fuel swelling and fuel-cladding chemical interactions of Sphere-Pac and pellet (U,Pu)O₂ fuels. These capsules have been irradiated to a peak burnup of approximately 4.4% FIMA (as of May 9, 1971). Each capsule contains four fuel pins, with two thermocouples at the axial midplane of each pin. The peak cladding inside surface temperature is 540°C with the reactor at 175 MW. All thermocouples appear to be operating satisfactorily.

The second set of tests in this series consists of three instrumented capsules, each designed to measure fission gas pressure during testing and each containing one fuel pin with a 20-in.-long column of fuel. One capsule contains FTR-type pellets of the highest permissible density (94% of theoretical), the second contains FTR pellets of the lowest permissible density (88% of theoretical), and the third contains a packed bed of Sphere-Pac U-fines fuel. In the latter fuel, all the plutonium is contained in the coarse fraction (approx 400 μ m diam), and a fine fraction (<44 μ m diam) of depleted UO₂ is infiltrated into the coarse bed.

Hardware for the three capsules has been machined, inspected, and cleaned. The FTR pellets have been received from WADCO and will be completely characterized.

ORR Instrumented Thermal Performance Tests

R. B. Fitts

The ORR instrumented tests are designed⁴² to monitor the thermal performance of fuel pins as they operate in the Oak Ridge Research Reactor Poolside Facility.⁴³ The temperatures of the cladding and fuel center line and the rates of heat generation are continuously monitored and recorded. The general results from the first three capsules were reported last

year.⁴⁴ They showed that within $\pm 8\%$ the central temperature developed in pellet and Sphere-Pac fuels is the same at identical operating conditions.

The fuel microstructures developed in the pellet and Sphere-Pac fuel pins from capsule SG-3 have been analyzed in detail.^{45,46} A typical cross-section from each fuel pin is shown in Fig 13.7 with the calculated⁴⁶ temperature profiles superimposed on the fuel structures. The first discernible outlining of the grain boundaries in both fuels occurs at 1300°C, and complete restructuring takes place above 1700°C.

This analysis has also led to a preliminary conclusion that the fuel-to-cladding thermal conductance in a Sphere-Pac pin ($1.93 \text{ W cm}^{-2} \text{ }^{\circ}\text{C}^{-1}$) is higher than that in a pellet fuel pin ($0.73 \text{ W cm}^{-2} \text{ }^{\circ}\text{C}^{-1}$) with a small (0.0015 in. radial) initial fuel-cladding gap. This conclusion is based upon small differences in the measured heat generation rates and temperatures for the two fuel pins, and, although we believe these differences to be real, we have begun to statistically analyze the data to assess the significance of these measured differences.

The chemical compatibility of stainless steel cladding with the (U,Pu)O₂ fuels was better for Sphere-Pac than pellet fuel.⁴⁷ This observation was supported by the results from the pellet and Sphere-Pac fuels tested in the SG-3 capsule. Although the test times and fuel burnup were low in this test, the pellet fuel pin contained several areas of very localized cladding attack,⁴⁶ whereas the Sphere-Pac fuel pin contained no such areas.

The performance of the tungsten-rhenium thermocouples used in these tests was generally good, although at 2000°C some chemical attack was observed on the wires and sheaths. This attack appears to be a result of the vaporization of oxides of tungsten and rhenium.⁴⁸

42 R. B. Fitts and V. A. DeCarlo, *Metals and Ceramics Div Annu Progr Rept June 30, 1968*, ORNL-4370, pp. 145-49.

43 D. B. Trauger, *Some Major Fuel Irradiation Test Facilities of the Oak Ridge National Laboratory*, ORNL-3574 (April 1964).

44 R. B. Fitts, V. A. DeCarlo, and D. R. Cuneo, *Metals and Ceramics Div Annu Progr Rept June 30, 1970*, ORNL-4570, pp. 56-57.

45 R. B. Fitts, V. A. DeCarlo, and D. R. Cuneo, *Fuels and Materials Development Program Quart Progr Rept. Sept 30, 1970*, ORNL-4630, pp. 35-36.

46 R. B. Fitts, E. L. Long, Jr., and J. L. Miller, Jr., *Fuels and Materials Development Program Quart Progr Rept Dec 30, 1970*, ORNL-TM-3300, pp. 23-29.

47 C. M. Cox, R. B. Fitts, A. R. Olsen, and E. L. Long, Jr., *Trans. Amer. Nucl. Soc.* **14**, 173-75 (1971).

48 R. B. Fitts, J. L. Miller, Jr., and E. L. Long, Jr., "Observations on Tungsten-Rhenium Thermocouples used in Reactor in (U,Pu)O₂ Fuel Pins," to be published in the Transactions of the 5th Symposium on Temperature, its Measurement and Control in Science and Industry, held in Washington, D.C., June 21-24, 1971.

Fig. 13.7. Fuel restructuring in ORR instrumented tests of $U_{0.8}Pu_{0.2}O_{1.99}$. The structure of Sphere-Pac and pellet fuel is compared with calculated temperature profiles from the type 304 stainless steel cladding to the inner surface of the annular fuel.

Fuel-Cladding Mechanical Interaction Tests

R. B. Fitts   B. Fleischer   R. L. Senn⁴⁹

This series of irradiation tests⁵⁰ is intended to measure in-reactor the axial extension of the fuel column and cladding and the internal gas pressure developed in LMFBR-type fuel pins during operation under carefully controlled prototypic LMFBR power and temperature conditions. The tests, lasting for 1 to 2 years and producing burnups in the $(U,Pu)O_2$ fuels of 5 to 9%, will include programmed power cycles and occasional overpower cycles. The measurements will provide information on the frequency and mode of fuel-cladding mechanical interaction and the buildup of fuel pin internal gas pressure during irradiation. This

information is important to the economics and safety of the LMFBR.

The design^{51,52} and fabrication^{53,54} of the first capsule, which contains a prototypic Fast Test Reactor fuel pin (except for fuel length), is nearly complete. This capsule will begin operation in the ORR poolside facility in June 1971.

49. Reactor Division.

50. R. B. Fitts, J. D. Jenkins, J. G. Morgan, and R. L. Senn, *Metals and Ceramics Div. Annu. Progr. Rept. June 30, 1970*, ORNL-4570, p. 60.

51. R. B. Fitts, R. L. Senn, J. G. Morgan, and J. D. Jenkins, *Fuels and Materials Development Program Quart. Progr. Rept. June 30, 1970*, ORNL-4600, pp. 58-63.

52. R. B. Fitts and R. L. Senn, *Fuels and Materials Development Program Quart. Progr. Rept. Sept. 30, 1970*, ORNL-4630, pp. 36-38.

53. R. B. Fitts and R. L. Senn, *Fuels and Materials Development Program Quart. Progr. Rept. Dec. 31, 1970*, ORNL-TM-3300, pp. 29-33.

54. R. B. Fitts, R. L. Senn, and R. A. Bradley, *Fuels and Materials Development Program Quart. Progr. Rept. March 1971*, ORNL-TM-3416, pp. 25-26.

ANALYSIS OF FUEL ELEMENT PERFORMANCE

C. M. Cox

We are developing analytical models for predicting and evaluating the performance of LMFBR fuel pins and are examining irradiated fuel pins in detail. The models have emphasized the thermal, chemical, and mechanical performance of the fuel elements, particularly during startups, power cycles, and transients. This work includes direct support of the irradiation testing program in terms of optimizing experimental designs, interpreting results, and extrapolating these results to LMFBR conditions. Irradiated fuels are characterized in terms of redistribution of fuel components, porosity, and fission products and the quantitative identification of chemical interactions of fuel and cladding. This involves electron microscopy, electron microprobe analysis, and quantitative metallography.

Performance Model Development

F. J. Homan

The FMØDEL code described last year⁵⁵ was essentially a steady-state performance model, which we had begun to modify for power cycling calculations. This modification is now complete, and the code is suitable for steady-state, power cycling, and limited transient applications. Rapid cooldowns and other off-normal operating conditions can also be evaluated. In addition, the reactor power history can now be followed in detail. The empirical fuel restructuring model used previously⁵⁶ has been discarded in favor of a dynamic model based on a vaporization-condensation mechanism of pore migration.⁵⁷ Other additions to FMØDEL during the past year include Lackey's treatment of grain growth⁵⁸ and plutonium redistribution,⁵⁹ a fuel crack-

ing model,⁶⁰ and improvement of the cladding mechanical model to include flux enhanced creep.⁶¹

FMØDEL has been used recently in a variety of applications. First was the modeling round robin exercise,⁶² where the performance characteristics of a number of pins were predicted by several AEC contractors, and the results were compared. Then a summary of comparisons between predicted and measured fuel pin behavior was presented at the American Nuclear Society topical meeting on Fast Reactor Fuels.^{63,64} Included in the comparisons were fuel pin diametral expansions, restructuring, center-line temperatures, and porosity distributions. Figure 13.8 compares measured and predicted diametral expansions, and Fig. 13.9 measured and predicted fuel restructuring for a series of fuel pins irradiated by the General Electric Company⁶⁵ in EBR-II. These fuel pins had fuel densities ranging from 84 to 98% of theoretical and operated with peak heat rates of 10 to 17 kW/ft to burnups of about 50,000 MWd/metric ton. Most recently, FMØDEL was used to predict the results of the PNL-19 heat rate to melting experiment.⁶⁶

FMØDEL currently exists as two versions. A single-node version is used in the detailed analysis of one axial section of fuel. A multinode version calculates performance at several axial positions. The multinode version also has the capabilities of the single-node version, but computer running times may be excessive for a very complex case involving fuel-cladding mechanical interaction and perhaps a detailed following of the reactor history. For this reason the multinode version will be most useful in broader, less detailed analyses.

Electron Microscopy of Irradiated (U,Pu)O₂

W. J. Lackey

Replica electron microscopy of irradiated (U,Pu)O₂ is being conducted to improve our understanding of

55. F. J. Homan, *Metals and Ceramics Div. Annu. Progr. Rept. June 30, 1970*, ORNL-4570, p. 68.

56. C. M. Cox and F. J. Homan, *PRØFIL - A One-Dimensional FØRTRAN IV Program for Computing Steady-State Temperature Distributions in Cylindrical Ceramic Fuels*, ORNL-TM-2443 (March 1969); Addendum (August 1969).

57. F. J. Homan, *LMFBR Fuel Cycle Studies Progress Report for December 1970*, No. 22, ORNL-TM-3281, pp. 56-62.

58. J. L. Miller, Jr., and W. J. Lackey, *LMFBR Fuel Cycle Studies Progress Report for January 1971*, No. 23, ORNL-TM-3312, pp. 101-3.

59. W. J. Lackey, *LMFBR Fuel Cycle Studies Progress Report for July 1970*, No. 17, ORNL-TM-3095, pp. 61-65.

60. F. J. Homan, *LMFBR Fuel Cycle Studies Progress Report for September 1970*, No. 19, ORNL-TM-3180, pp. 72-73.

61. F. J. Homan, *LMFBR Fuel Cycle Studies Progress Report for March 1971*, No. 25, ORNL-TM-3375, pp. 65-71.

62. F. J. Homan, *Oak Ridge National Laboratory Solutions to a Modeling Round-Robin Exercise*, ORNL-TM-3360 (in press).

63. F. J. Homan, W. J. Lackey, and C. M. Cox, *Comparison Between Predicted and Measured Fuel Pin Performance*, ORNL-TM-3386 (May 1971).

64. F. J. Homan, W. H. Bridges, W. J. Lackey, and C. M. Cox, *Trans. Amer. Nucl. Soc.* 14 (suppl 1), 8-10 (April 1971).

65. R. C. Nelson et al., *Performance of Plutonium-Uranium Mixed-Oxide Fuel Pins Irradiated in a Fast Reactor (EBR-II) to 50,000 MWd/Te*, GEAP-13549 (August 1969).

66. F. J. Homan et al., "Heat Rate to Melting Predictions," *LMFBR Fuel Cycle Studies Progr. Rept. June 1971*, No. 28, ORNL-TM-3487 (in press).

Fig. 13.8. Postirradiation profilometer traces and ORNL-predicted expansions for five fuel pins from General Electric F-2 series.

Fig. 13.9. Summary of comparisons between predicted diameters for central void, columnar, and equiaxed grain regions.

restructuring, fuel swelling, and fission gas release. Previously we reported⁶⁷ the examination of fuel irradiated to a burnup of 0.7% FIMA. Similar fuel after irradiation in the ETR with a cladding inner surface temperature of about 370°C at a time-averaged linear heat rate of 14 kW/ft to a burnup of 4.2% FIMA is shown in Fig. 13.10. The microstructure of the fuel immediately adjacent to the cladding appears to be unchanged from that of the unirradiated material. This is strong evidence that intergranular pores as large as 0.2 μm in diameter do not disappear during irradiation.⁶⁸ This is not to say that a large number of considerably smaller fission gas bubbles do not disappear as a result of resolution processes. There were indications that fission gas bubble migration and coalescence were influenced by movement of columnar grain boundaries perpendicular to the thermal gradient as well as by the presence of subgrains 1 to 3 μm across within the equiaxed grain region.^{68,69}

(U,Pu) O_2 Grain Growth

W. J. Lackey R. A. Bradley

Because of the influence that grain size is expected to have on release of fission gas, fuel swelling, and Nabarro-Herring creep of (U,Pu) O_2 , we investigated the

67. W. J. Lackey, *Metals and Ceramics Div. Annu. Progr. Rept. June 30, 1970*, ORNL-4570, pp. 68–69.

68. W. J. Lackey, *LMFBR Fuel Cycle Studies Progr. Rept. April 1971, No. 26*, ORNL-TM-3412, pp. 79–83.

kinetics of in-reactor and out-of-reactor grain growth.^{69,70} The size of the equiaxed grains was determined as a function of radial position for three Sphere-Pac $\text{U}_{0.85}\text{Pu}_{0.15}\text{O}_{2.00}$ fuel pins after irradiation in the ETR. The initial grain size of the fuel was 1.2 μm . Data for two low-burnup pins were combined and analyzed as shown in Fig. 13.11. The least-squares equations given in the figure relate the observed grain size in microns (D) to the initial grain size (D_0), the irradiation time in hours (t), and the irradiation temperature in degrees centigrade (T). In the higher temperature region, solid fission products or gas bubbles apparently retard the rate of grain growth. The low activation energies indicate that in-reactor grain growth is not nearly as temperature dependent as out-of-reactor grain growth of UO_2 and ThO_2 . Comparisons of the grain size after a burnup of 4.2% FIMA with the grain size of the two low burnup pins showed that grain growth was not complete at the conclusion of the low burnup irradiations.

Out-of-reactor isothermal annealing of archive fuel resulted in extensive agglomeration of porosity in conjunction with grain growth. In addition, annealing at 1550°C apparently caused the fuel density to actually decrease. Such a decrease in density is unusual, but it has been observed for ThO_2 isothermally annealed out-of-reactor.⁷¹ Thus, this mechanism of swelling may be a contributing factor to fuel swelling in the equiaxed grain region of oxide fuel pins.

Actinide and Oxygen Redistribution in Irradiated (U,Pu) O_2

W. J. Lackey D. K. Bates⁷²
J. L. Miller, Jr. A. R. Olsen

Because of the anticipated influence of component redistribution on the thermal and compatibility behavior of fast reactor fuel pins, we have measured^{73,74}

69. W. J. Lackey, *Fuels and Materials Development Program Quart. Progr. Rept. March 31, 1971*, ORNL-TM-3416, pp. 33–38.

70. W. J. Lackey, *Fuels and Materials Development Program Quart. Progr. Rept. Sept. 30, 1970*, ORNL-4630, pp. 47–54.

71. K. H. McCorkle and C. S. Morgan, *Metals and Ceramics Div. Annu. Progr. Rept. June 30, 1970*, ORNL-4570, p. 26.

72. Summer employee sponsored by Oak Ridge Associated Universities.

73. J. L. Miller, Jr., and W. J. Lackey, *Fuels and Materials Development Program Quart. Progr. Rept. March 31, 1971*, ORNL-TM-3416, pp. 39–44.

74. W. J. Lackey, A. R. Olsen, and J. L. Miller, Jr., "Actinide Redistribution in Irradiated (U,Pu) O_2 ," *LMFBR Fuel Cycle Studies Progr. Rept. May 1971, No. 27*, ORNL-TM-3456, in press.

Fig. 13.10. Selected-area replica electron micrographs of irradiated $\text{U}_{0.85}\text{Pu}_{0.15}\text{O}_{2.00}$.

Fig. 13.11. Grain growth of $U_{0.85}Pu_{0.15}O_2$ in-reactor.

the radial distribution of uranium and plutonium as well as analytically modeled⁷⁵⁻⁷⁷ actinide and oxygen redistribution that occurs during irradiation of $(U,Pu)O_2$. Both electron microprobe⁷³ and alpha autoradiography^{75,76} studies showed that fuel that deposited from vapor in the region of transition from columnar to equiaxed grains was rich in uranium. This is strong evidence, at least for stoichiometric fuel, that

75. A. R. Olsen, R. B. Fitts, and W. J. Lackey, "In-Reactor Restructuring Temperatures and Kinetics for $(U,Pu)O_2$," paper presented at the Conference on Fast Reactor Fuel Element Technology, New Orleans, April 13-15, 1971, American Nuclear Society.

76. W. J. Lackey, A. R. Olsen, J. L. Miller, Jr., and D. K. Bates, *Trans. Amer. Nucl. Soc.* **14**, 180-82 (1971).

77. W. J. Lackey, "Actinide Redistribution in Irradiated $(U,Pu)O_2$," *LMFBR Fuel Cycle Studies Progr. Rept. June 1971*, No. 28, ORNL-TM-3487, in press.

actinide redistribution occurs by an evaporation-condensation mechanism.

The analytical model is kinetic. The commonly observed depletion in uranium near the central void is accounted for by the formation and subsequent transport down the temperature gradient of a vapor rich in uranium compared to the initial solid. The actinide composition of each of a set of radial increments is calculated as a function of time from a series of calculations of the quantity and plutonium-to-uranium ratio of the material that condenses into and evaporates from the increment during a short time period. Contrary to what occurs for slightly substoichiometric and hyperstoichiometric fuel, the model predicts preferential evaporation of plutonium and thus concentration of uranium at the central void for appreciably hypo-stoichiometric material.

Radial Porosity Distribution and Its Influence on the Fuel Temperature Profile

W. J. Lackey   F. J. Homan   T. M. Kegley, Jr.

Knowledge of the radial porosity distribution of the fuel as a function of time is necessary to accurately calculate fuel temperatures, creep rate, and other structure-sensitive properties. We measured⁷⁸ the radial porosity profile for an irradiated (U,Pu)O₂ fuel pin and developed a computer model that calculates⁷⁹ the porosity profile based on the evaporation-condensation mode of material transport down a temperature gradient. Additionally, we determined the influence of the porosity profile on fuel temperatures.⁸⁰

The measured and predicted porosity profiles are shown to compare favorably in Fig. 13.12. The columnar grain region is shown to be considerably more porous than previously generally believed. The calculated fuel center temperature was 200°C higher when based on the observed porosity distribution rather than the previously generally assumed three-zone porosity distribution model.

Fuel-Cladding Chemical Interaction

R. B. Fitts   A. R. Olsen
C. M. Cox   E. L. Long, Jr.

Chemical interactions between mixed oxide fuel, fission products, and cladding materials may be a major factor limiting the life of fuel rods in oxide fueled fast breeder reactors. We have examined in- and out-of-reactor tests at ORNL and the available literature for evidence of such chemical interactions and have summarized our findings^{81,82}. An overall summary of this information is given in Fig. 13.13. The ORNL Sphere-Pac data, represented by the diamond symbols, are obviously well below the data from other sites for pellet

and Vi-Pac fuels. The principal conclusions from this work follow.

1. Stainless-steel-clad mixed-oxide fuel pins fabricated with Sphere-Pac fuel have shown no fuel-cladding chemical interaction, in marked contrast to some fuel pins made with pellet fuels and operated under the same conditions.
2. Fuel-cladding chemical interaction is primarily due to oxidation of the cladding material.
3. Hastelloy X appears to be able to operate at 50 to 100°C higher temperature than stainless steel without excessive fuel-cladding chemical interaction.

Discrete Element Analysis of Cladding Deformation

B. R. Dewey⁸³

As a specialized form of finite element stress analysis, the discrete element method was developed and programmed⁸⁴ for hollow cylindrical solids subjected to pressure and thermal loading. The solution allows arbitrary radial variation of mechanical properties and temperature, computes elastic and inelastic stresses and displacements, and predicts time-dependent deformation based on empirical creep laws. This work was undertaken to extend the method to axial as well as radial variation of temperature, loading, and material properties. The two-dimensional loading is of particular interest at fuel element spacers, where it cannot be analyzed with the finite difference method used in the FMØDEL code.

Mechanical Properties of Stainless Steel Tubing

R. W. Swindeman   R. D. Waddell, Jr.

Exploratory tests were performed on annealed and cold-worked type 316 stainless steel tubing in support of the fuel element modeling activity. The purpose was to gain some insight regarding the response of 316 stainless steel under conditions that are not being investigated elsewhere but are anticipated during start-up of a fast breeder reactor. Into this category fall: (1) low-strain-rate tensile conditions, which may result from fuel thermal expansion straining the cladding, (2) relaxation of thermally induced stresses, and (3) creep at high stresses under changing thermal and load conditions. For a "low-strength" heat of type 316

78. W. J. Lackey and T. M. Kegley, Jr., *Fuels and Materials Development Program Quart Progr Rept Dec 31, 1970*, ORNL-TM-3300, pp 40-43.

79. F. J. Homan, *Fuels and Materials Development Program Quart Progr Rept Dec 31, 1970*, ORNL-TM-3300, pp 33-39.

80. W. J. Lackey and F. J. Homan, *Fuels and Materials Development Program Quart Progr Rept March 31, 1971*, ORNL-TM-3416, pp 31-34.

81. R. B. Fitts, E. L. Long, Jr., and J. M. Leitnaker, "Observations of Fuel-Cladding Chemical Interactions as Applied to GCBR Fuel Rods," presented at ANS Conference on Fast Reactor Fuel Element Technology, April 1970, New Orleans, ORNL-TM-3385 (July 1971).

82. C. M. Cox, R. B. Fitts, A. R. Olsen, and E. L. Long, Jr., *Trans Amer Nucl Soc* 14, 173-75 (1971).

83. Consultant from the University of Tennessee.

84. B. R. Dewey, *Discrete Element Analysis of the Creep of Stainless Steel Tubing for LMFBR Application*, ORNL-TM-3294 (March 1971).

Fig. 13.12. Comparison of calculated and measured radial porosity distribution for $U_{0.85}Pu_{0.15}O_2$ irradiated at 13.6 kW/ft to 0.7% FIMA.

Fig. 13.13. Summary of fuel-cladding interaction data from stainless-steel-clad fuel pins.

Fig. 13.14. Creep rate of type 316 stainless steel tubing under thermal cycling conditions.

stainless steel sheet, we found⁸⁵ little or no short-term influence of thermal and load cycling on the creep rate. We have extended testing to include $\frac{1}{4}$ -in.-diam $\times$ 0.015-in.-wall tubing. The creep rates obtained from thermal cycling are compared for the two materials in Fig. 13.14. The thermal dependence of creep around 15,000 psi appears quite similar for these two materials. Strain or time has some effect on creep rate, but the time duration is of questionable significance since irradiation effects will probably dominate not long after startup of a reactor. Low-strain-rate tensile testing of annealed tubing has shown very little strain rate sensitivity.⁸⁶ However, we found significant relaxation in annealed tubing at 1100 and 1200°F. Curves are shown in Fig. 13.15. In contrast to annealed tubing, we found a significant strain rate effect on the tensile yield of cold-worked tubing.⁸⁷ Relaxation tests on this material are being planned.

85. R. W. Swindeman, *Metals and Ceramics Div. Annu. Progr. Rept. June 30, 1970*, ORNL-4570, pp. 71-73.

86. R. W. Swindeman, *Fuels and Materials Development Program Quart. Progr. Rept. March 31, 1970*, ORNL-4560, pp. 81-84.

87. R. W. Swindeman, *ibid.*, pp. 83-85.

Fig. 13.15. Relaxation curves for annealed type 316 stainless steel tubing starting from 0.2% total strain.

14. Advanced Fast Breeder Reactor Fuels Development

J. L. Scott   P. Patriarca

The goals of this program are to investigate the properties and behavior of those uranium- and plutonium-base ceramic fuels that we term conductors — such as the mononitrides, carbonitrides, and monocarbides — and to compare their potential as liquid-metal fast breeder reactor (LMFBR) fuel with that of (U,Pu)O₂, which by comparison is an insulator. Since the thermal conductivity of the ceramic conductors is about ten times that of (U,Pu)O₂, one could theoretically operate a conductor at ten times the power density with the same central temperature. In practice, heat transfer limitations, thermal stresses in the cladding, and high rates of swelling at high temperatures limit the power density to about two or three times that of (U,Pu)O₂ — still a challenging improvement. Additionally, the margins for transient overpower are much higher in the ceramic conductors than in (U,Pu)O₂.

To evaluate the true potential of these fuels, we need to define the structures, composition, and quality control required to achieve 150,000 MWd/metric ton at peak linear heat ratings of 30 to 50 kW/ft. We must also demonstrate the possibility of a low-cost fuel cycle for manufacturing fuel with the needed properties. Our work is oriented primarily toward demonstrating the irradiation performance of (U,Pu)N at high burnups and high heat ratings. Therefore, much of our effort is devoted to fabricating and characterizing fuel for irradiation testing.

Other work on nitride fuels is reported in Chaps. 6, 8, and 26.

IRRADIATION TESTING

T. N. Washburn

Thermal Flux Tests

The initial series of irradiation tests are two noninstrumented capsules of four pins each in the ETR. These "screening" tests are to determine the performance of nitride fuel synthesized from metal. The peak

linear heat rating is 30 kW/ft to burnups of 30,000 and 60,000 MWd/metric ton. The fuel is cold-pressed pellets with densities from 86 to 91% of theoretical, and the fuel pins have a 0.010-in. radial gap between the fuel pellet and cladding, filled with NaK-19 to enhance heat transfer.

Capsules 43-N1 and 43-N2 were neutron radiographed at TREAT before insertion into the ETR. The reactor went to full power on December 9, 1970; as of May 9, 1971, the capsules have operated for 102 effective full-power days to a burnup of approximately 2% FIMA.

Fast Flux Tests

E. J. Manthos   M. K. Preston   J. H. Erwin

Seven unencapsulated fuel pins, five for testing in the EBR-II and two spares, are being fabricated. The 19-pin subassembly will be shared with Battelle Memorial Institute, Columbus Laboratories. The ORNL fuel pins are described in Table 14.1.

Table 14.1. Characteristics of unencapsulated Fuel Pins for testing in EBR-II

Fuel	
Composition	(U-18% Pu)N
Enrichment, % ²³⁵ U	93
Pellet diameter, in.	0.260
Pellet density, % of theoretical	90
Cladding	
Material	Type 316 stainless steel
Outer diameter, in.	0.310
Wall thickness, in.	0.015
Cold work, %	20
Fuel Pin	
Smear density, % of theoretical	78
Sodium bond thickness, in.	0.010
Fuel column length, in.	13.5
Overall length, in.	40
Operating Conditions	
Linear heat rating, kW/ft	30
Specific power, W/g	220
Peak cladding temperature, °C	650
Fuel center-line temperature, °C	1050

FABRICATION OF (U,Pu)N FUEL

Fuel for EBR-II Tests

E. S. Bomar V. J. Tennery

We completed a campaign to synthesize and fabricate mixed nitride fuel for loading eight pins for irradiation in the EBR-II. This material consisted of 117 in. of fuel, 0.26 in. in diameter, weighing 1.36 kg, and fabricated into 413 pellets. Additional nitride fuel was produced for characterization and archives. The quantitative chemical and x-ray characterization data are given in Table 14.2. The microstructure showed a single mononitride phase. The fuel pellets were centerless ground in an inert atmosphere glove box to diameters of 0.260 ± 0.001 in. Also, 20 in. of high-purity UN was produced and machined for use as insulator material in the ends of the EBR-II irradiation pins.

Sintering Experiments on (U,Pu)N

V. J. Tennery E. S. Bomar

We confirmed the role of the nitrogen pressure in the sintering of compacts of (U,Pu)N by experiments with powders derived from uranium-plutonium alloy as well as those produced by mechanically blending UN and PuN powders. For the alloy-source nitride powders, sintering conditions corresponding to points A, B, C, and A', B', and C' shown on the phase diagram in Fig. 14.1 were selected. The samples were heated to the temperatures indicated, while the nitrogen pressure was maintained at the value shown. The $U_{0.81}Pu_{0.19}N$ samples were maintained at temperature for 300 min, then cooled to $1400^{\circ}C$, and the furnace was evacuated before further cooling to room temperature. The densities of the specimens after sintering are shown in

Fig. 14.2, and the sintering enhancement due to the reduced nitrogen pressure is clearly indicated.

Similarly, compacts made from mechanically mixed UN and PuN powders were sintered under conditions shown in Fig. 14.3, with the low P_{N_2} runs corresponding roughly to line "Y" and the higher pressure sintering runs corresponding to the line designated as "X." Two different UN powders were used to determine if variations in the sinterability of the UN powder significantly affected the densification of the UN-PuN blend.

The data for the densification of these mechanical mixtures are shown in Fig. 14.4. For the blend of UN

Fig. 14.1. Temperature-pressure conditions used for sintering $U_{0.81}Pu_{0.19}N$ specimens derived from alloy powders.

Table 14.2. Analytical chemistry and x-ray data for (U,Pu)N fuel for EBR-II irradiation study

Sample	Content (wt %)					Mass balance (%)	Lattice parameter (Å)
	U	Pu	N	O	C		
510	79.26	15.24	5.42	0.043	0.034	99.997	4.8905
570	79.23	15.30	5.40	0.040	0.043	100.014	4.8907
630	79.24	15.32	5.40	0.044	0.055	100.06	4.8911
690	79.49	15.20	5.42	0.040	0.030	100.18	4.8907
750	79.49	15.30	5.44	0.040	0.030	100.30	4.8905
809	79.49	15.34	5.46	0.050	0.020	100.36	4.8905
869	79.39	15.32	5.47	0.030	0.020	100.23	4.8906
926	79.39	15.16	5.44	0.020	0.020	100.03	4.8906
981	79.19	15.25	5.44	0.030	0.020	99.93	4.8908
1011	79.39	15.07	5.48	0.020	0.020	99.98	4.8907

Fig. 14.2. Sintered densities of $U_{0.81}Pu_{0.19}N$ specimens sintered under conditions of Fig. 14.1.

Fig. 14.3. Temperature-pressure conditions used for sintering $U_{0.80}Pu_{0.20}N$ specimens derived from mechanical mixtures of UN and PuN.

(4 + 5) and PuN (4) sintered along lines "X" or "Y," the sintered density was essentially a linear function of the sintering temperature. Again, sintering under lower nitrogen pressures improved the densification. In the case of the mechanical mixture of UN (3S-3) and PuN (4), the densification was a nonlinear function of the

Fig. 14.4. Sintered densities of $U_{0.8}Pu_{0.2}N$ from mechanical mixtures of UN and PuN powders. Powder 3S-3 was finer than 4 + 5. Letters X and Y refer to sintering conditions in Fig. 14.3.

sintering temperature and achieved a limit about 84% of theoretical. In fact, all the mechanical mixtures approached a density about 84% of theoretical at the highest practical sintering temperature ($\leq 2300^{\circ}C$). The reason for these relatively low densities is evident in the microstructure of a sintered mechanically blended sample. Numerous large voids exist in the microstructure and are apparently at sites of the original PuN particles, and the presence of these low-density regions effectively limits the ultimate density that can be achieved in the sintered compacts.

CHARACTERIZATION OF (U,Pu)N

Analytical Methods for Determining Nitrogen in Mononitride and Sesquinitride Phases

V. J. Tennery J. L. Botts¹

The Kjeldahl method is the standard technique used in the FFTF program for nitrogen analysis of the oxide and nitride fuels. However, this technique characteristically gives significantly lower results when sesquinitride phases are present. Lindemer and Bradley² have shown that the use of nitrogen-hydrogen mixtures for reducing mixed oxides can result in the solution of

1. Analytical Chemistry Division.

2. T. B. Lindemer and R. A. Bradley, private communication.

nitrogen into the fluorite lattice and the subsequent precipitation of an M_2N_3 -type phase. Consequently, the dissolution step in the Kjeldahl analysis may result in low nitrogen values since the M_2N_3 phase is very difficult to dissolve in acids. When a mononitride phase is present the dissolution procedure used is of utmost importance if nitrogen losses are to be avoided before the distillation and titration steps of the Kjeldahl analysis.

We have compared the nitrogen values determined for a sample of $U_{0.8}Pu_{0.2}N$ using $HCl + HF$ and H_3PO_4 . The use of copper selenate in the dissolution was also investigated. The results obtained for a number of nitrogen determinations of $(U,Pu)N$ are given in Table 14.3. The use of H_3PO_4 is superior. Copper selenate was unsatisfactory.

The Dumas method for nitrogen determinations has been found to be satisfactory for both mononitride and sesquinitride phases. Because the Kjeldahl method is unsatisfactory for samples containing the M_2N_3 phase, we assembled a Dumas facility and tested it by analyzing several uranium nitride samples, including UN and U_2N_3 . The sample is oxidized to release nitrogen gas, which is quantitatively collected and measured. This method is capable of analyzing the nitrogen in U_2N_3 phases as easily as mononitride phases since it does not depend upon dissolution. Typical results for

nitrogen as well as the other major elements are given in Table 14.4 for three samples. Obviously, sesquinitride phases can be analyzed readily for nitrogen by the Dumas technique.

The Lattice Parameter of $(U,Pu)N$ Solid Solutions³

V. J. Tennery E. S. Bomar

Anselin⁴ reported that UN and PuN form a continuous solid solution of the NaCl structure and that the lattice parameter obeys a Vegard relationship.^{4,5} Considerable work has been reported⁴⁻¹⁰ on the lattice parameters of UN and PuN.

We measured the lattice parameters of the cubic solid solutions from the system $U_{1-x}Pu_xN$ at 25°C in samples in which the oxygen contents were measured at the time the x-ray specimens were prepared. The lattice constants and the analyzed chemical contents of the samples are given in Table 14.5. The composition dependence is shown in Fig. 14.5.

Table 14.3. Comparison of dissolution methods for $U_{0.8}Pu_{0.2}N$

Dissolution acid	Analyzed nitrogen ^a content (wt %)	Total nonmetal ^b content (wt %)
H_3PO_4	5.44, 5.45, 5.46	5.53
$HCl + HF$	5.14, 5.15, 5.01	5.24

^aTriplicate aliquots were analyzed as shown.

^bOxygen plus carbon content of sample was 0.093 wt %.

3. Paper presented at the Annual Meeting of the American Ceramic Society, Chicago, April 24–29, 1971. Published in *J. Amer. Ceram. Soc.* 54, 247–49 (1971).

4. F. Anselin, *J. Nucl. Mater.* 10, 301–20 (1963).

5. F. Anselin, *Preparation and Study of the Nitrides and Mixed Carbides Nitrides of Uranium and of Plutonium*, CEA-R-2988 (June 1966); ORNL-tr-1722.

6. J. M. Leitnaker, R. A. Potter, K. E. Spear, and W. R. Laing, *High Temp. Sci.* 1, 389–400 (1969).

7. P. E. Evans and T. J. Davies, *J. Nucl. Mater.* 10, 43–55 (1963).

8. R. Lorenzelli, *Contribution to the Study of the System $(U,Pu)C,N$* , CEA-R-3536 (May 1968); ORNL-tr-3019.

9. W. M. Pardue, V. W. Storhok, and R. A. Smith, pp. 721–38 in *Plutonium 1965*, ed. by A. E. Kay and M. B. Waldron, Chapman and Hall, London, 1967.

10. M. W. Shupe, R. L. Nance, and D. Kelley, *Nitrides, Advanced Plutonium Fuels Program*, LA-4284-MS (June 1969).

Table 14.4. Chemical analysis results for UN and UN_x phases

Sample	Dumas			Kjeldahl ^b			Content (wt %)			Percent mass balance ^d	Mole ratio ^d N + O + C/U
	Determinations	% N	% S ^a	Determinations	% N	% S ^a	U ^c	O	C		
Sintered UN	36	5.47	0.35	19	5.49	0.90	94.48	0.029	0.04	100.02	0.997
UN powder	17	5.46	0.34				94.44	0.049	0.04	99.99	0.000
UN_x	17	8.40	0.32				91.55	0.028	0.03	100.01	1.571

^a% S = relative standard deviation; % S = $100s/\bar{x}$, where s = standard deviation of a set and $\bar{x}$ = mean of the set.

^bPhosphoric acid dissolution was used.

^cUranium was determined gravimetrically.

^dThe Dumas nitrogen results were used for this calculation.

Fig. 14.5. Dependence of the lattice parameter of (U,Pu)N composition.

Table 14.5. Lattice parameters and chemical compositions of $U_{1-x}Pu_xN$ solid solutions

Composition ^a x	Lattice parameter ^b (a_0 at 25°C) (Å)	Element (wt %)					(N + C + O)/(U + Pu) ^f (mole ratio)
		Uranium ^c	Plutonium ^c	Nitrogen ^d	Oxygen ^e	Carbon ^e	
0.00	4.88920 ± 0.00017	94.45	0	5.41	0.09	0.030	0.998
0.19	4.89060 ± 0.00022	77.00	17.40	5.47	0.08	0.026	1.004
0.38	4.89470 ± 0.00015	58.60	35.90	5.45	0.05	0.020	0.999
0.58	4.90020 ± 0.00025	40.20	54.80	5.45	0.04	0.030	0.993
0.79	4.90380 ± 0.00013	21.35	73.10	5.30	0.04	0.020	0.968
1.00	4.90480 ± 0.00008	0	94.39	5.40	0.10	0.020	0.9972

^aUncertainty in x as a result of uncertainties in element determinations.

^bThe error is the standard deviation as computed by the machine.

^cUncertainty is ±0.3%.

^dUncertainty is ±5%.

^eUncertainty is ±10%.

^fAccumulated uncertainty in (N + C + O)/(U + Pu) is ±0.02.

Mercury Pycnometer Facility

J. P. DeLuca

The ability to determine the bulk density is of great importance and practical use in developing and characterizing a sintered ceramic nuclear fuel body. For this purpose we installed a mercury pycnometer in an inert atmosphere in a glove box to determine the bulk density of sintered pellets of (U,Pu)N and other plutonium-bearing ceramics.

The pycnometer is an improved version of an earlier design¹¹ and employs a precision hydraulic cylinder

and piston. The movement of the piston is measured by a micrometer, and the mercury pressure is shown on a digital display.

The sample chamber is approximately 1 cm in diameter × 1 cm high. The ultraprecision syringe can displace 2.5 cm³ of Hg, and the mercury pressure can be read to 1400 torr by a stainless steel diaphragm transducer. The electronic readout and control system

11. S. E. Dismuke, "Vacuum Pycnometer Using Mercury with Plunger Displacement for Hot Cell Use," pp. 37-39 in *Proc. 17th Conf. on Remote Systems Technol.*, 1969, American Nuclear Society, Hinsdale, Illinois.

consists of the vacuum readout of the sample chamber, the mercury pressure readout, and the remote drive for the syringe. The system also includes a mercury vapor detector and filter to continuously monitor mercury vapor in the off-gas stream and remove it.

An analytical balance in the same glove box permits a complete density determination within the one box. The pycnometer was calibrated against steel balls of known volumes over a range typical of fuel pellets. The precision of the volume determination is $\pm 0.001 \text{ cm}^3$.

COMPATIBILITY OF CLADDING WITH NITRIDE FUELS

J. P. DeLuca J. M. Leitnaker

The compatibility of nitride fuels with candidate cladding alloys must be thoroughly investigated and understood if these fuel materials are to be considered seriously for use in LMFBR systems. The problem is complicated because of the several multicomponent cladding alloys under consideration and the important effects of burnup on the composition, constitution, and nitrogen activity of the fuel. Our approach is to investigate systematically the thermodynamics and kinetics of those interactions that are pertinent to the compatibility problem. Such interactions involve components of the fuel and cladding.

Phase Investigations in the Pu-Cr-N System

J. P. DeLuca J. M. Leitnaker

The solid-state phase behavior of the Pu-Cr-N system was investigated from 790 to 1700°C and over a hydrogen pressure range from 2.6×10^{-10} to 1 atm. A partial phase diagram of the system at 1 atm total pressure and 1700°C is shown in Fig. 14.6; Cr, Cr₂N, and CrN all form a two-phase region with PuN under the conditions investigated. No ternary compound was found as reported by Spear and Leitnaker¹² for the U-Cr-N system.

The heat treatments were carried out in an induction furnace that was installed in an alpha glove box. The samples were analyzed metallographically and with x rays.

Review of the Chromium-Nitrogen System

J. P. DeLuca J. M. Leitnaker

The known thermodynamic data in the chromium-nitrogen system were analyzed. The high-temperature

12. K. E. Spear and J. M. Leitnaker, "Phase Investigations in the U-Cr-N System," to be published.

Fig. 14.6. Partial ternary phase diagram of the Pu-Cr-N system.

heat content measurements of Satoh¹³ were reevaluated, and the molar heat of Cr₂N was determined to be $15.05 + 6.58 \times 10^{-3} T$ (°K); that for CrN was $11.10 + 1.58 \times 10^{-3} T$ cal mole⁻¹ °C⁻¹. Using these heat capacities and an estimated $\Delta S_{298,f}^{\circ} = 20 \pm 1$ cal/°C per gram atom N for the formation of the two nitrides, second- and third-law calculations were made for all available vapor pressure data. Excellent agreement between the two calculations was found for Mills¹⁴ data. The third law ΔH_{298}° for the formation of Cr₂N from metal and nitrogen was -32.18 ± 0.05 kcal/mole Cr₂N, and the second-law calculation gave -31.51 ± 0.56 kcal/mole. For the formation of CrN from Cr₂N and nitrogen, the third law gave $\Delta H_{298}^{\circ} = -24.91 \pm 0.03$ kcal/mole of CrN, and the second-law calculation gave $\Delta H_{298}^{\circ} = -24.87 \pm 0.74$ kcal/mole. Because of this good internal consistency, Mills' data was taken to be the most reliable. A partial phase diagram of the chromium-nitrogen system was also prepared from all available data.

Compatibility of (U,Pu)N with LMFBR Stainless Steels, a Literature Review

J. P. DeLuca

We compiled the available data on compatibility experiments to determine whether compatibility problems exist between the nitrides and candidate claddings. Considerable work has been done on compatibility, both in and out of reactor.

13. S. Satoh, "The Heat of Formation and Specific Heat of Chromium Nitride," *Sci. Papers, Inst. Phys. Chem. Res. (Tokyo)* 34, 819, 1001 (1938).

14. T. Mills, *J. Less Common Metals* 22, 373 (1970).

Two major conclusions were drawn from the review. The first is that mixed nitrides and stainless steel can and do react at reactor temperatures. One needs to understand what controls the elemental activities to be able to prevent or limit nitriding of stainless steel in a reactor.

The second conclusion is that if nitride fuels are to be made on a large scale and if they are to be clad in commercial-grade stainless steel, a minimal oxygen contamination will have to be accepted, and an understanding of the quantitative effects of oxygen on the compatibility of mixed nitrides with stainless steel is important. Reports that conclude that the pure, stoichiometric, mixed nitrides are compatible out-of-reactor with low-oxygen-content stainless steel have taken only the first step. The second step should be the acquisition of enough information to allow one to determine and control what effect the associated impurities (C and O) will have on the compatibility of mixed nitrides with LMFBR claddings.

Thermodynamic Properties of Uranium Mononitride¹⁵

F. L. Oetting¹⁶ J. M. Leitnaker

The high-temperature enthalpy, $H_T^\circ - H_{298}^\circ$, of uranium mononitride has been determined from 298 to 1700°K by a copper block drop calorimeter of the isoperibol type. The experimental data may be expressed by the following equation:

$$H_T^\circ - H_{298}^\circ = 11.681T + 1.3291 \\ \times 10^{-3}T^2 + 9.812 \times 10^4/T - 3.930 \times 10^3.$$

The heat capacity of uranium mononitride is expressed as

$$C_p^\circ = 11.681 + 2.6582 \times 10^{-3}T - 9.812 \times 10^4 T^{-2}$$

in the same temperature range. Combination with data at 298°K available from the literature made it possible to construct a table of thermodynamic functions for uranium mononitride. An evaluation of the published vaporization data on uranium mononitride combined with the present enthalpy data indicates that the $\Delta H_{f,298}^\circ$ of uranium mononitride is -70.6 ± 1.0 kcal/mole and the heat of vaporization of uranium metal is 128 ± 2 kcal/mole.

Kinetic Studies of the Synthesis of Carbides, Carbonitrides, and Hypostoichiometric Oxides in the U-Pu-O-C-N System

T. B. Lindemer

An attractive process for producing carbides, nitrides, and carbonitrides in the uranium-plutonium system is the carbothermic conversion of oxide-carbon mixtures produced by the sol-gel process. Consequently, the kinetics of the reactions are being studied to ascertain the mechanisms controlling the conversion; this information is then applied to the design parameters of specific conversion equipment. Particular kinetic studies reported¹⁷⁻¹⁹ during the last year include UC with N_2 , UC_2 with N_2 , and UO_2 with C, and the information was used to analyze the fluidized-bed conversion of oxide-carbon mixtures to fuel compounds in the U-Pu-C-N system.²⁰ The latter analysis was tested by converting 250 g of sol-gel $U_{0.8}Pu_{0.2}O_2$ -C shards to (U,Pu)(C,N) in a fluidized-bed reactor. These shards were pressed and sintered into 89% dense, 0.63-cm-OD $\times$ 0.535-cm-long pellets that contained no second-phase compounds.²¹

A current kinetic study involves the simultaneous reaction of UO_2 , C, and N_2 to produce U(C,N). This is being accomplished with oxide pellets, so that quantitative weight change and metallographic techniques can be used to follow the progress of the reaction. At 1700°C, with $P_{CO} = 10$ torr and $P_{N_2} = 380$ torr, the conversion is accomplished by two successive chemical reactions:

in which the $UO_{1.22}N_{0.54}$ is a composition in a

17. J. M. Leitnaker, T. B. Lindemer, and C. M. Fitzpatrick, "Reaction of UC with Nitrogen from 1475° to 1700°C," *J. Amer. Ceram. Soc.* 53, 479-81 (1970).

18. T. B. Lindemer, J. M. Leitnaker, and M. D. Allen, "Kinetics of the Reaction of UC_2 and Nitrogen from 1500° to 1700°C," *J. Amer. Ceram. Soc.* 53, 451-56 (1970).

19. T. B. Lindemer, M. D. Allen, and J. M. Leitnaker, "Reply to 'Discussion of Kinetics of the Graphite-Uranium Dioxide Reaction from 1400° to 1765°C,'" *J. Amer. Ceram. Soc.* 53, 581 (1970).

20. T. B. Lindemer, "Rate Controlling Factors in the Carbothermic Synthesis of Advanced Fuels," *Nucl. Appl. Technol.* 9, 711-15 (1970).

21. T. B. Lindemer, *LMFBR Fuel Cycle Studies Progress Report for October 1970, No. 20*, ORNL-TM-3217, pp. 43-46.

15. Submitted to *Journal of Chemical Thermodynamics*.

16. Dow Chemical Co., Rocky Flats, Colo.

solid-solution field that includes²²⁻²³ UO_2 . This sequence of reactions in the synthesis of U(C,N) has apparently never been reported. It is significant to note that UO_2 is converted to $\text{UO}_{1.22}\text{N}_{0.54}$ by the approximate replacement of each three atoms of oxygen by two of nitrogen and that the nitrogen present in the final U(C,N) appears to be incorporated in the system by the initial reaction.

PERFORMANCE CAPABILITY OF ADVANCED FUELS FOR FAST BREEDER REACTORS

T. N. Washburn J. L. Scott

We studied²⁴ the practical performance limits of $(\text{U,Pu})\text{C}$ and $(\text{U,Pu})\text{N}$ relative to that of $(\text{U,Pu})\text{O}_2$ for use in an LMFBR. The boundary limits of fuel performance are best shown on plots of specific power (W/g) against linear power (kW/ft). For $(\text{U,Pu})\text{O}_2$ fuels, as shown in Fig. 14.7, these boundaries form a triangle with borders of about 100 W/g minimum specific power, about 0.200 in. minimum fuel diameter, and a maximum linear power of about 12 kW/ft for the core

22. J. M. Martin, *J. Nucl. Mater.* 34, 81-85 (1970).
 23. R. Benz, G. Balog, and B. H. Baca, *High Temp. Sci.* 2, 221-51 (1970).
 24. T. N. Washburn and J. L. Scott, *Performance Capability of Advanced Fuels for Fast Breeder Reactors*, ORNL-TM-3388 (May 1971).

Fig. 14.7. Performance boundaries of stainless-steel-clad, helium-bonded $(\text{U,Pu})\text{O}_2$ fuel pins in an LMFBR.

average or about 19 kW/ft for the highest rated fuel pin in which the fuel temperature would be near melting at the fuel center line. For $(\text{U,Pu})\text{C}$ and $(\text{U,Pu})\text{N}$ fuels, the minimum specific power and minimum fuel diameter are the same as for the oxides. However, the higher thermal conductivity of these advanced fuels permits linear powers to about 30 kW/ft core average and about 45 kW/ft for the highest rated pin, as shown in Fig. 14.8, when a sodium bond is used between the fuel and cladding to prevent excessive fuel temperatures and to provide space to accommodate fuel swelling. Also included are comparisons of the fuel performances specified in the LMFBR in follow-on studies²⁵⁻²⁹ to our more generalized study. There is substantial economic advantage in operating fuel at highly rated conditions, but a large amount of development work and irradiation testing must be performed with both the carbides and nitrides to permit an absolute comparison of their worth relative to oxides.

25. General Electric Company, *1000 Mw(e) Liquid Metals Fast Breeder Reactor Follow-On Study*, GEAP-5710, vol. 1.
 26. Atomics International, *1000 Mw(e) Liquid Metals Fast Breeder Reactor Follow-On Study*, AE-AEC-12792, vol. 1.
 27. Babcock and Wilcox Company, *1000 Mw(e) Liquid Metals Fast Breeder Reactor Follow-On Study*, BAW-1328, vol. 1.
 28. Combustion Engineering, *1000 Mw(e) Liquid Metals Fast Breeder Reactor Follow-On Study*, CEND-337, vol. 1.
 29. Westinghouse Electric Corporation, *1000 Mw(e) Liquid Metals Fast Breeder Reactor Follow-On Study*, WARD-2000-97.

Fig. 14.8. Performance boundaries of stainless-steel-clad, sodium-bonded $(\text{U,Pu})\text{C}$ or $(\text{U,Pu})\text{N}$ fuel pins in an LMFBR.

15. Cladding and Structural Materials

J. R. Weir, Jr.   H. E. McCoy, Jr.

This work is concerned with the development of suitable fuel cladding materials for LMFBR's. The cladding material chosen for the FFTF is 20%-cold-worked type 316 stainless steel. However, most of the data for material exposed to high fluences of fast neutrons has been for type 304 stainless steel, since it is used as a structural material in EBR-II. These data, although not directly applicable to FFTF, do contribute to the general understanding of austenitic stainless steels. A cladding material with better resistance to irradiation damage is needed. We have developed and are studying modified compositions of types 304 and 316 stainless steel with small additions of titanium.

High fluences of fast neutrons can cause two property changes of concern. The numerous atomic displacements can result in void formation and a density decrease. The dislocations and other defects produced by the displacements and the helium produced by transmutations can cause significant changes in the mechanical properties, a decrease in the fracture strain being of major concern.

SWELLING OF AUSTENITIC STAINLESS STEELS

E. E. Bloom   J. O. Stiegler

The swelling that occurs in stainless steels during neutron irradiation has been shown to be a sensitive function of the irradiation conditions and of the microstructure and composition of the steel.¹ We are evaluating the effects of these variables by the use of quantitative transmission electron microscopy and immersion density measurements on a variety of materials irradiated in EBR-II and HFIR. Significant findings of

work completed during the past year are described below.

Effect of Irradiation Temperature on Void Formation in Type 304 Stainless Steel

Previous work¹ has shown that in the range between about 370 and 500°C void concentration increases with increasing fluence, at least up to 7×10^{22} neutrons/cm². The mean void size increases with increasing irradiation temperature but is relatively insensitive to fluence, increasing as about the 0.15 power² of fluence. Maximum void sizes increase with increasing temperature, but not with fluence above about 5×10^{21} neutrons/cm² (ref. 1).

During the past year we found essentially opposite behavior in material irradiated at 590°C. Void concentrations saturated and void sizes increased with no evidence of the limiting void size found at lower irradiation temperatures. Void concentration measurements at 375, 465 and 590°C are shown in Fig. 15.1, and void size distributions for specimens irradiated to three different fluences at 590°C are given in Fig. 15.2. The latter figure shows that the void concentration increases very little on increasing the fluence from 2.25 to 3.5×10^{22} neutrons/cm² but that the distribution shifts to larger void sizes. The absence of voids smaller than 180 Å in diameter supports the contention that nucleation has ceased. Over the fluence range covered in Fig. 15.2 both maximum and mean diameters increased as the 0.5 power of fluence. This value is considerably higher than that observed at lower temperatures or in high purity aluminum.³ It is, however, in agreement with the model of diffusion-controlled growth of the

1. E. E. Bloom, *An Investigation of Fast Neutron Radiation Damage in an Austenitic Stainless Steel*, ORNL-4580 (August 1970).

2. H. R. Brager et al., "Irradiation Produced Defects in Austenitic Stainless Steel," *Metallurgical Transactions* (to be published).

3. N. H. Packan, "Fluence and Flux Dependence of Void Formation in Pure Aluminum," *Journal of Nuclear Materials* (to be published).

Fig. 15.1. Void concentration as a function of neutron fluence for annealed type 304 stainless steel irradiated at three temperatures. The solid lines represent the empirical equation developed by Brager et al.²

Fig. 15.2. Effect of fast neutron fluence on the void size distribution in annealed type 304 stainless steel irradiated at 590°C.

voids under conditions of constant vacancy supersaturation.⁴

On the logarithmic plot in Fig. 15.1 the slopes of the straight lines that can be drawn through the data points increase with irradiation temperature, from 0.66 at 375°C to about 5 at 590°C. The data may alternately be plotted on a linear scale. Then the slope decreases with increasing temperature, but the fluence intercept (threshold below which voids are not found) increases with increasing temperature. Threshold fluences for void formation are about 1×10^{20} neutrons/cm² at 375°C, 1.2×10^{21} neutrons/cm² at 465°C and 1.5×10^{22} neutrons/cm² at 590°C. Other observations indicate that the threshold may be composition sensitive.

Comparison of Standard and Titanium-Modified Type 316 Stainless Steel

Preliminary examination of specimens of annealed standard and modified (0.23% Ti) type 316 stainless steel have shown that the modified alloy swells significantly less than the standard material. Electron microscopy of specimens irradiated at 580°C indicate that the reason for the reduced swelling in the modified alloy is a large reduction in the concentration of voids. The concentration of voids in the standard steel is about 1×10^{13} , and all voids are associated with precipitate particles. The distribution of void sizes is bimodal, with large voids located on the large, blocky precipitate particles and smaller ones associated with the needle-like precipitate. No precipitate particles were found in the modified alloy, and the concentration of voids was less than 10^{12} /cm³. By comparison, the void concentration in standard type 304 stainless steel irradiated under these conditions would be about 1.8×10^{14} voids/cm³ (ref. 2), which further illustrates the strong dependence of the damage state on composition.

Dislocation structures also depend on composition. The standard steel contained Frank loops and a loose dislocation structure probably formed by glide and climb of loops that had unfaulted. Only a few faulted loops were found in the modified alloy. Small loops were observed in association with the dislocation structure.

Effects of Microstructure

We have already pointed out that at the higher irradiation temperatures voids were often associated

4. T. T. Claudson et al., "Fast-Reactor Radiation-Induced Changes in Cladding and Structural Materials," vol. 2, p. 165 in *Radiation Damage in Reactor Materials, proceedings of a Symposium, Vienna, June 2-6, 1969*, International Atomic Energy Agency, Vienna, 1969.

with precipitate particles and that specimens that contained fewer particles also contained fewer voids. In many of these cases the voids and precipitate particles both formed during the irradiation, and it is not clear which came first. We have found one clear example in which the voids nucleated on precipitate particles. For specimens of titanium-modified type 304 stainless steel, annealing 1 hr at 952°C following cold working produced a high density of coherent precipitate particles aligned in rows, as shown in Fig. 15.3(a). The microstructures after irradiation to fluences of 2.0 and 3.0×10^{22} neutrons/cm² at 590°C are displayed in Figs. 15.3(b) and 15.3(c). There is an obvious association of voids with the aligned noncoherent precipitate particles. Areas having high precipitate concentrations also have high void concentrations, and larger particles have larger voids attached to them. Apparently the voids nucleated at the sites of the original precipitate, although it is not clear whether this happened when they were coherent or noncoherent. The correlation between precipitate and void size indicates that the voids and precipitate grew simultaneously, suggesting that one or more of the elements present in the precipitate have been bound strongly to the vacancies and dragged to the void-precipitate complexes.

Swelling is also modified by the presence of a dislocation structure, but in a complex way. Cold worked materials show small but consistent increases in density during irradiation. Electron microscopy indi-

cates the presence of voids, which should contribute to a density decrease. The overall increase is evidently due to the overriding effect of densification as a result of precipitation reactions.

The swelling of heavily cold worked materials from void formation was appreciably less than that of annealed materials because of a large reduction in the concentration of voids; sizes were only slightly decreased. Different behavior was found in lightly deformed or recovered materials containing moderate dislocation densities, about 10^{10} /cm². Void concentrations were not affected, but void sizes were increased resulting in a greater overall swelling. This apparent anomaly can be rationalized by considering the roles of both the vacancies and the interstitials generated by the irradiation. Void formation is believed to occur because dislocations have a greater attraction for interstitials than vacancies and thus preferentially remove them from the system, leaving a net excess of vacancies available for void formation. Dislocation densities increase excessively in the annealed, recovered, and cold worked materials. In the cold worked material, dislocation densities are high enough that both vacancy and interstitial concentrations are depressed. In recovered materials the dislocations are far enough apart that they reduce interstitial concentrations but only slightly perturb the vacancy population. In annealed materials the grown-in dislocations are so far apart that they have little effect on the interstitial concentrations.

PHOTO 1087-71

Fig. 15.3. Effect of irradiation at 590°C on the microstructure of titanium-modified (0.2% Ti) type 304 stainless steel. (a) Annealed at 925°C. (b) Irradiated at 590°C to 2.0×10^{22} neutrons/cm². (c) Irradiated at 590°C to 3.0×10^{22} neutrons/cm².

In the latter two cases the major interstitial sink is probably the radiation-produced dislocation structure. This interstitial sink is augmented enough in the recovered material to increase the net vacancy concentration, and it swells more than an annealed structure. It is not clear whether the reduced void concentrations in cold worked materials are due to the reduced vacancy concentration or to trapping of helium atoms on the dislocations and thus inhibiting void nucleation.

Effect of a Thermal Neutron Environment

Significant differences have been found in swelling between specimens irradiated in a fast reactor (EBR-II) and those irradiated in a thermal reactor (HFIR). For example, specimens of standard type 316 stainless steel irradiated in HFIR to a fluence of 2.9×10^{22} neutrons/cm² at 575°C swelled 3.9%, as measured by immersion density and confirmed by electron microscopy. In comparison, irradiation in EBR-II to a fluence of 2.7×10^{22} neutrons/cm² at 575°C resulted in a volume change of only 0.68%. Most, if not all, of this difference can be attributed to increased helium production in HFIR. Weitman, Däverhög, and Farvolden⁵ recently pointed out an anomalously high production rate of helium in nickel irradiated in a mixed fast-thermal spectrum. They suggested that a fast-neutron reaction produced an intermediate, short lived product that had a very high thermal neutron (n,α) cross section. This was verified in this experiment, in which 1800 at. ppm He was found in the sample irradiated in HFIR, compared with an expected 2 ppm for a comparable EBR-II irradiation. In the specimen irradiated in HFIR many of the cavities were found on grain boundaries, suggesting that they were helium bubbles rather than voids.

Composition also affected swelling in specimens irradiated in HFIR. The addition of 0.33% Ti to type 316 stainless steel reduced the swelling from 3.9 to 0.9%. A further increase of titanium content to 0.46% reduced the density decrease to 0.8%.

MECHANICAL PROPERTIES OF AUSTENITIC STAINLESS STEELS

E. E. Bloom	R. E. Gehlbach
J. O. Stiegler	D. Fahr

As discussed previously, the microstructural damage that is produced as a result of a given irradiation is a

function of the irradiation temperature and fast neutron fluence. Below about 350°C small defect clusters, a few tens of angstroms in diameter, are formed. Irradiation at 350 to 650°C produces voids and dislocations, and above 650°C the only visible damage is helium bubbles formed by the precipitation of (n,α)-produced helium. Precipitation of carbides and various intermetallic phases as well as recovery of dislocation structures, such as those introduced by cold work, occur as a result of aging at elevated temperatures. These processes may be accelerated and modified during neutron irradiation. The effects of irradiation on mechanical properties are thus sensitive to alloy composition, initial microstructure, irradiation temperature, fast neutron fluence, and irradiation time.

Type 304 Stainless Steel

The effect of irradiation on the yield strength and uniform elongation of annealed type 304 stainless steel is shown in Fig. 15.4.⁶ The specimens were irradiated and tested at approximately the same temperatures. The yield strength was increased by irradiation for temperatures up to about 650°C. The magnitude of the change is strongly sensitive to the irradiation temperature. Uniform strain was reduced over the entire temperature range. At 450°C the reduced uniform strain was primarily a result of the reduced ability of the material to strain harden, leading to plastic instability early in the deformation. At 750°C the stress-strain behavior of the material was unaffected, but the ductility was reduced by premature grain boundary fracture. These observations are in agreement with the microstructural observations. At 450°C a high density of irradiation-produced voids and dislocations caused a large change in stress-strain behavior (increased yield stress and reduced work hardening) and thus reduced uniform strain. As the irradiation temperature was increased the void and dislocation concentrations decreased and the changes in yield strength became less. At 750°C no displacement damage was observed, but helium bubbles were present in the matrix and at grain boundaries. For this condition the stress-strain behavior was essentially unaffected by irradiation. However, the ductility was reduced by premature grain boundary fracture, indicating grain boundary embrittlement due to transmutation-produced helium.

5. H. Weitman, N. Däverhög, and S. Farvolden, *Trans. Amer. Nucl. Soc.* 13, 577 (1970).

6. E. E. Bloom and J. O. Stiegler, "Effects of Fast Neutron Irradiation of the Tensile Properties of Austenitic Stainless Steels," pp. 768-72 in *Second International Conference on the Strength of Metals and Alloys, Conf. Proc.* vol. II, The American Society for Metals, Metals Park, Ohio, 1970.

Fig. 15.4. Effect of fast neutron irradiation on the tensile properties of type 304 stainless steel when irradiated and tested at approximately the same temperature. The numbers by the points indicate the fast fluence in units of 10^{22} neutrons/cm².

The effects of irradiation on creep properties are of concern over the entire temperature range in the LMFBR. Below about 500°C the major process is radiation-enhanced creep. This phenomenon must of course be investigated during irradiation. Above about 500°C thermal creep processes are expected to dominate. Thus above 500°C postirradiation tests on samples irradiated at the test temperature can be used to estimate the in-reactor behavior of the material at the particular fluence in question. The effects of irradiation on the creep-rupture properties of annealed type 304 stainless steel irradiated to 1.5 to 3.5×10^{22} neutrons/cm² (>0.1 MeV) are shown in Fig. 15.5. At 550 and 600°C, irradiation to these fluences produced no

major change in the rupture life. Creep rates of the irradiated samples tended to be slightly lower than those of the unirradiated samples, with the effect being more pronounced at 550°C than at 600°C. The ductility, as measured by total elongation, was significantly reduced. At 704°C an increase in minimum creep rate was observed. This effect might result from the precipitation of carbon from solution during irradiation. The combination of increased creep rate and reduced ductility at high temperatures leads to a rather large reduction in rupture life.

Studies⁷ on material irradiated at 370 to 470°C to a range of fluences and then tested at 550 and 600°C have shown that for irradiation temperatures at which voids and dislocations are formed, the reductions in rupture life and ductility become more severe with increasing fluence. Scanning electron microscopy and optical metallography have shown that for these conditions the fractures are intergranular and that essentially no grain boundary cracks are formed along the gage section. It thus appears that a crack once initiated propagates rapidly to cause failure.

Type 316 Stainless Steel

Type 316 stainless steel is being investigated over a wider range of experimental variables than type 304 stainless steel because it is the cladding alloy for the FFTF. As already discussed, a high dislocation density such as that produced by cold working appears to reduce the swelling. Cold working also produces significant changes in the mechanical properties and in the phase transformation and precipitation reactions that occur in both unirradiated and irradiated material.

We identified the phases formed in both solution-treated (1 hr at 1050°C) and 20%-cold-worked samples during aging 4000 hr at 350, 450, 550, and 650°C. Very little precipitation is present after aging at the two lower temperatures and significantly greater amounts at 550 and 650°C. The $M_{23}C_6$ carbide and intermetallic compounds are formed in solution-treated material during aging at 550°C or above. Cold work before aging has a marked effect on precipitation. In 20%-cold-worked material the formation of the $M_{23}C_6$ carbide is drastically suppressed and sigma and laves phase are formed, particularly at 650°C.

7. E. E. Bloom and J. O. Stiegler, "Effect of Fast Neutron Irradiation on the Creep Rupture Properties of Type 304 Stainless Steel at 600 C," pp. 451–67 in *Irradiation Effects on Structural Alloys for Nuclear Reactor Applications*, Spec. Tech. Publ. 484, American Society for Testing and Materials, Philadelphia, March 1971.

Fig. 15.5. Effect of fast neutron irradiation on the creep rupture properties of type 304 stainless steel, (a) Rupture life, (b) minimum creep rate, (c) ductility

When type 316 stainless steel is irradiated in the annealed condition the changes in tensile properties are similar to those discussed for annealed type 304 stainless steel. When the material is cold worked 20% the yield stress is increased and the elongation decreased over the range 350 to about 750°C, as

illustrated in Fig. 15.6. Aging 20%-cold-worked material for 4000 hr at 450, 550, or 650°C or irradiation in the range 450 to 750°C caused a reduction in yield stress, which became more pronounced with increasing temperature. The effects of irradiation on the ductility of 20%-cold-worked material are complex. At 450 to

Fig. 15.6. Effect of thermal aging and irradiation on the tensile properties of annealed and 20%-cold-worked type 316 stainless steel. (a) Yield stress, (b) total elongation.

550°C and fluences of 1.5 to 2.3×10^{22} neutrons/cm² (>0.1 MeV) the postirradiation tensile ductility was actually higher than in the as cold worked condition, presumably because of recovery during irradiation. In the range 600 to 800°C the ductility was low and exhibited a minimum. Over this temperature range significant microstructural changes occurred. Some void and dislocation formation was observed in the range 600 to 650 or 700°C, significant recovery of the cold worked structure occurred at all temperatures, and above about 700°C some recrystallization occurred. Carbide precipitation and σ -phase formation occurred over the entire temperature range. These complex microstructural changes, acting in combination with the transmutation-produced helium, give the resultant properties.

The effects of irradiation on creep-rupture properties of annealed and cold worked type 316 stainless steel are being investigated. Initial results indicate that irradiation to a fluence of 2 to 3×10^{22} neutrons/cm² (>0.1 MeV) significantly reduces the ductility, with the most pronounced effects occurring in the range 550 to 650°C, where total elongations are generally in the range 1 to 5%.

Other Austenitic Alloys

Investigation of the effects of fast neutron irradiation on the properties of alloys that show promise as cladding and structural materials in LMFBR's has continued. Alloys included are titanium-modified types 304 and 316 stainless steel, type 318 stainless steel, SANDVIK 1272HV, and 19-9-DL.

The tensile properties of titanium-modified type 304 stainless steel after irradiation were measured. The strength properties do not differ significantly from those of standard type 304 stainless steel irradiated and tested under similar conditions.⁶ Ductility, as measured by uniform strain, total elongation, or reduction in area, is higher for irradiation and test temperatures above about 450°C. Figure 15.7 compares the total elongation of standard and titanium-modified type 304 stainless steel after irradiation in the EBR-II. The modified alloy had much greater elongation at test temperatures above 450°C.

The creep-rupture properties after irradiation have been measured. At 600°C, the rupture life of modified type 304 stainless steel was one-tenth that of the standard type 304 stainless steel irradiated at the same temperatures; its minimum creep rate was about ten times higher. These differences in strength properties were a result of the finer grain in the titanium-modified type 304 stainless steel (annealed 1 hr at 925°C before

Fig. 15.7. Tensile ductility of standard and titanium-modified type 304 stainless steel after irradiation in EBR-II.

irradiation) as compared to the standard type 304 stainless steel (annealed 1 hr at 1050°C before irradiation). The ductility of the modified alloy after irradiation, in terms of elongation at the end of second-stage creep, total elongation, or reduction in area, was significantly higher than that of the standard type 304 stainless steel.

Metallographic examination of titanium-modified type 304 stainless steel, annealed 1 hr at 925°C, irradiated at about 590°C to 3.0×10^{22} neutrons/cm² (>0.1 MeV), and then tested at 600°C and 27,500 psi stress, was completed. The material strained about 11% before going into third-stage creep. Transmission electron microscopy of specimens removed from the stressed gage section revealed that a dislocation cell structure had formed, with the voids and precipitate particles acting as pinning points. Most significant was the observation by scanning electron microscopy that the specimen had failed in a very ductile, predominantly transgranular mode. This was compared to the brittle intergranular fracture of standard type 304 stainless steel. Irradiated titanium-modified type 304

stainless steel is significantly more ductile at temperatures where helium embrittlement predominates. The present results demonstrated that the improved ductility was retained under irradiation and test condition where both displacement damage (voids and dislocation structure) and helium affect mechanical properties, particularly ductility.

Similar differences in properties occur between standard and titanium-modified type 316 stainless steel. For all conditions where comparative data were available,

the titanium-modified alloy had significantly higher total elongation. At lower temperatures the modified alloy was also stronger. As the irradiation and test temperatures were increased, the differences in strength properties diminished. After holding for long periods of time at 600°C or higher the modified alloy may be somewhat weaker than the standard alloy because of a finer grain size and the precipitation of carbon from solution. Improved strength can be obtained if necessary by using a higher annealing temperature.

16. Fabrication Development of Fast Breeder Reactor Cladding

W. R. Martin

High-quality but economical tubing is required to meet the performance requirements for liquid-metal fast breeder reactors. Our goal is to develop methods of fabrication that meet the needs of the FBR. This program is currently concentrating on type 316 stainless steel.

EVALUATION OF PLANETARY SWAGING FOR PRODUCING HIGH-QUALITY CLADDING

G. A. Reimann

We have evaluated the planetary swaging process. Although it affords a unique method for producing tubing, certain characteristics of the technique restrict its application as a production tool for fabricating the quantity of high-quality cladding envisioned for the Fast Breeder Reactor.

Planetary swaging was most effective when limited to several light ironing passes to produce tubing of finished size. Dimensional control was precise and surface finish was superior. But the inherent slowness of the process at rates of 4 ft/min cannot compete with the higher rates obtained in conventional drawing. Planetary swaging frequently produces a surface with hardness values that correspond to 50% cold work while reducing the cross-sectional area of the tube only 20%.

Attempts to swage at higher speeds and heavier reductions to improve the economics produced surface defects in the tubing. The principal cause for such defects was the formation of a pronounced circumferential ridge just ahead of where the swaging balls first contacted the tube surface. The development of this ridge, shown in Fig. 16.1, was a major factor limiting the reduction obtainable from a single pass.

ULTRAFINE GRAIN SIZE TYPE 316 STAINLESS STEEL TUBING

G. A. Reimann   A. C. Schaffhauser

Using the successful procedures developed previously¹ to obtain a fine grain size (ASTM 14) as a base,

we have attempted to refine that grain size to ASTM 20. A powder metallurgy approach using small-diameter atomized type 316 stainless steel powder was not successful. Temperatures required to sinter the product increased the grain size of the starting product. Oxide particulates from the surface of the atomized powders did not restrict grain growth. Additionally, the presence of some large particles caused microcracking in the alloy at high levels of cold work.

ELEVATED-TEMPERATURE DRAWING

G. A. Reimann

Type 316 stainless steel was successfully drawn at temperatures within the range 200 to 760°C with carbide plugs and dies. Deformations equal to a 40% reduction in cross-sectional area were completed without intermediate heat treating. Surfaces of the tubing produced would require chemical or mechanical treatment to meet the quality level now specified for reactor tubing. This method of drawing develops, particularly at 760°C, a fine cellular dislocation structure that may result in improved properties.

GENERATION AND EVALUATION OF ARTIFICIAL DEFECTS

W. R. Martin

As-Machined Notch Studies

K. V. Cook   R. W. McClung

The purpose of the as-machined notch study is to produce flaws of various sizes by electro-discharge machining in type 316 stainless steel tubular specimens for mechanical property testing. Notches such as these are normally used to establish test sensitivity for both ultrasonic and eddy-current tests and are as narrow as we can machine them at the present time (0.0023 in.).

1. G. A. Reimann, *Metals and Ceramics Div. Annu. Progr. Rept. June 30, 1970*, ORNL-4570, p. 86.

Fig. 16.1. Circumferential ridge formed by subjecting tubing to "heavy" reductions by planetary swaging. (a) Partially planetary swaged tubes. (b) Cross section at the ridge. 75X. Etch: HCl, HNO₃, H₂O.

We prepared approximately 120 samples from ORNL-fabricated tubing and 15 from tubing fabricated by the Carpenter Technology Company. Preparation of specimens required zero-defect tubing; thus, very sensitive penetrant and ultrasonic techniques were used to inspect the material. Following the nondestructive testing and documentation, we selected, labeled, and marked the 4-in.-long sections for the burst specimens. After sectioning, we machined those specimens requiring notches and documented the notch location and size as well as the wall thickness variations on each specimen.

Altered Notch Studies

K. V. Cook   G. A. Reimann   R. W. McClung

The goal of the altered notch study is to establish methods for fabricating artificially produced flaws in tubing to resemble natural defects. These simulated flaws are being used in studies involving the fabrication,

inspection, and mechanical properties groups to evaluate and upgrade tubing fabrication and inspection methods as well as to establish the effect of the simulated flaws on mechanical properties.

We have established procedures to produce altered notches in drawn or sunk tubing and can reliably predict final notch dimensions. The program has produced enough ORNL-fabricated tubing, containing altered notches, to supply approximately 30 tube burst specimens. The smallest altered notches produced thus far are approximately 0.0001 in. wide $\times$ 0.270 in. long $\times$ 0.0018 in. deep, as shown in Fig. 16.2.

Study of Fabrication-Introduced Discontinuities

K. V. Cook

The primary objective of this study was to establish a size of discontinuity that might be introduced in fuel tube cladding while the fuel pellets are being inserted or removed. Mechanical testing results on as-machined and

ORNL-DWG 70-13052

ALTERED NOTCH

- (a) MADE BY SINKING TUBE WITH
AS-MACHINED NOTCH

- (b) MADE BY SINKING AND IRONING
0.043-in. WALL TO 0.015-in. WALL

Fig. 16.2. Representation of as-machined notch and the altered notch in type 316 stainless steel.

altered EDM notches should establish the importance of such discontinuities induced during loading of the fuel

A 0.230-in.-OD $\times$ 0.015-in. wall type 316 stainless steel tube fabricated by the Carpenter Technology Company was selected for this study. The tube had been purchased in accordance with FFTF specifications which required ultrasonic inspection using a 0.001 in. deep $\times$ 0.030 in. long EDM reference notch. We ultrasonically tested the tube using such a notch to confirm the integrity before fuel loading. After fueling and introducing scratches, the tube was rechecked in the ultrasonic inspection setup. The deepest scratch detected was 0.0002 to 0.0003 in. A metallographic cross section of this scratch confirmed the depth measurement and established that the defect was about 0.002 in. wide.

CREEP RUPTURE OF TYPE 316 STAINLESS STEEL TUBING WITH ARTIFICIAL DEFECTS

R. T. King   G. A. Reimann   K. V. Cook

Previous investigators^{2,3} have recommended that the maximum defect depth allowed in stainless steel nuclear-grade tubing be 10% of the tube wall thickness, basing their conclusion on short-term tests of tubes containing artificial or natural defects. We are attempting to learn whether these conclusions are applicable to 0.23-in.-diam $\times$ 0.016-in.-wall-thickness type 316 stainless steel tubing, which is the proposed fuel cladding for liquid-metal fast breeder reactors.

Tubing fabricated from one heat of type 316 stainless steel was ultrasonically inspected to guarantee that no natural flaws existed in 4-in. specimen lengths of 20% cold-worked material. Longitudinal notches 0.0025 in. wide were then electro-discharge machined into either the inner or outer surfaces of some of these tubes, the notch depths were about 10, 33, and 66% of the tube wall thickness, and the notches were machined to 0.030- or 0.250-in. lengths. The notches were machined on the thin side of the tube wall, whenever thickness variations were found. Some of the tubes were then annealed at 925°C for 1 hr in hydrogen, while others were left in the cold-worked condition. Creep-rupture tests were performed in He-1% O₂ at 650°C at stresses that caused rupture after a few tenths of an hour to several hundred hours. The results for 20% cold-worked

tubing containing notches may be summarized as follows:

- 1 Notches accelerate the intergranular fracture process in the metal beneath the notch, reducing the rupture lifetime of the tubing (see Fig. 16.3) and the amount of circumferential strain that occurs before failure.
- 2 Within the limits of experimental error, the detectable effects of notches on the inner and outer wall are the same.
- 3 As notch length increases, the notches become more detrimental to properties, because the constraint provided by the rest of the tube decreases with increasing notch length.
- 4 Both rupture time and strain decrease with increasing notch depth.

The results for annealed tubing presently available indicate the following:

- 1 Notches of depth equal to about 10% of the wall thickness of annealed tubing cause less reduction in the rupture time or circumferential fracture strain than in cold-worked tubing.
- 2 Notches of depth equal to about 33 and 66% of the wall thickness seriously reduce both the rupture time and circumferential fracture strain of annealed tubing.

These significant differences in the behavior of annealed and cold-worked tubing are compelling reasons for reexamining the inspection standards of stainless steel fuel cladding materials. Other factors that may be important but which have not yet been investigated include the test environment, the test temperature, the notch geometry or origin, and the combination of irradiation and defect effects on cladding properties.

Fig. 16.3. Effect of notches on the rupture times of cold-worked type 316 stainless steel tubing tested at 650°C in He-1% O₂.

2 R. F. Kirby, *Evaluation of 300 Series Stainless Steel Tubing for Fuel Cladding* GEAP-4095 (October 1962)

3 T. Lauritzen, A. Montes, and A. Conti, *The Influence of Surface Defects on the Short Term Mechanical Properties of Austenitic Stainless Steel Tubing*, GEAP-13550 (December 1969)

17. Welding Development

G. M. Slaughter

The LMFBR welding development program is concentrated on two types of materials, austenitic stainless steels and ferritic steels.

STAINLESS STEEL

G. M. Goodwin   N. C. Binkley
N. C. Cole   R. G. Berggren

We are studying the effect of both welding process and variables within a process on the behavior of weldments in austenitic stainless steels at 370 to 650°C for application to LMFBR vessels and components. The solidification substructure (the structure in its finest microscopically resolvable detail) markedly influences the mechanical properties of a weldment at elevated temperatures. Since the size and type of substructure in a weldment are significantly influenced by factors that the welding operator can control, we determine the effects of composition, individual welding process, and the welding variables (current, voltage, travel speed, etc.) on the observed microstructure and, subsequently, on elevated-temperature mechanical properties. In all instances, highly pedigreed materials are used, and all of the variations in composition are within allowable specifications. The effects of postweld heat treatment and neutron irradiation are also investigated.

We reviewed the published data concerning the elevated-temperature mechanical properties of austenitic stainless steel weldments. Little information was available, and it showed a high degree of scatter, particularly in ductility.¹ For type 347 stainless steel weld metal, for example, the total elongation values from stress-rupture tests at 650°C, plotted as a function of rupture life, show an essentially random pattern. Most of the total elongation values are less than 10%, and many are 1% or less. Thus, our welding programs were undertaken to augment the meager literature data and to determine the individual effects of some of the variables that we feel are responsible for the above

situation, such as changes in welding input parameters and minor composition variations. The information generated in these programs was influential in the selection of a "controlled residual element" filler metal for the Fast Flux Test Facility (FFTF) vessel, and characterization studies indicate that this filler metal possesses superior strength and ductility.

Submerged-Arc Process

We are investigating the effects of variations in welding parameters and minor compositional changes due to flux composition variations for the submerged-arc process. Eleven different weldments are included in the study, each having an intentional variation in either welding parameters or flux composition. Figure 17.1 shows stress plotted against rupture life for submerged-arc weldments at 650°C. The upper scatter band represents literature data for type 304 stainless steel base material. Note that the weld metal is generally weaker than base metal, with only a few weld metal data points falling within the base metal scatter band. Figure 17.2 shows total elongation plotted against rupture life for the same tests shown in Fig. 17.1. Note the relatively high degree of scatter, but the total elongation values are generally greater than 10% and there is only a moderate trend toward decreasing ductility with increasing rupture life. These results will be compared in the next section with those for the shielded metal-arc process.

Shielded Metal-Arc Process

Our objective is to determine the effects of electrode coating variables on the shielded metal-arc (stick electrode) welding process. We are comparing the substructures and elevated-temperature mechanical properties of 23 shielded metal-arc weldments made with type 308 stainless steel electrodes.² Included are the three most

1. G. M. Goodwin, *Fuels and Materials Development Program Quart. Progr. Rept. Sept. 30, 1969*, ORNL-4480, pp. 105-8.

2. N. C. Binkley, G. M. Goodwin, and D. G. Harman, *Fuels and Materials Development Program Quart. Progr. Rept. Dec. 31, 1969*, ORNL-4520, pp. 165-72.

Fig. 17.1. Stress plotted against rupture life for type 308 stainless steel submerged-arc welds at 650°C.

Fig. 17.2. Elongation in stress-rupture tests of type 308 stainless steel submerged-arc welds at 650°C.

Fig. 17.3. Effect of composition on the creep ductility of shielded metal-arc welds at 650°C.

popular electrode coatings produced by a commercial supplier: lime, titania, and lime-titania. The last mentioned is the most widely used, and we are studying the effects of minor changes in C, Si, P, S, and B contents of the electrode coating and subsequent deposited weld metal (deposit composition is within the allowable type 308 composition limits in all cases). Significant variations in creep strength and ductility were observed. Figure 17.3 shows total elongation plotted against rupture life for a series of weld metals. Note that what

appears to be a broad scatter band of ductility values can now be resolved into a family of curves for the individual weldments. Although some of the individual weldments show decidedly superior ductility, all show markedly decreasing ductility with increasing rupture life at 650°C.

Fig. 17.4. Stress plotted against rupture life for type 308 stainless steel shielded metal-arc welds at 650°C.

Based on these initial test results, several heats of "second-generation" weld metal were produced containing controlled amounts of certain beneficial residual elements — namely, boron and phosphorus. Additional testing showed these filler metals to have superior strength and ductility and led to the selection of an optimized "controlled residual element" filler metal for the FFTF vessel.

Figure 17.4 summarizes the stress vs rupture life data for shielded metal-arc welds at 650°C. Note, in contrast to the results for the submerged-arc welds, that the stress-rupture properties fall within the scatter band for type 304 base material. The total elongation values for these same tests are shown vs rupture life in Fig. 17.5. In this figure, test results from 20 standard type 308 weldments are shown as solid symbols, enclosed by a scatter band; the open symbols represent data from the two second-generation filler metals and the actual FFTF filler metal. Note the significant improvement in ductility with no significant sacrifice in strength. A more detailed analysis shows the FFTF filler metal to be superior to both of the second-generation filler metals, with respect to both strength (rupture life) and ductility (total elongation).

Heat Treatment Studies

A comprehensive study of heat treatments was initiated to determine the effects of time and tempera-

Fig. 17.5. Elongation in stress-rupture tests of type 308 stainless steel shielded metal-arc welds at 650°C.

ture exposure upon the microstructure and properties of welds in austenitic stainless steels. Three general types of heat treatments are being investigated: (1) solution annealing, (2) solution annealing followed by an intermediate-temperature carbide agglomeration treatment, and (3) long-term aging.

As would be anticipated, each of the different weld metals, having a slightly different composition and microstructure, responds differently to heat treatment.

In general, solution treating dissolves and agglomerates the δ -ferrite phase to a degree dependent upon the amount and distribution of ferrite in the as-welded structure, solution-treating temperature, and time at temperature. This, in turn, affects the response of the material to carbide agglomeration treatments. The finer ferrite phase in the shielded metal-arc weld dissolves more readily, allowing extensive grain-boundary migration and, subsequently, extensive carbide precipitation at lower temperatures. The submerged-arc weld, on the other hand, is more resistant to ferrite dissolution and agglomeration and shows carbide precipitation predominantly at remaining austenite-ferrite boundaries.

Long-term aging studies have shown that the rate of formation of σ -phase and rate of carbide precipitation depend in a complex fashion upon starting microstructure (as welded or as heat treated), composition, aging temperature, and time at aging temperature. In general, σ -phase formation is accelerated by a coarser ferrite distribution.

Metallographic techniques were developed for the selective identification of ferrite, σ -phase, and precipitated carbides.

Corrosion Studies

The relative corrosion resistance of stainless steel weldments, both as welded and in various heat treated conditions, is of interest for the fabrication, shipment, installation, and service of a stainless steel reactor vessel. We have performed Strauss tests on 56 composite wafers representing five different weld-metal compositions, four base metal compositions, and nine heat-treatment conditions.

All specimens in the as-welded condition passed the Strauss test. Heat treatments typical of those being considered for the FFTF vessel³ caused all base metals (except low-carbon ones) to fail the Strauss test. This indicates that it is highly likely that any reasonable heat treatment that may be applied to the FFTF vessel (0.05–0.07% C) would cause it to fail the Strauss test.

Irradiation Studies

We prepared 226 composite weldment specimens for irradiation in the Experimental Breeder Reactor II. Of these specimens, 168 make up a statistically designed experiment that involves eight weld metal compositions, five specimen locations, and three heat-treatment

conditions. The remaining 58 specimens represent additional welds, heat-treatment conditions and specimen locations that could not be included in the main experiment because of the number of variables involved. The irradiation exposure will be completed in FY 1973, and postirradiation testing will include tensile and creep-rupture tests.

FERRITIC STEELS

D. A. Canonico   N. C. Binkley

The successful operation of a steam generator depends upon the mechanical properties, corrosion resistance, and weldability of the materials from which it is fabricated. Currently, a number of commercial steam generator designs are being considered. This program is concerned with several types of ferritic steels that are candidates for use in their construction. The low-carbon grades of low-alloy steels and the stabilized low alloy steels are emphasized in our study because little basic information is known about them and because they eliminate the carbon transport problem, which is one of the primary concerns in steam generators heated by liquid sodium.

The purpose of the program is to determine the weldabilities of the various steels and determine the advantages and limitations of each. The assessment of weldability includes microstructural studies as well as mechanical property measurements. Determination of susceptibility to cracking as a consequence of welding and the effects of welding on the mechanical properties is of prime importance.

Stabilized Grades

Carbon in the low-alloy steels has been stabilized with a number of carbide-forming elements, however, the use of all except niobium has been abandoned. A state-of-the-art review of the weldability of the stabilized low-alloy steels has been completed.⁴ An abstract of the report follows.

Stabilized 2 $\frac{1}{4}$ % Cr–1% Mo low alloy steels have been proposed as materials for the construction of sodium-to-water steam generators for LMFBR applications. Stabilizing elements such as Ti, Nb, V, and Ta have been used by various manufacturers to "tie up" the carbon (about 0.10% C) and thereby prevent its loss to the flowing sodium. For various reasons, such as poor impact properties, most stabilized versions have been abandoned, the primary exception is the alloy with 0.5% Ni added to improve impact strength. This alloy is

³ G. M. Goodwin and N. C. Cole, *Fuels and Materials Development Program Quart. Progr. Rept. March 31, 1971*, ORNL-TM-3416, pp. 137–42.

⁴ N. C. Binkley, *State of the Art Review – Weldability of Stabilized 2 $\frac{1}{4}$ % Cr–1% Mo Steel*, ORNL-TM-3490 (in press).

available commercially as Sandvik HT8X6 and carries the German designation of 10CrMoNiNb910.

While this HT8X6 alloy shows considerable promise in regard to impact properties and resistance to loss of carbon, there is some doubt about its general weldability and fabricability. Problems in welding could arise primarily from weld-associated cracking due to the formation of a eutectic composition between iron and niobium. In general, the European sources have produced the bulk of literature on this alloy, and they seem to be quite optimistic about its use. They believe that cracking as a result of welding will not occur. On the other hand, some sources in the United States seem to think that this material has poor weldability from the standpoint of U.S. codes and specifications. However, since little actual experience with this alloy exists in the United States, a thorough weldability study is warranted.

The recommended heat treatment for tubing manufactured from this steel is to austenitize at 1050°C for 20 min, cool in air to 500°C, and then temper at 750°C for 1 hr. The resulting microstructure is similar to that of unstabilized 2.25% Cr–1% Mo tubing (ASTM A213-T-22) except for the occurrence of angular precipitate particles. Hardenability studies employing the Jominy end quench test showed that these steels respond to a heat treatment similarly to the 2.25% Cr–1% Mo alloy (ASTM A387, grade D) plate except that the overall hardness is lowered. Electron-beam microprobe studies of the base metal show the niobium to be associated with the precipitate, thereby explaining the lower hardness values. This association (which appears to satisfy the NbC stoichiometry) results in a material whose mechanical properties should be similar to those of a low-carbon 2.25% Cr–1% Mo steel.

Initially we used the TIGAMAJIG weldability testing device on 1/4-in.-thick commercial plate. Both high- and low-heat-input welds were made, and a metallographic investigation revealed cracks in the specimens. These cracks were partially filled with a lower melting phase, as shown in Fig. 17.6. Further, in the low-heat-input welds the grain boundaries in the heat-affected zone appeared to have been melted during welding. Also, a eutectic microstructure was associated with the niobium-rich precipitate in the region close to the fusion line. The presence of a constituent that melts below the melting temperature of the bulk steel could easily account for the reported weldability problems cited in the state-of-the-art review.

An electron-beam microprobe analysis of these liquidated phases showed them to be rich in niobium. Figure 17.7 shows the results of the microprobe study of the cracks. A semiquantitative analysis of the back-filled structure corresponded to the Fe₂Nb- α eutectic. The

eutectic temperature, 1370°C, is in good agreement with the temperature of observed melting in a hot-ductility study. The hot ductility study showed excellent on-heating ductility for this steel. Further, the recovery of ductility after heating to the zero-ductility temperature, 1330°C, was excellent.

Chromium-Molybdenum Low-Alloy Steel with Low Carbon Content

Another alternative to the elimination of the carbon migration problem in ferritic steels lies in decreasing the carbon levels to near the solid solubility limit. An investigation of the weldability and mechanical properties of weldments of this grade of material is also under way. Carbon contents of 0.003, 0.045, and 0.11% in a nominal 2.25% Cr–1% Mo low-alloy steel are included in the study. (The 0.11% C is typical for a 2.25% Cr–1% Mo steel, ASTM A213-T-22 and ASTM A387, grade D.)

Fully restrained gas tungsten-arc welds made with filler metal from each carbon level show a factor of 2 difference between the tensile strength of the 0.003% C and 0.11% C at 565°C. Postweld heat treating at 700°C for 1 hr had essentially no effect on the low-carbon welds but appreciably lowered the strength of the high-carbon steel. Table 17.1 contains tensile results at room temperature and 565°C for the weld metal. These data indicate that the medium- and high-carbon steels may suffer from a decrease in strain rate. The reduction-in-area values, in particular, dropped precipitously.

Microhardness traverses were made across weldments made with these filler metals, and Table 17.2 contains the results. We studied areas from both the last and early passes (weld metal that had been exposed to thermal excursions due to the multipass weld technique employed). The strengthening effect of the multipass weld technique on the heat-affected zone (HAZ) of the low-carbon welds is noteworthy. The last pass has a diamond pyramid hardness (DPH) number of 129, whereas the reheated HAZ is strengthened considerably (DPH of about 165). Further, the weld metal of the high (0.11%) carbon is softened by the multipass technique.

The use of the low-carbon 2.25% Cr–1% Mo steel may require that a cosmetic pass (or passes) be employed to avoid what may be a metallurgical notch due to the low strength in the HAZ. These passes could be subsequently removed by grinding.

Fig. 17.6. Cracks in welds in niobium-stabilized low-alloy steel. (a) Backfilling of cracks. (b) Crack tips and backfilled phase at higher magnification.

Fig. 17.7. Results of electron-beam microprobe analysis of liquated phase in heat-affected zone of a niobium-stabilized low-alloy steel weld. Note enrichment of niobium in backfilled portion of cracks. (a) Image shown by secondary electrons. (b) Display of Nb $L\alpha$ x rays from same area.

Table 17.1. Results of all-weld-metal tensile tests on low-carbon low-alloy steel welds

Specimen designation ^a	Test temperature (°C)	Stress (psi)		Ductility (%)	
		Yield	Ultimate	Total strain	Reduction in area
		$\times 10^3$	$\times 10^3$		
1A1-1	room	88.5	101.4	14.35	79.5
1A1-2	565	53.8	56.7	12.05	80.5
1A1-3 ^b	565	57.8	61.0	8.75	69.4
1A4-1A ^c	room	60.2	74.0	20.1	88.7
1A4-2A ^c	565	46.3	50.1	15.9	86.3
1B-1	room	82.0	104.5	15.65	80.4
1B1-2	565	68.8	92.4	17.8	69.7
1B1-3 ^b	565	74.6	90.7	12.55	52.5
1B6-1A ^c	room	72.2	86.1	18.6	81.2
1B-2A ^c	565	55.0	57.5	13.1	87.5
1C1-1	room	135.2	157.6	14.5	72.0
1C1-2	565	102.5	118.4	13.1	60.8
1C1-3 ^b	565	101.5	116.9	7.7	13.1
1C7-1A ^c	room	90.7	101.6	15.65	84.0
1C7-2A ^c	565	66.0	68.6	13.85	85.0

^aThe A, B, C middle letter designation refers to 0.003%, 0.035%, and 0.11% C, respectively.

^bTests conducted at head speed of 0.002 in./min. All others at 0.05 in./min.

^cDesignation describes a postweld heat treatment of 700°C for 1 hr.

Table 17.2. Hardness measurements in low-carbon low-alloy steel welds

Weld designation	Carbon (%)	Hardness (DPH)			
		Heat-affected zone		Weld metal	
		Last pass	Early pass	Last pass	Early pass
1A	0.003	129	161–171	224–257	162–210
1B	0.03	182	193	251–297	219–263
1C	0.11	245	251	339–401	276–305

18. Corrosion of Advanced Steam Generator Alloys

J. P. Hammond

The program on corrosion behavior of steam generator alloy weldments was expanded to give greater emphasis to materials being considered for LMFBR use and stress corrosion as the mode of failure.

The program currently includes two areas of investigation: (1) general corrosion (uniform scaling, including pitting and knife-edge attack at fusion lines) at 595 and 650°C (1100 and 1200°F); and (2) stress corrosion cracking (induced by chloride or caustic as contaminants) at 480°C (900°F) and higher.

GENERAL CORROSION

The general corrosion specimens of the similar- and dissimilar-alloy weldments in Table 18.1 recently accumulated a total exposure of 16,000 hr (about two years) in superheated steam at 595 and 650°C. Details of the preparation of specimens, whose surface finish was belt-ground, were given previously.¹ The various corrosion data were interpreted, and 20-year base-metal penetrations were calculated for the similar-metal weldments from weight gain as had been done after one year of exposure.²

Table 18.1. General corrosion specimens

Base metal	Base metal	Filler metal
Inconel 625	Inconel 625	Inconel 625
Inconel 625	Incoloy 800	Inconel 625
Inconel 625	Incoloy 800	Inconel 82
IN 102	IN 102	IN 102
IN 102	Incoloy 800	IN 102
IN 102	Incoloy 800	Inconel 82
Hastelloy X	Hastelloy X	Hastelloy X
Hastelloy X	Incoloy 800	Hastelloy X
Hastelloy X	Incoloy 800	Hastelloy W
Hastelloy X	Incoloy 800	Inconel 82
Incoloy 800	Incoloy 800	Inconel 82
Inconel 600	Inconel 600	Inconel 82
Type 304	Type 304	Type 308
stainless steel	stainless steel	stainless steel

The penetrations calculated for 20 years from the 16,000-hr exposure data were generally somewhat less than those from 8000 hr, reflecting shallower curve slopes (second-stage corrosion) for the former. Except for the stainless steel samples, specimens of the respective weldments showed no physical evidence of scale flaking. Therefore, we view the trend toward shallower slopes as favorable. The penetrations calculated³ for 20 years for the Inconel 625, Hastelloy X, IN 102, and Incoloy 800 similar-metal weldments at 595 and 650°C did not exceed 0.0005 in. Inconel 600 welded to itself with Inconel 82 was penetrated about 0.0015 in. at 595°C and 0.002 in. at 650°C. Penetrations were not determined on the stainless steel weldments since they flaked badly.

The structural characteristics of the scales that formed on the various base metals and weld deposits did not appear to have changed significantly as a result of the longer exposure.³ Neither were any indications of aggravated attack noted at fusion lines.

A comparison of our corrosion results on weldments with those of the General Electric Company (Vallecitos Laboratory) on wrought alloys showed that our materials corroded only one-third to one-half as much as theirs.² Since a difference in surface treatment of the specimens could have been a factor in this discrepancy, we assessed the importance of surface finish as a corrosion variable.

1. J. P. Hammond, *GCR Program Semiannu. Progr. Rept. Mar. 31, 1969*, ORNL-4424, pp. 63-72.

2. J. P. Hammond et al., "Corrosion of Advanced Steam Generator Alloy Weldments in 1100 and 1200°F (595 and 650°C) Steam," paper 46 presented at the National Association of Corrosion Engineers 26th National Conference, March 2-6, 1970, Philadelphia; to be published in the proceedings.

3. J. P. Hammond et al., "Corrosion of Nickel Base Alloy Weldments in Steam at 1100 and 1200°F (595 and 650°C)," paper presented at American Welding Society 52nd Annual Meeting, San Francisco, Calif., April 26-30, 1971 (submitted for publication).

Fig. 18.1. Typical scales formed on a dissimilar-metal weldment after 8000 hr exposure at 650°C (1200°F). Top-to-bottom are plate (Inconel 625), filler metal (Inconel 625), and plate (Incoloy 800). Microspecimens unetched.

Identical studies were made with specimens ground on a 100-mesh-grit belt and with ones electropolished to remove the effects of surface grinding (0.002 in. removed). The electropolishing slightly improved the corrosion resistance of some base metals but greatly increased the corrosion of others. Figure 18.1 illustrates the effects of these surface finishes for one of the dissimilar-metal weldments (Inconel 625 welded to Incoloy 800 with Inconel 625 filler metal) after 8000 hr exposure at 650°C. The extent of scaling of the Inconel 625 both as base and filler metal is diminished by electropolishing, whereas that of Incoloy 800 is greatly increased.

To better analyze the effects of these finishes, specimens of the individual base metals were exposed in

duplicate for periods up to 14,000 hr. The weight-gain results for electropolished specimens exposed at 650°C are compared with belt-ground specimens in Fig. 18.2. Figure 18.3 gives the same results on an expanded scale and includes curves for Incoloy 800 at 595°C as well. The corrosion resistance of Hastelloy X as well as Inconel 625 apparently is somewhat improved with electropolishing, whereas that of Incoloy 800 and Inconel 600 is substantially reduced. The corrosion resistance of type 304 stainless steel also was vastly decreased by electropolishing, but results for it are not included in the graphs because of spallation.

A mathematical analysis of the individual alloy specimens represented in Fig. 18.3 indicates that the corrosion of electropolished Incoloy 800 is of a

Fig. 18.2. Corrosion of base metal alloys at 650°C, as-ground and electropolished. Specimen area is 20 cm².

different form than that generally depicted for intermediate- and high-nickel alloys of this general class.³ Instead of its second-stage corrosion conforming to the usual linear equation, the data best fitted an equation of the form

$$Y = A + (1/B + CT)T,$$

where Y is the weight gained, T is time, and A , B , and C are constants. Features prominent in the corrosion of electropolished Incoloy 800 thus are unusually large first-stage corrosion, followed by slowly diminishing corrosion rates during the second stage. The calculated

Fig. 18.3. Corrosion of Incoloy 800 as-ground and electropolished in comparison with other base metals.

20-year corrosion of electropolished Incoloy 800 at 595 and 650°C was comparable with that of the ground alloy. This finding, coupled with the fact that scale-retention tests showed electropolished Incoloy 800 to have extremely high resistance to flaking and spallation,³ reflects encouragingly on Incoloy 800 for high-temperature steam applications.

STRESS CORROSION CRACKING

Five test runs were conducted⁴ in the loop developed for the investigation of stress corrosion of weldments in

4. J. P. Hammond, *Fuels and Materials Development Program Quart. Progr. Rept. Sept. 30, 1970*, ORNL-4630, pp. 281-86.

steam contaminated with NaCl and oxygen. The materials tested, except for several stainless steels and chromium-containing ferritic materials, were much the same as those previously examined for general corrosion.³ The test specimens included welded and non-welded samples $3\frac{1}{4} \times \frac{1}{2} \times \frac{1}{16}$ in., and were statically stressed as U-bends by bending to a $\frac{1}{2}$ -in. radius. They were tested as ground, ground and annealed, and ground, annealed, and pickled.

Table 18.2 summarizes these tests. The first two tests, which were conducted to determine whether cracking occurs under superheated steam conditions, failed to produce cracks. A third run, identical to the first except

that the loop was cycled to the steam saturation temperature (280°C) periodically to introduce entrained moisture, also failed to produce cracks. The chloride level in these runs was held at 0.25 ppm, which is believed to be its saturation concentration in superheated steam at the test pressure (900 psi). In the fourth run, the chloride level was increased to 1.5 ppm, but still no failures occurred.

Finally, a substantially more severe test produced a large number of specimen failures. In this run, the NaCl and oxygen levels were 25 and 50 ppm, respectively, and the time at the steam saturation temperature was increased. Table 18.3 summarizes the information on the steam generator alloy weldments that cracked.

It should be noted that, whereas a considerable number of different alloy weldments with ground surfaces failed, cracks were not generally found in the same alloys when ground and annealed or ground, annealed, and pickled. Weldments of Inconel 625 welded with itself did not fail in any condition.

Figure 18.4 illustrates the failed Hastelloy X U-bend specimens and the microstructural characteristics of the stress-corrosion crack. The cracks in the various alloys were generally intergranular and usually initiated alongside the root pass in the heat-affected zone. Occasionally cracks propagated into the weld deposits.

Our test results on weldments generally confirm findings of other investigators working with wrought materials — namely, that some high-nickel alloys do fail by stress corrosion under adverse conditions in steam containing high concentrations of NaCl and oxygen.

Table 18.2. Stress corrosion tests in steam with NaCl and oxygen as contaminants

Run	Conditions of test		Contaminants (ppm)		Results
	Time (weeks)	Temperature (°C)	NaCl	O ₂	
1	5	540	$\frac{1}{4}$	20	No cracks
2	5	315	$\frac{1}{4}$	20	No cracks
3	5	540–280 (2 hr at 280, 5 times per week)	$\frac{1}{4}^a$	20	No cracks
4	5	480–280 (2 hr at 280, 5 times per week)	$1\frac{1}{2}^a$	20	No cracks
5	7	480–280 (24 hr at 280, 3 times per week)	25 ^a	50	Some cracks

^aContamination level at 280°C only.

Table 18.3. Steam generator alloy weldment specimens cracked by stress corrosion in steam containing 25 ppm NaCl and 50 ppm O

Base metal	Filler metal	Surface conditions	Crack time (weeks)	Number of failures	Crack length (in.)	Location ^a
Type 304 stainless steel	Type 308 stainless steel	Ground	2	3 of 3	1/2	B and W
18-18-2 stainless steel	18-18-2 stainless steel	Ground	2	2 of 3	1/2	W
Hastelloy X	Hastelloy X	Ground	2	3 of 3	3/32–1/2	B through W
Hastelloy N	Hastelloy N	Ground	1	4 of 4	1/2	W
Incoloy 800	Inconel 82	Ground	2–7	3 of 3	1/8–1/4	B
IN 102	IN 102	Ground	5	1 of 3	1/8–1/4	B
Inconel 600	Inconel 82	Ground ^b	7	3 of 3	1/8–1/4	B through W

^aB = base metal; W = weld metal.

^bSpecimens had a prior steam exposure as U-bend specimens without cracking. They were retightened and then tested.

Fig. 18.4. Characteristics of chloride stress corrosion in Hastelloy X weldment. (a) U-bend specimens after failure. (b) Microstructural features of the crack. Etched with mixture of H_2O_2 and HCl . 100X.

19. Sodium Corrosion in LMFBF Systems

J. H. DeVan   W. O. Harms

The purpose of this program is to determine the corrosion properties of fuel cladding and structural materials for liquid-metal fast breeder reactor (LMFBR) systems. Our studies are concerned with the effects of interstitial impurities in sodium on the corrosion properties of vanadium alloys

EFFECT OF OXYGEN IN SODIUM ON THE CORROSION OF VANADIUM AND VANADIUM ALLOYS

R. L. Klueh

We continued our studies¹ to determine the effect of alloying elements on the solubility of oxygen in vanadium. We concluded that Cr, Mo, Fe, Ta, and Nb — none of which form internal oxides — lower the solubility of oxygen in vanadium — chromium, molybdenum, and iron much more than tantalum and niobium. By varying the chromium content, we determined the thermodynamic interaction parameter $\epsilon_0(\text{Cr}) \cong 7.5$.

We derived equations to determine the effect of alloying components in vanadium on the oxygen diffusion coefficient. We tested these equations using data from studies of the redistribution of oxygen between vanadium and vanadium alloy specimens that had been doped to various oxygen levels. The diffusion equations were derived under the assumption that the diffusion of oxygen was the rate controlling step in the oxygen transfer. However, our experiments showed that a surface reaction may control the transfer in some instances

OXIDATION OF VANADIUM AND VANADIUM ALLOYS

R. L. Klueh

Studies of the effect of sodium on vanadium and vanadium alloys clearly demonstrate that corrosion is

directly related to the oxygen concentration of the sodium, and that oxidation studies can be used to augment sodium studies.² We therefore studied the oxidation kinetics of vanadium and V-20% Ti at 600 and 1000°C under reduced oxygen pressures (from 8×10^{-6} to 8×10^{-4} torr)

Under all conditions tested, oxidation occurred in two stages — an initial linear stage and a subsequent stage in which the rate decreased with time (parabolic-like). The initial state is symptomatic of a reaction rate determined by the rate of oxygen adsorption on the specimen surface. During the second stage a surface scale forms, and the reaction is probably controlled by diffusion through the scale. However, oxygen continues to dissolve in the metal matrix, so this stage is not completely parabolic. At 600°C, where the oxidation rate is significantly lower than at 1000°C, the length of the first stage is substantially reduced because of the lower oxygen diffusion coefficient at 600°C.

Simple microstructural studies on V-20% Ti have demonstrated the utility of oxidation studies for sodium applications. Studies of V-20% Ti in sodium reveal what investigators have described as a "hardened zone" immediately below the external surface. We showed² that the kinetics of penetration of the "hardened zone" follow that predicted for internal oxidation and concluded that a precipitate was not observed metallographically because the temperature of oxidation was too low (about 650°C) for appreciable titanium diffusion. Thus, oxidation and precipitation occurred in place, with little or no agglomeration.

To verify this, we oxidized V-20% Ti specimens for various times at 1000°C at an oxygen pressure of 5×10^{-5} torr and followed the progress of the internal oxidation zone into the specimen interior. For oxidation times longer than 2 hr, the initial precipitation zone was accompanied by the formation of a zone of different etching characteristics that started at the specimen surface and also moved inward with time,

¹ R. L. Klueh, *Metals and Ceramics Div. Annu. Progr. Rept.* June 30, 1970, ORNL-4570, p. 92

² R. L. Klueh and J. H. DeVan, *J. Less Common Metals* 22, 389-98 (1970)

consuming the internal oxidation zone. A similar microstructure was observed at 600°C, a temperature similar to that in sodium studies, and is shown in Fig. 19.1. This microstructure is identical to that observed by Levin and Greenberg³ on V-10% Ti exposed to zirconium-gettered sodium at 650°C. Knoop microhardness measurements reveal a constant hardness of 1290 through the light-etching region followed by a rapid decrease through the dark zone (apparently a zone of fine precipitate particles) and then a constant hardness of about 250 in the oxygen unaffected zone.

The darker zone apparently is formed as oxygen diffuses into the alloy and reacts with the titanium to precipitate titanium oxide. As this zone moves into the specimen interior, a concentration gradient develops between the specimen surface (oxygen concentration determined by the oxygen partial pressure) and the precipitation front (oxygen concentration near zero). Eventually, the concentration of oxygen near the surface increases enough to induce the α (bcc, solid solution) $\rightarrow$ β (bct, solid solution) phase transformation.⁴ Evidently the extreme hardness of the β phase makes it impossible to resolve the precipitate. This conclusion is supported by the hardness measurements, which are consistent with measurements made at Ames Laboratory on α and β solid solutions. Since the phase transformation has not been observed on similarly oxidized vanadium (in a sodium or gaseous environment), it appears that the oxygen concentration for the transformation is lower in the vanadium-titanium system, perhaps as a result of the internal stresses generated by the oxide precipitate.

3. H. A. Levin and S. Greenberg, *An Exploratory Study of the Behavior of Niobium- and Vanadium-Base Alloys in Oxygen-Contaminated Sodium*, ANL-6982 (January 1968)

4. J. L. Henry et al., *J. Less-Common Metals* 21, 115-35 (1970).

Fig. 19.1. Alloy V-20% Ti oxidized for 400 hr at 600°C and an oxygen pressure of 5×10^{-5} torr. A superimposed hardness profile shows the hardness difference between material affected and unaffected by oxygen

20. Sodium Removal and Caustic Effects

W. O. Harms   J. H. DeVan

The purpose of this program is to evaluate the corrosion of structural components caused by the products of sodium oxidation or hydrolysis. The program deals with oxidation problems arising from sodium-water reactions and from the leakage or spillage of sodium on metal surfaces that are in contact with mixtures of nitrogen and air. It is also concerned with corrosion effects that result from the cleaning and storage of materials after exposure to sodium.

EXAMINATION OF ALCO/BLH STEAM GENERATOR

G. M. Slaughter   R. H. Jones¹
J. H. DeVan   P. Patriarca

We are examining the ALCO/BLH steam generator,^{2,3} which failed while under test at the Liquid Metal Engineering Center (LMEC). After installation at the Sodium Components Test Installation of the LMEC in 1965, the steam generator operated intermittently with sodium for 7600 hr and with steam for 4100 hr. A water leak on the feedwater chest was found in May 1970, and was traced to an area of extensive cracking in the lower tube sheet. In view of the vital role of steam generators in the LMFBR demonstration-plant program and the well-documented fabrication and operational history of this unit, it is being examined to determine the mechanism of failure and to study other metallurgical features of interest.

The steam generator arrived at ORNL on December 7, 1970, and was placed in the Experimental Gas Cooled Reactor turbine building for examination. All tube-to-tube-sheet welds were dye-checked and found to be free of cracks. Flow tests on open tubes (those not previously welded shut with plugs) revealed them to be

essentially unblocked. However, leaks were found in two tubes that had been in service at the time of test termination. We observed a massive collection of reaction products in the argon cover gas space above the sodium level. These deposits covered the underside of the tube sheet, tube interstices, thermocouples, and the inner surface of the shell. Surfaces underlying these deposits showed corrosion effects typical of those caused by fused sodium hydroxide.

A detailed analysis of the 6 $\frac{5}{8}$ -in.-thick lower tube sheet, both nondestructive and metallographic, is currently under way. We found an extensive system of cracks in this region (Fig. 20.1), and a step-by-step procedure is being followed to determine the mechanism.

STUDY OF METHODS FOR CLEANING SURFACES OF MATERIALS EXPOSED TO SODIUM^{4,5}

J. H. DeVan   D. H. Jansen

The effectiveness of various sodium removal techniques was tested by exposing several potential LMFBR structural alloys in static sodium for short periods of time, stripping the specimens of residual sodium, and re-exposing in sodium. Alloys chosen for investigation were types 304L and 321 stainless steel, 2.25% Cr-1% Mo steel, Incoloy 800, Inconel 625, and IN 102. These alloys were tested in one of two geometries: either as tubes fillet-welded into a small block or as side-by-side sheets welded on two opposite edges. Both designs provided built-in crevices typical of those existing in sodium heat exchangers. Sodium was removed from the specimens by hydroxide-forming solvents (steam, water, and alcohol), anhydrous ammonia, and vacuum distillation. An additional set of specimens was simply drained

1. Plant and Equipment Division.

2. J. H. DeVan and G. M. Slaughter, *Fuels and Materials Development Program Quart. Progr. Rept. Dec. 31, 1970*, ORNL-TM-3300, pp. 182-84.

3. J. H. DeVan, G. M. Slaughter, and R. H. Jones, *Fuels and Materials Development Program Quart. Progr. Rept. March 31, 1971*, ORNL-TM-3416, pp. 155-61.

4. J. H. DeVan, *Fuels and Materials Development Program Quart. Progr. Rept. Dec. 31, 1970*, ORNL-TM-3300, pp. 185-87.

5. J. H. DeVan, *Fuels and Materials Development Program Quart. Progr. Rept. March 31, 1971*, ORNL-TM-3416, pp. 161-65.

Fig. 20.1. Gross cracking in segment of lower tube sheet of ALCO/BLH steam generator. Tube sheet was $6\frac{5}{8}$ in. thick.

and exposed to air, with no attempt made to remove the residual sodium before the final sodium test. Two heating schedules were selected for the final sodium tests: (1) 100 hr at 700°F plus 900 hr at 1100°F and (2) 1000 hr at 1100°F.

Metallographic examinations of the specimens following these exposures showed significant corrosion of all specimens except those cleaned by water or steam. Corrosion was the result of a coating of Na_2O that remained on the specimen surface following cleaning, and corrosion was no heavier in the built-in crevices than on other surfaces. There were no indications in these studies of caustic attack occurring during sodium removal, even in the crevices.

The stainless steels and nickel-base alloys exhibited equivalent attack, and the $2\frac{1}{4}\%$ Cr–1% Mo steel was attacked more than the other alloys. We saw no differences in attack as a function of the initial oxygen concentration of the sodium (up to 100 ppm), which

confirms that the attack was due to a locally high concentration of caustic at the specimen surface. Also, the extent of attack was the same for both of the final heating schedules cited above.

CORROSION EFFECTS OF SODIUM LEAKS OR SPILLS IN GASES CONTAINING OXYGEN^{4,5}

J. H. DeVan

Sodium in both the liquid and solid states oxidizes rapidly when exposed to atmospheres that contain O_2 , CO_2 , or H_2O . The resultant oxidation products are potentially damaging to structural components used in LMFBR systems. At 500°C or higher, damage accrues from the fluxing effects of sodium oxides on otherwise protective base-metal oxides. At lower temperatures, damage can result from dissolution and stress-corrosion effects of hydrated caustic residues.

Accordingly, we began a series of tests to evaluate the debilitating effects of sodium (or sodium compounds) on stainless steel in mixtures of nitrogen and air. Since the tests were aimed specifically at the problem of a leak or spill in the annulus between the containment vessel and the outer guard vessel of the FFTF reactor, we constructed a test apparatus that would maintain a controlled flow of sodium through a simulated defect in

a type 304 stainless steel specimen and into an atmosphere representative of that surrounding the exterior of the FFTF vessel. The test system was designed to provide a leakage rate of sodium through the specimen in the range 1 to 200 g/hr. In four test runs we verified the adequacy of the specimen design and the analytical capability of the gas analysis system. Work on this task was then discontinued.

21. Nondestructive Testing Techniques for LMFBFR

W. O. Harms   R. W. McClung

We are developing new methods, techniques, and equipment for nondestructively inspecting materials and components for the Liquid-Metal Fast Breeder Reactor (LMFBR) program. Among the methods studied are electromagnetic induction, ultrasonics, and penetrating radiation. Special emphasis is being given to developing techniques for measuring the degree of cold work in small-diameter type 316 stainless steel tubing.

DEVELOPMENT OF ADVANCED NONDESTRUCTIVE TESTING

Eddy-Current Instrument

C. V. Dodd

We derived the theoretical equations and wrote computer programs for determining both the depth and size of defects in cylindrical conductors. We also constructed a phase-shifting network to calibrate the modular phase-sensitive eddy-current instrument within 0.02° for the experimental verification.

Dual-frequency modules were designed, constructed, and tested for use with the modular instrument. With these modules, two parameters (e.g., conductivity and thickness) can be measured simultaneously.

Ultrasonic Schlieren Technique for Inspection of Welds

H. L. Whaley   K. V. Cook

We continued our study of the response of ultrasound to various types of defects in stainless steel welds. A new type of transducer unit using multiple receiving elements was constructed and tested. With an increase of the signal-to-noise ratio, this device should be practical in situations where there is less dependence on exact flaw orientation. The weld samples were examined radiographically and then ultrasonically by the

Delta technique.¹ Results with the Delta technique were poor, apparently due to excessive scatter caused by the large grains of the welds. The optical system has been enlarged and improved so that placement of the heavy weld samples in the test tank no longer disarranges the optics. Examination of the stainless steel samples by the schlieren technique is under way. Visual observation of the interaction of ultrasonic pulses with the sample should give improved insight into the optimum test conditions for inspection of such samples.

MEASUREMENT OF COLD WORK IN STAINLESS STEEL

C. V. Dodd   W. A. Simpson, Jr.

We are investigating methods for nondestructively measuring the degree of cold work in small-diameter stainless steel tubing for application to inspection of FFTF fuel-pin cladding. We emphasize the use of electromagnetic induction for detecting the changes in magnetic permeability produced by cold work.

We have designed, constructed, and tested a low-frequency eddy-current bridge system to measure the cold work in type 316 stainless steel tubing² at an inspection speed of 200 ft/min. Computer calculations indicated that we could measure cold work of 0.250-in.-diam tubing within 3.75% for the worst combination of variables, and experimental measurements gave results within 1.5%.

Our bridge system was used to test a set of 0.300-in.-OD type 316 stainless steel rods fabricated at Argonne National Laboratory to contain a range of cold

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1. H. L. Whaley and K. V. Cook, *Fuels and Materials Development Program Quart. Progr. Rept. June 30, 1970*, ORNL-4600, pp. 153-55.

2. C. V. Dodd and W. A. Simpson, Jr., "Measurements of Small Magnetic Permeability Changes by Eddy-Current Techniques," paper presented at the 30th National Fall Conference for Nondestructive Testing in Cleveland, and to be published in *Materials Evaluation*.

work. A smooth curve of magnetic permeability vs cold work was obtained, although the change in permeability for a given difference in cold work was smaller for the rods than for the tubes.

A computer analysis was made on a new type of coil system for measuring cold work in tubing. The new system consists of two driving coils and two receiving coils. It had a calculated error of 2.4% for the worst combination of variables for measuring 0.230-in.-diam

tubing. The coils have been constructed and are being tested.

A computer study is being made on the use of reflection coils (such as those used with the phase-sensitive eddy-current instrument) to measure permeability changes on flat stainless steel specimens, such as the faces of the FFTF fuel subassembly shroud. Preliminary studies indicate high sensitivity with only small error due to variations in lift-off.

22. Fast Breeder Neutron Absorber Materials

W. R. Martin

Boron carbide has been used extensively as a neutron absorber in thermal reactors. For the fast breeder test and demonstration reactors, boron carbide and tantalum are presently the prime candidate materials. However, little is known about the performance of these or other absorber materials at the temperature and fluence expected in fast breeder reactors. The purpose of our current program has been to characterize boron carbide, investigate its basic irradiation behavior, and use this information to optimize its performance in fast reactor service. The key points are to identify the important materials variables and to determine what effect these have on performance in a fast reactor.

INDEXING OF X-RAY DIFFRACTION POWDER PATTERNS OF BORON CARBIDE

H. L. Yakel

We have completely indexed the Cu K α x-ray diffraction powder patterns of boron carbide¹. Some of the previously unidentified lines were due to impurities. Due to the complexity of the Cu K α patterns of the boron carbide in the high-angle regions that are required for accurate lattice parameter measurements, we indexed patterns using the K α x rays from Cr, Fe, Co, and Ni. These longer wavelength x rays simplify the pattern in the high angle regions and thus simplify the measurement of lattice parameters with no loss of accuracy.

X-ray diffraction of boron carbide is also described in Chap. 12 of this report.

X-RAY DIFFRACTION FROM IRRADIATED BORON CARBIDE POWDERS AND CRYSTALS

G. L. Copeland   V. J. Tennery   H. L. Yakel

Lattice parameters calculated from Debye-Scherrer x-ray powder patterns of boron carbide powders irradiated at 350 to 500°C in the ORR to burnups of about 8% of ¹⁰B (1.6×10^{21} atoms/cm³) reveal a large

amount of strain in the lattice. In one case, the *a* parameter increased significantly and the *c* parameter decreased slightly (*a* and *c* are the hexagonal indices corresponding to the rhombohedral boron carbide structure). In another case, the *a* parameter decreased slightly and the *c* parameter increased. In both cases the volume of the unit cell increased 0.5%.

Single crystals of boron carbide have been irradiated to fluences of 1.8×10^{20} neutrons/cm² (thermal) in the ORR at 350 and 550°C. Results to date show a significant variation from those reported in 1955 by Tucker and Senio² for boron carbide crystals irradiated to 3×10^{20} neutrons/cm² at an unspecified temperature. Like the earlier data, our patterns are a composite of sharp Bragg maxima (unbroadened relative to the unirradiated crystal reflections) and diffuse reflections located at or near these sharp maxima. Again like the earlier data, a highly anisotropic Debye-Waller factor diminishes the intensities of reflections with *l* large compared to *h* and *k* (hexagonal indices). But whereas Tucker and Senio reported an anisotropic lattice expansion (*a* increases, *c* decreases on irradiation), we noted that both *a* and *c* increase over their unirradiated values if the sharp maxima alone are considered. The lattice parameters estimated from the positions of the diffuse reflections correspond to an increase in *a* and a decrease in *c*.

We suggest a tentative model of a damaged structure that might produce these observed x-ray diffraction effects. It imagines the crystal to be a composite of regions in which individual defects (displaced atoms, vacant icosohedral or chain sites) are located and regions containing extended planar collections of defects. The former give rise to the sharp Bragg maxima, the latter produce the diffuse peaks.

1 H. L. Yakel, *Fuels and Materials Development Program Quart. Progr. Rept. Dec. 31, 1970*, ORNL-TM-3300, pp 188-91.

2 C. W. Tucker, Jr., and P. Senio, *Acta Cryst.* 8, 371 (1955).

TRANSMISSION ELECTRON MICROSCOPY OF IRRADIATED BORON CARBIDE

G. L. Copeland C. K. H. Dubose D. N. Braski³

We have produced thin films of irradiated boron carbide for transmission electron microscopy by two techniques.⁴ One consisted of preparing thin foils (0.003 in. thick) from a high-density pellet, irradiating the foils in a capsule, and then loading them directly into the ion-bombardment micromilling machine for further thinning. The second method was to irradiate boron carbide particles in a capsule, disperse the particles in an aluminum matrix, and then thin the composite. The ion milling machine attacks the aluminum and boron carbide at the same rate, so that uniform thin films may be obtained.

The microstructures are the same in each case for the ranges investigated. The burnups were about 8% of the ^{10}B (1.6×10^{21} atoms/cm³) at irradiation temperatures of 350 to 400°C. Figure 22.1 shows a grain boundary in a particle. The high density of black spots indicative of a large amount of lattice strain is uniform over the entire field, but the spots are out of contrast in one grain. The foil sample showed a large amount of microcracking and was extremely brittle. The high irradiation damage density was uniform throughout all the samples, with no observable differences near grain boundaries, twin boundaries, intragranular voids, or particle edges. No helium bubbles or other evidence of reaction product agglomeration was observed. Electron microscopy of boron carbide is also discussed in Chap. 5 of this report.

EFFECT OF ELEMENTAL BORON ON GAS RELEASE FROM IRRADIATED BORON CARBIDE POWDERS

G. L. Copeland

Irradiation of boron carbide powders containing different levels of elemental boron resulted in additional gas release over that expected from powders in which all the boron was combined with carbon. Elemental boron powder was blended with boron carbide powder and annealed at temperatures of 1000 to 2000°C. This treatment resulted in boron carbide containing free boron ranging from 0.6 to 11.6 wt %. Irradiation of the powders containing 11.6 wt % free boron in the ORR at 300 to 550°C resulted in helium

3. Isotopes Division.

4. C. K. H. Dubose, D. N. Braski, and G. L. Copeland, *Fuels and Materials Development Program Quart. Progr. Rept. Dec. 31, 1970*, ORNL-TM-3300, pp. 202-8.

Fig. 22.1. Transmission electron micrograph of irradiated boron carbide particle, showing uniform damage up to grain boundary. 90,000X.

release up to 30% of that generated. Boron carbide powders with no free boron have exhibited helium release of about 5% under the same irradiation conditions. These results show that uncombined boron is an undesirable constituent for any nonvented fast reactor control rod.

IN-REACTOR GAS PYCNOMETER FEASIBILITY EXPERIMENT

G. W. Keilholtz⁵ R. E. Moore⁵ D. A. Dyslin⁶

A gas pycnometer that can measure the swelling of boron carbide specimens during irradiation is being tested. The measurement is based upon the ideal gas laws with a system containing helium. A specimen chamber in the reactor core will be connected by a capillary tube to a bellows volume changer and accurate pressure gage located outside the reactor. The specimen would operate at elevated temperatures, for example 700°C, and the capillary tube and bellows will be near room temperature. It is desirable to detect specimen swelling of 5% during a three-month irradiation.

A preliminary error analysis of the system has shown that the volume of a 1-in.³ specimen could be determined within $\pm 0.6\%$. This predicted error is due to inaccuracies in pressure and temperature measurements as well as the initial volume of the system.

A gas pycnometer bench test with the entire system at room temperature has been run. The system pressure stabilized within 2 to 5 min after the system volume was changed, and the volume of a 1-in.³ specimen can be determined within $\pm 0.3\%$. Additional tests will be required to establish the accuracy of the method at

elevated temperatures, since temperature changes between pressure readings are a major factor in this experiment.

FAST REACTOR IRRADIATION TESTING OF ABSORBER MATERIALS

G. L. Copeland R. E. Moore⁵
G. W. Keilholtz⁵ D. A. Dyslin⁶
R. G. Donnelly

An irradiation experiment described previously⁷ was built, was inserted in the EBR-II, and is proceeding on schedule.

A second test of seven capsules and a third test of four capsules are being prepared for insertion in the EBR-II. These tests are designed to determine: (1) the effects of neutron capture rate on solid swelling and gas release of boron carbide, (2) comparative irradiation performance of TaB₂ and Ta₂B, (3) effect of sodium bonding on the irradiation performance of boron carbide, (4) comparison of cold-pressed boron carbide pellets, and (5) effect of neutron irradiation on the physical and mechanical properties of tantalum and its alloys.

5. Reactor Chemistry Division.

6. General Engineering Division.

7. G. L. Copeland and G. W. Keilholtz, *Metals and Ceramics Div. Annu. Progr. Rept. June 30, 1970*, ORNL-4570, p. 102.

Part III. Space Power Technology

23. Materials Development for Isotopic Power Programs

R. G. Donnelly

Materials studies on isotopic power programs have been primarily in support of space activities, with only strontium compound compatibility and plasma-arc welding studies in support of terrestrial isotopic power. The development of new cladding alloys is aimed specifically at ^{238}Pu -fueled heat sources but could apply to ^{244}Cm when missions arise requiring this isotope

Our cermet fuels studies have centered on determining fabricating methods to optimize specific properties. In these activities we have confined our efforts to molybdenum cermets containing ThO_2 as a stand-in for $^{238}\text{PuO}_2$ and $^{244}\text{Cm}_2\text{O}_3$. The lessons learned with these cheaper, more easily handled materials will be applied next year to fueled cermets and cermets containing noble metals.

In addition to the subjects reported here we also provided materials consultation on the Isotope Kilowatt Program.

CLADDING MATERIALS PROGRAM

New Platinum-Rhodium-Tungsten Cladding Alloys for Space Isotopic Heat Sources¹

C. T. Liu   H. Inouye   R. G. Donnelly

The radioisotopic fuel used for space power systems must be clad in a highly reliable material, not only to contain the fuel for normal operation of several years, but to survive launch abort situations, severe aerodynamic heating on re-entry, high-velocity impact, and postimpact environment. Because no single alloy of

current manufacture can meet the severe service and safety requirements, multiple layers of refractory alloys clad with a platinum-rhodium alloy, so that one alloy compensates for the shortcomings of another, are now being considered. However, recent studies indicate that the performance of refractory alloy components in such capsule assemblies is not as reliable as desired from the standpoint of oxidation resistance and compatibility. Moreover, the available platinum-base alloys (Pt-20% Rh and Pt-30% Rh) possess adequate oxidation resistance and fabricability but lack the desired mechanical strength and high melting point. Our program objective has been to develop fabricable alloys with better strength, excellent oxidation resistance, improved compatibility, and a high melting point. This paper summarizes the above properties in terms of the effect of tungsten content on the platinum-rhodium base.

Ingot of the platinum-base alloy designated as Pt-3010, containing 26 to 30% Rh and 6 to 10% W (wt %), are readily fabricable to sheet material by hot forging in air followed by cold rolling. Figure 23.1 shows the tensile properties as a function of testing temperature. The Pt-26% Rh-8% W alloy has about 15% elongation at room temperature, and this increases to 47% at 1316°C. This alloy is substantially stronger than Pt-30% Rh at all temperatures, stronger than T-111 and TZM to 1093°C, and equivalent to TZM at 1316°C.

Alloying with up to 10% W did not significantly impair the excellent oxidation resistance of the platinum-rhodium base. For example, the Pt-30% Rh-10% W alloy oxidized in air at an average rate of 7.5, 2.2, and $0.26 \times 10^{-6} \text{ g cm}^{-2} \text{ hr}^{-1}$ at 1200, 1000, and 760°C, respectively. These rates are four orders of magnitude lower than those for molybdenum- and tantalum-base alloys and only 6 times those for

¹ Abstracted from paper submitted for the 1971 Winter American Nuclear Society Meeting, Miami Beach, Oct. 17-21, 1971.

Fig. 23.1. Comparison of the tensile properties of Pt-26% Rh-8% W alloy with Pt-30% Rh, T-111, and TZM. Data for T-111 and TZM are from General Electric Company, *Multi-Hundred Watt, Radioisotope Thermoelectric Generator Program*, GESP-7034 (March 1970).

platinum. Furthermore, metallographic examination of the specimens oxidized at 1000°C showed no grain boundary oxidation.

In the binary alloy systems platinum-tungsten and rhodium-tungsten, an increase in the tungsten content increases the melting point. We found that Pt-3010 has a melting point above 2000°C, which fulfills the current requirement for space cladding material. The alloys have good weldability. Metallographic examination of TIG welds on sheet material showed no cracking as welded or after bending 90°. Also, Pt-3010 alloys are more compatible than the Pt-30% Rh alloy with T-111, tungsten, and molybdenum from 900 to 1700°C.

Atomic Ordering and Structural Transformation in the V-Co-Ni Ternary Alloys²

C. T. Liu

The transition behavior of the close-packed ordered nine-layered structure (K phase) existing in the V-Co-Ni

ternary alloys was investigated. Both neutron and x-ray diffraction indicate that atomic ordering and structural transformation take place separately. The first step of transition is to form the AuCu_3 -type ordered structure (α' phase), and the apparent activation energy for atomic ordering is estimated to be 76 kcal/mole. The α' to K transition proceeds by nucleation and growth; however, both mode and morphology of transition vary with reaction temperature. These observations have been discussed in terms of temperature dependence of nucleation and growth processes. The structural transformation produces massive substructures, which harden the alloy substantially.

CERMET FUELS

Evaluation of Fabrication Techniques for Cermet Isotope Fuel Simulants¹

L. E. Poteat   R. W. Knight
R. G. Donnelly   J. I. Federer

The heat source used in the thermoelectric generator for the Pioneer and Transit programs contains ^{238}Pu in the form of a plutonium oxide-molybdenum cermet (PMC). The molybdenum matrix improves the mechanical properties and increases the thermal conductivity. The heat source consists of a stack of 22 cermet disks, each about 2 in. in diameter $\times$ 0.25 in. thick. Because of the limited quantities of plutonium available and because of the safety hazard involved in handling this highly radioactive material, thorium-molybdenum cermet disks are being used to simulate the plutonium-molybdenum cermet during capsule qualification and generator testing.

Three different techniques for fabricating thorium-molybdenum cermets were investigated. The first was hot pressing of thorium powders coated with molybdenum by chemical vapor deposition, as used in the fabrication of PMC. For comparison, two less expensive alternate techniques, (1) cold pressing and sintering of blended molybdenum and thorium powders and (2) hot pressing of blended powders, were also investigated.

The microstructure of the hot pressed coated thorium particles shows low porosity and an almost continuous molybdenum phase. In this technique the 105- to 177- μm thorium powder is coated with molybdenum by chemical vapor deposition in a fluidized bed. A 3- μm coating is produced by the reduction of MoF_6 with hydrogen at 625°C and 1 atm to give 17.5% Mo. When hot pressed at 1800°C and 6600 psi for 1 hr, a 98%-dense cermet disk is produced.

The most economical alternate method of producing the cermet is blending the two powders followed by

2. Abstract of paper submitted for publication.

cold pressing and sintering. To develop high strength and high thermal conductivity, a continuous metal phase is desirable. To obtain the most continuous phase with a fixed amount of metal (17.5%), large grains (105 to 177 μm) of thoria were blended with fine (0.565 μm average) molybdenum powder. An 85%-dense cermet was produced by pressing at 63,000 psi and sintering in vacuum at 2200°C for 4 hr. The addition of 0.5% CaO to the thoria to increase its sinterability led to 90%-dense disks. The microstructure shows excessive porosity, and the molybdenum does not appear to be continuous.

To reduce the porosity, blended fine molybdenum powder and coarse thoria powder were hot pressed at various temperatures and pressures. Hot pressing at 1800°C and 6600 psi for 1 hr produced 99%-dense disks. The microstructure shows very little porosity and a more continuous metal phase.

Electrical resistivity was measured on structures produced by the three different techniques. The resistivity was about the same for the hot-pressed blended powder disks and the cold-pressed-and-sintered disks and was almost 50% greater than that of the hot-pressed CVD-coated particles. This would indicate that the thermal conductivity of the disks from the CVD-coated particles is greater than that of disks produced by the other two techniques. The mechanical strength of the cermets was determined by three-point bend tests. The disks produced from the CVD coated particles were 25% stronger than the others.

Of the three techniques investigated, the disks produced by hot pressing the CVD-molybdenum-coated thoria powders appear to have superior strength and conductivity. These superior properties are a result of the thoria grains being essentially encapsulated in a continuous matrix of molybdenum.

Controlled Porosity Cermets for Application to Curium Fuel Forms¹

M. M. Martin   R. G. Donnelly

Because $^{244}\text{Cm}_2\text{O}_3$ has about 5 times the power density of $^{238}\text{PuO}_2$, it permits greater flexibility in the fuel form design. For instance, either a $^{244}\text{Cm}_2\text{O}_3$ cermet can have 5 times the power density of a $^{238}\text{PuO}_2$ cermet with an equivalent metal content, or additional metal can be used to improve the impact resistance and postimpact fuel containment and still allow a significant power density advantage. We have investigated ranges of fabrication conditions for molybdenum-ThO₂ as a stand-in for molybdenum- $^{244}\text{Cm}_2\text{O}_3$ and noble metal- $^{244}\text{Cm}_2\text{O}_3$ cermets. Our aim has

been to develop fuel forms with the most desirable combination of properties and to reduce the in-cell development requiring curium. We have specifically attempted to structure the cermet to provide for release of helium so that the fuel form should not swell and thereby be physically degraded.

Two fabrication approaches have been pursued: hot pressing, and cold pressing and sintering. Small cylindrical pellets of molybdenum with 0, 20, 40, 60, and 80 vol % ThO₂ powder were compacted and tested under varying conditions for porosity, helium permeability, compressive yield strength, and microstructure. Cold pressing and sintering parameters studied were pressure (25,000, 50,000, 100,000 psi), temperature (1400, 1600, 1800, 2000°C), and duration at temperature (60, 120, 240 min). Hot pressing parameters were temperature (100, 1300, 1600°C) and duration of 6000-psi applied load (15, 30, 60 min) at temperature.

The density of cold-pressed-and-sintered molybdenum-ThO₂ pellets depended primarily upon the pressing pressure and to a lesser extent upon the ThO₂ concentration. The pressing temperature established the degree of consolidation for the hot-pressed cermets, and pressing time produced little, if any, effect. Similar appearing microstructures produced by the two techniques also correspond to equivalent compressive yield strengths at 5% offset strain. During the 400°C compressive test, most specimens exhibited sufficient ductility to minimize the release of activity on testing. However, pellets hot pressed at 1000°C and cold-pressed-and-sintered cermets containing 40 vol % ThO₂ crumbled at low stress and strain. We can control the void content of both types of cermets over a rather wide range. More importantly, most of the voids are interconnected, resulting in a structure permeable to helium.

Both techniques have some drawbacks. The cold-pressed-and-sintered molybdenum-ThO₂ pellets contain numerous matrix fissures, which are perpendicular to the pressing direction. These flaws can be minimized by compacting at reduced pressure, but this maximizes void content.

Data on strength, permeability, and microstructures as a function of fabrication parameters are presented.

COMPATIBILITY

J. R. DiStefano

We have conducted experiments over the past several years to determine the compatibility of potential container materials with $^{244}\text{Cm}_2\text{O}_3$ at temperatures from 750 to 1850°C. For thermionic applications

(>1500°C) W-26% Re, TZM, and Mo appear to be satisfactory container materials.^{3,4} After 10,000 hr at 1250°C, Nb, Nb-1% Zr, Ta, Ta-10% W, Mo, and V appearing promising, but pure zirconium reacted extensively with $^{244}\text{Cm}_2\text{O}_3$.

Two strontium compounds, SrTiO_3 and Sr_2TiO_4 , seem to be very compatible with Haynes alloy No. 25, Hastelloy C, and type 316 stainless steel,⁵ even after 10,000 hr at 1100°C. Strontium oxide reacts with these alloys but significantly less at 900°C than at 1100°C. In Hastelloy C the reaction is perhaps related to the presence of one or more intermetallic phases and appears to cease⁶ after 5000 hr. In laboratory heats containing very low silicon and relatively high carbon or in alloys containing very high silicon, these phases do not form, and no attack was observed. Potassium in SrO also decreased its compatibility with Hastelloy C.

PLASMA-ARC WELDING OF AN ISOTOPE CAPSULE¹

G. M. Goodwin   B. F. Early⁷

A certain thermoelectric generator uses a ^{90}Sr titanate fuel form contained in a heavy-walled capsule of Hastelloy C, a nickel-base alloy with excellent strength, oxidation, and corrosion properties. The capsule design uses a threaded end cap, with a closure weld to ensure containment. Based upon a maximum anticipated seawater corrosion rate, a minimum weld penetration of 0.055 in. is required.

Autogeneous gas-tungsten arc (GTA) welding has been used to produce the closure; however, for certain weldment designs and materials, the attainment of the required penetration by GTA welding presents problems. Sample welds made before and after the fueled capsule weld are used to indicate the penetration of the actual capsule seal weld. The weld penetration by the GTA process is sensitive to electrode separation from work, alignment, variation of alloy composition, and welding parameters. We found that the plasma-arc process produces the required penetration with minimum sensitivity to these variables.

3. J. R. DiStefano, *Metals and Ceramics Div. Annu. Progr. Rept. June 30, 1970*, ORNL-4570, pp. 107-108.

4. J. R. DiStefano, "Compatibility of $^{244}\text{Cm}_2\text{O}_3$ with Refractory Metals at Thermionic Temperatures," pp. 26-33 in *IEEE Conference Record of 1970 Thermionic Conversion Specialist Conference, October 26-29, 1970*, The Institute of Electrical and Electronics Engineers, New York, 1970.

5. J. R. DiStefano, *Metals and Ceramics Div. Annu. Progr. Rept. June 30, 1970*, ORNL-4570, p. 111.

6. J. R. DiStefano and R. E. McHenry, *Compatibility of Strontium Alloys with Superalloys at 900 and 1000°C*, ORNL-4625 (to be published).

7. Isotopes Division.

A plasma-arc welding procedure was developed and successfully applied to four of these capsules, achieving an average penetration of at least twice the minimum requirement. The plasma-arc welding process is relatively new and is normally used in the "keyholing" mode, a technique involving a full-penetration weld in sheet or thin plate. This is, to our knowledge, the first application of the plasma process to a "blind" (non-full-penetration) weld.

The plasma-arc welding process provides increased penetration over that obtainable with the gas-tungsten-arc process through a constricted, highly ionized plasma — in this case, of argon gas. Careful control of the welding variables is required, however, since the plasma produces a depression in the molten weld puddle, which, under certain undesirable conditions, results in voids and cold shuts in the weld metal. The development effort therefore concentrated on selection of parameters to give adequate penetration with a minimum probability of entrapped voids.

Bead-on-plate test welds were produced with intentional variations in speed of travel (10 and 15 in./min), welding current (140, 155, 170 A), orifice size ($\frac{1}{8}$ and $\frac{3}{32}$ in.), and plasma gas flow (2.4 and 3.2 ft³/hr). Each of these conditions yielded a depth of penetration greater than 0.100 in., and entrapped voids occurred only with the more severe conditions — that is, high travel speed, high current, small orifice, or high plasma gas flow.

Based upon these tests, three actual test pieces were welded with 10-in./min travel speed, 140-A welding current, $\frac{1}{8}$ -in. orifice, and 2.4-ft³/hr plasma gas flow. Depth of penetration achieved exceeded 0.100 in. No entrapped voids were observed upon sectioning.

We welded the four fueled capsules in-cell with the above conditions, using a programmable power supply that permitted entirely automated operation. No significant difficulties were encountered.

The advantages of the plasma welding process for this application include (1) ease of alignment — a low-current pilot arc can be used to align the torch with the weld joint before welding; (2) freedom from stubout and possible tungsten inclusions — the plasma process does not use an exposed tungsten electrode as does the GTA process; (3) freedom from arc-length considerations — torch-to-work distance can vary from approximately $\frac{1}{8}$ to $\frac{1}{2}$ in. without appreciable effect; and, most important, (4) increased penetration — because of the inherent characteristics of the plasma-arc welding process, sufficient penetration could easily be achieved to provide a factor of safety over the minimum penetration requirement.

24. Metallurgy of Refractory Alloys

R G Donnelly   P Patriarca

The purpose of this program is to provide a broad, base-technology evaluation of high-temperature alloys for use in high-performance nuclear reactors and isotopic heat sources for advanced space, terrestrial, and civilian power applications. Principal emphasis is placed on tantalum-, niobium-, and molybdenum-base alloys. Our work on tungsten and its alloys is reported in Chap 25.

BASIC PHYSICAL METALLURGY

H Inouye

Nitrogen Solubility in T-111

H Inouye

The purpose of this study is to determine the feasibility of using T-111 (nominal composition Ta-8% W-2% Hf) as the cladding for UN fuel in a Rankine-cycle space reactor. The equilibrium nitrogen pressures over T-111 as a function of the nitrogen content were measured with a calibrated mass spectrometer. The nitrogen pressure over T-111 in the range 1200 to 1500°C is higher than that over tantalum¹ by up to two orders of magnitude. In terms of the nitrogen uptake, T-111 appears to be more compatible than tantalum with UN. Because Hf lowers the nitrogen pressure over Nb-rich Nb-Hf alloys by several orders in magnitude,² similar effects were also expected for T-111 since it contains about 2% Hf. These unexpected results are tentatively attributed to the tungsten in T-111.

Creep of T-111 in Low-Pressure Nitrogen

H Inouye

Creep of T-111 is being measured in low-pressure nitrogen to determine if ultrahigh-vacuum creep data

apply to performance as cladding for UN. Testing at 1200 and 1400°C in vacuum and in low-pressure nitrogen showed moderate strengthening of T-111 by nitrogen at 1400°C. According to solubility studies (this chapter) the maximum nitrogen content at 4.7×10^{-6} torr and 1400°C is about 300 ppm.

The nitrogen environment also strengthens T-111 at 1200°C, however, the improvement was greater at 4.4×10^{-6} torr nitrogen than at 9.6×10^{-6} torr nitrogen. A rupture strain of only 2.2% for the specimen tested at the higher nitrogen pressure indicates that nitrogen embrittles the alloy.

Effects of Oxygen Contamination on the Tensile Properties of T-111

C T Liu

The objective of this study is to provide the necessary information for the use of T-111 in isotopic heat sources for space power. The T-111 alloy containing 7.98% W, 2.02% Hf, and 26 ppm O was doped with controlled amounts of oxygen in a dynamic system at oxygen pressures of 1 to 2×10^{-5} torr at 1000°C. The contaminated specimens were then tested in tension at two different conditions: annealed 15 min at 1700°C to simulate re-entry heating or as doped. The results for the annealed specimens are shown in Fig 24.1. An initial reduction of ductility and increase in strength were observed at all temperatures. Calculations based on the lattice-parameter measurement indicate that the solubility of oxygen in T-111 is around 100 ppm at 1700°C. Beyond the 100 ppm level, surprisingly enough, both the strength and ductility were almost independent of oxygen level. The data in Fig 24.1 indicate that annealed T-111 can tolerate oxygen contamination to 3000 ppm but loses its ductility completely at 4300 ppm.

In contrast the as-doped T-111 exhibits a much lower tolerance for oxygen contamination. Figure 24.2 shows the initial increase in strength and continuous decrease in ductility with oxygen level. At above 750 ppm O,

¹ R. Griffith and J. A. Pryde, *Trans. Faraday Soc.* **63**, 2599-2604 (1967).

² A. Taylor and N. J. Doyle, *J. Less Common Metals* **13**, 413-30 (1967).

Fig. 24.1. Tensile properties of T-111 annealed 15 min at 1700°C after doping with various levels of oxygen at 1000°C.

Fig. 24.2. Tensile properties of T-111 as doped with various levels of oxygen at 1000°C.

T-111 fractured in an extremely brittle manner; that is, within the elastic limit at temperatures as high as 1316°C. The contaminated specimens were also examined metallographically. All the results lead to the conclusions that the thermal history, by altering the form and distribution of the oxide precipitate, has a greater effect than the oxygen content on the mechanical properties of T-111.

Simple Method of Determination of the Distribution and Solubility Limit of Interstitials in Substitutional Solid Solutions³

C. T. Liu H. Inouye R. W. Carpenter

A simple method for calculation of the solubility limit of certain interstitial species in solid solutions from a single lattice parameter measurement is described. The calculation is based on thermodynamic considerations, and the result allows qualitative conclusions to be made about the randomness of the solute distribution. The method is used to calculate oxygen solubility limits in Nb-Zr and Nb-Hf alloys and to explain previously reported but apparently quite different solubility limits in the two chemically similar alloys.

Solid-Solution Theory and Spinodal Decomposition⁴

C. T. Liu B. T. M. Loh

The free energy of solid solution varies with the atomic arrangement or degree of mixing in solution. The change of free energy with solution state in an alloy system with a miscibility gap was examined step by step from the random state toward the equilibrium state by a series of approximations provided by the cluster-variation method. As equilibrium is approached, the gap corresponding to the nonequilibrium state gradually shrinks to the equilibrium gap, while the chemical spinodal region expands and eventually approaches the solubility limits. The effects of these features on the spinodal decomposition are discussed. Several experimental observations of spinodal decomposition that cannot be explained satisfactorily by previous theory can be accounted for when the free energy is considered to vary with the state of solution.

3. Abstract of paper accepted for publication in *Journal of the Less-Common Metals*.

4. Abstract of paper accepted for publication in *Philosophical Magazine*.

JOINING STUDIES

G. M. Slaughter

Refractory Alloy Welding Development

A. J. Moorhead C. D. Lundin⁵

Hot-cracking. As part of our program to determine the mechanisms and tendency of hot-cracking in refractory alloys, we have been examining the fracture surfaces of cracks in various refractory metals. We examined cracks that occurred during gas tungsten-arc welding of molybdenum alloy TZM test coupons in a glove box and during orbiting-arc welding of molybdenum tubing outside the box. Examination was by optical microscopy, scanning electron microscopy, and electron microprobe analysis. The results showed that (1) hot cracking that involves a liquid phase (illustrated in Fig. 24.3) can occur in both TZM and Mo, (2) hot cracking can and does influence subsequent cracking at temperatures well below the solidus, and (3) porosity at grain boundaries in the fusion zone and heat-affected zone of Mo welds leads to weld cracking.

The grain-boundary porosity is believed to result from lack of complete exclusion of air from the weld area during arc welding. The porosity observed in several welds tended to link in wormhole fashion (as shown in Fig. 24.4) to produce fissures in both the fusion and heat-affected zones. This, coupled with the large grain

5. Consultant from the University of Tennessee, Knoxville.

Fig. 24.3. Scanning electron micrograph of a portion of the fracture surface of a hot crack in a TZM weld. Note the protuberances, which solidified from liquid necks formed during cracking. 1000X. Reduced 23%.

Fig. 24.4. Scanning electron micrograph showing porosity in a portion of the fracture surface of a crack in an orbiting-arc weld on a molybdenum tube. 1000X. Reduced 23%.

size inherent in the weld area, makes the welds exceedingly brittle.

The fracture surfaces of the TZM welds (which have both hot and cold cracks) were carefully examined with a scanning electron microprobe analyzer. Modest amounts of oxygen were in the hot-cracked areas, especially in the protuberances formed by liquid-metal necks during cracking. No significant oxygen concentrations were found in the cold-cracked areas of the weld. Carbon was also detected in small particles on the hot-cracked surfaces and in areas that produced a dark structure in the scanning micrographs.

Component fabrication. Molybdenum and T-111 thermal-convection loops were fabricated by welding. Both are of the same design, but the tubing of the T-111 loop is $\frac{7}{8}$ in. OD $\times$ 0.050 in. wall. Both loops were welded in a vacuum-purged, argon-filled glove box by the manual gas tungsten-arc process using similar filler metal wire. Both were constructed with stringent cleaning, handling, and welding procedures; and the T-111 loop passed the radiographic inspection and was helium leaktight after welding. However, during leak checking of the molybdenum loop, a 1.5-in.-long crack was found in the upper crossover arm. This defect was apparently a previous flaw in the base metal that was propagated by the thermal stresses developed during welding. The crack was machined out and manually rewelded, resulting in a leaktight system. Although this type of defect is undesirable, the result was beneficial in that it demonstrated our ability to repair very large defects in molybdenum structures by welding.

Brazing Alloy Remelt Studies

D. A. Canonico

The use of filler metals for joining refractory metals quite often requires that the brazement function at or near its melting point. This requirement raises the question of remelt temperature. Ideally, two components would be brazed at a low temperature and then the brazement would be capable of withstanding temperatures considerably above the brazing temperature. We have attempted to determine the mechanisms by which the melting point is changed on a number of alloys developed at ORNL⁶ covering a broad range of temperatures.

The program was initiated on the premise that the melting point of the filler metal can be increased primarily by volatilization of an element and solution of a refractory element. Our initial studies centered on three alloys: (1) Ti-48% Zr-4% Be, (2) Ti-46% Zr-8% Ge, and (3) Ti-25% Cr-21% V. All three possess excellent wettability and flowability on refractory metals. Alloy 3 is excellent for the direct brazing of ceramics and graphite; alloy 2 is recommended for joining graphite. Miller-Peaslee shear specimens with a 3-mil joint opening were prepared for tantalum and brazed in a resistance furnace in a vacuum of 10^{-6} torr. After brazing, the specimens were returned to the furnace, stressed, and reheated until failure was observed.

For Ti-48% Zr-4% Be the brazing cycle lowered the melting point from 1800°F to about 1680°F. Electron-beam microprobe analysis showed areas enriched in Zr and, therefore, probably in the melting-point depressant Be as well. The Ti-46% Zr-8% Ge remelt temperature (about 2485°F) was only slightly different from the original melting point (2420°F). This observation is supported by the electron-beam microprobe analysis, which showed very little segregation. However, the melting point of the Ti-25% Cr-21% V alloy increased from 2460 to 2700°F. This increase is attributed to both the solution of Ta into the filler metal and the loss of Cr by volatilization; this was verified by the electron-beam microprobe.

THERMAL CONDUCTIVITY OF REFRACTORY ALLOYS

R. K. Williams J. P. Moore

Combining high temperature electrical resistivity data with low-temperature thermal conductivity data can

6. D. A. Canonico, N. C. Cole, and G. M. Slaughter, "Direct Brazing of Ceramics, Graphite, and Refractory Metals," to be published in *Metals Progress*.

provide good high-temperature thermal conductivity estimates for metals and alloys. Above 1300°K our conductivity estimates for pure tungsten⁷ and tantalum,⁸ which are based on experimentally determined phonon conductivity and Lorenz function values, are probably more reliable than available measurements. The tantalum analysis was extended to include T-111. Estimated values of thermal conductivity to 1000°C were about 3% higher than those measured.

The accuracy of our low-temperature absolute linear heat flow apparatus was improved to permit determinations of phonon conductivity and Lorenz function values for molybdenum. Accuracies in thermal conductivity of $\pm 0.5\%$ and electrical resistivity of $\pm 0.1\%$ from 80 to 400°K are anticipated (see Chap. 8 of this report). Dilute Mo-Zr and Mo-Nb alloys were obtained and characterized for this study.

Room temperature resistivity measurements were used to evaluate ThO₂-17.5% Mo cermets produced by two processes. The high-temperature thermal conductivity was estimated from our previous measurements on molybdenum⁹ and thoria.¹⁰

MECHANICAL PROPERTIES OF COMMERCIAL REFRACTORY ALLOYS

R. L. Stephenson

Since most practical devices require joining, we consider the creep properties of welds to be of critical importance in evaluating materials for use at high temperatures. Stress-rupture data on transverse welds in Ta-10% W, T-111, and T-222 have been reported previously.¹¹⁻¹³ In all cases, the rupture times of the

welds were equal to those of controls at low stresses but much shorter at high stresses.

We have begun testing longitudinal welds in Ta-10% W. At high stresses, these welds fail at times shorter than those of unwelded control specimens, but at low stresses rupture times for welds are at least as long as those of control specimens.

We have creep tested specimens of SU-31 (Nb-17% W-3.5% Hf-0.12% C-0.03% Si) at 980, 1095, 1205, and 1425°C. This particular heat of material has the strongest stress-rupture properties¹⁴ of any niobium-base alloy we have tested to date.

ALKALI-METAL CORROSION OF REFRACTORY ALLOYS

J. H. DeVan

Forced Circulation Lithium Loop

R. L. Klueh

We are examining an engineering-scale, forced-circulation loop constructed of the tantalum-base alloy T-111 (Ta-8% W-2% Hf) that was operated for 3000 hr with lithium.¹⁵ The loop ran at a maximum temperature of 1370°C, a minimum temperature of 1200°C, and a flow rate of approximately 6 gal/min (maximum velocity at heater outlet: 20 fps). Specimens of the T-111 alloy were placed in the heater-economizer section and the pump inlet and outlet lines to measure the effects of mass transfer, including effects on the mechanical properties.

The specimens have been removed from the loop, visually examined, and weighed. Specimens that gained weight had a beige to gold surface coating; specimens that lost weight appeared highly polished, with grains sometimes clearly outlined.

From the weight change data, deposition apparently began somewhere in the radiator, continued through the pump, the pump outlet tube, and about the first 24 in. into the economizer. The specimens in the 1200°C pump inlet and outlet lines showed essentially constant weight gains of 0.6 to 0.7 mg/cm². The only other specimens to show weight gains were those just inside the economizer, where the weight gains decreased from about 0.7 mg/cm² at 1200°C to essentially zero at 1225°C. A maximum weight loss of about 0.9 mg/cm² was found at 1305°C; it did not occur in the maximum

7. R. K. Williams, J. P. Moore, W. P. Murray, and D. L. McElroy, *Metals and Ceramics Div. Annu. Progr. Rept. June 30, 1969*, ORNL-4470, pp. 61-62.

8. R. K. Williams, J. P. Moore, and D. L. McElroy, *Metals and Ceramics Div. Annu. Progr. Rept. June 30, 1970*, ORNL-4570, p. 115.

9. R. K. Williams, J. P. Moore, and D. L. McElroy, *Metals and Ceramics Div. Annu. Progr. Rept. June 30, 1968*, ORNL-4370, pp. 66-67.

10. J. P. Moore, R. S. Graves, and D. L. McElroy, *ibid.* p. 37.

11. R. L. Stephenson, *Fuels and Materials Development Program Quart. Progr. Rept. Sept. 30, 1970*, ORNL-4630, pp. 193-94.

12. R. L. Stephenson, *Fuels and Materials Development Program Quart. Progr. Rept. March 31, 1970*, ORNL-4560, pp. 181-82.

13. R. L. Stephenson, *Fuels and Materials Development Program Quart. Progr. Rept. Dec. 31, 1970*, ORNL-TM-3300, pp. 234-35.

14. R. L. Stephenson, *Fuels and Materials Development Program Quart. Progr. Rept. March 31, 1971*, ORNL-TM-3416, pp. 197-200.

15. B. Fleischer, *Metals and Ceramics Div. Annu. Progr. Rept. June 30, 1970*, ORNL-4570, pp. 103-4.

temperature zone because of the lower liquid velocity there.

Effect of Oxygen on the Compatibility of Refractory Metals with Alkali Metals

R. L. Klueh

We concluded our study of the effect of oxygen on the compatibility of tantalum with the alkali metals potassium, sodium, and lithium.¹⁶ Reactions with oxygen in these systems depend upon whether the oxygen is present in the refractory metal or the alkali metal. Oxygen added to the alkali metal promotes dissolution of the refractory metal. Oxygen added to the refractory metal above a threshold concentration renders the metal subject to penetration by the alkali metal.

The Tantalum-Oxygen-Sodium System¹⁷

The effect of oxygen, both in the sodium and in the tantalum, on the compatibility of tantalum and sodium was investigated at 600°C by static capsule tests.

16. R. L. Klueh, *Metals and Ceramics Div. Annu. Progr. Rept. June 30, 1970*, ORNL-4570, pp. 104-5.

17. Abstract of paper presented at the 1970 Fall Meeting of the Metallurgical Society of AIME, Cleveland, Oct. 19-22, 1970.

Increasing the oxygen concentration of the sodium led to increased dissolution of the tantalum in the sodium. Oxygen migrated from the sodium to the tantalum, and with increasing oxygen concentrations in the sodium, the specimens first gained and then lost weight. Most of the oxygen acquired by the tantalum was in a surface scale. The addition of oxygen to sodium produced a loosely adhering ternary oxide scale on the surface of the tantalum specimen. In high-oxygen sodium, the ternary oxide also formed along grain boundaries.

When the concentration of oxygen in tantalum before test exceeded a "threshold" level, the tantalum was penetrated by sodium. The threshold level was found to be about 200 ppm O. Penetration, as in other refractory metal-oxygen-alkali metal systems previously investigated, proceeds with the formation of a ternary oxide by a wedging mechanism. At low oxygen concentrations, attack proceeds along grain boundaries; as the oxygen concentration of the tantalum is increased, the number of grain boundaries attacked and the depth of attack increases. Still higher oxygen concentrations induce transgranular attack. The penetrated specimens were quite brittle and were easily fractured. Figure 24.5 shows a scanning electron micrograph of a freshly fractured tantalum specimen that contained 2000 ppm O before exposure to sodium and shows the voluminous amounts of corrosion products that form on grain boundaries.

Y-103067

Fig. 24.5. Scanning electron micrograph of a freshly fractured surface of a tantalum specimen that contained 2000 ppm O before exposure to sodium at 600°C.

25. Tungsten Metallurgy

P. Patriarca   A. C. Schaffhauser

The objective of this program is to provide the base technology on tungsten alloys for advanced space-power and general reactor technology applications. We are developing fabrication processes for tungsten alloys based on modification of conventional extrusion, chemical vapor deposition, and welding techniques. Since the primary criterion for the use of tungsten alloys for these applications is based on the creep properties, we are conducting extensive long-time tests at the temperatures of interest. We are also determining the mechanisms that control the creep behavior and the effect of interactions with the vapor species from an isotope or reactor fuel. The behavior of tungsten alloys under fast-neutron irradiation is also being evaluated.

EXTRUSION OF TUNGSTEN ALLOY TUBING

R. E. McDonald   A. C. Schaffhauser

We continued development of the floating-mandrel technique for the extrusion of tubing of advanced tungsten alloys. Previously we extruded $\frac{3}{4}$ - to 2-in. OD tubing with wall thicknesses between 0.06 and 0.3 in. of tungsten and W-25% Re from powder-metallurgy and arc-cast billets.¹ Recently we expanded our capability to arc-cast W-5% Re and powder-metallurgy W-2% ThO₂. The W-5% Re tubing $\frac{7}{8}$ in. OD $\times$ $\frac{1}{16}$ in. wall thickness was successfully extruded in a molybdenum alloy billet at 1700°C. Tubing of W-2% ThO₂ was successfully extruded to 1 in. OD $\times$ $\frac{1}{8}$ in. wall thickness in a molybdenum alloy billet and to $1\frac{1}{2}$ in. OD $\times$ $\frac{1}{4}$ in. wall thickness directly from a 3-in.-diam billet at 1750°C.

CHEMICAL VAPOR DEPOSITION OF TUNGSTEN ALLOYS

J. I. Federer

The optimum conditions for chemical vapor deposition of W-5% Re sheet by H₂ reduction of WF₆ and ReF₆ were determined. These conditions minimize nodules and associated porosity in the microstructure.

Previous attempts to minimize nodules by interrupting the deposition process were not successful.² Since a minimum temperature of 700°C is necessary for compositional uniformity, and since pressures in excess of 10 torr suppressed rhenium deposition, the effect of gas mixture was investigated.³ Small deposits (4 in.²) were prepared with gas mixtures having H₂/MF₆ ratios ranging from 1 to 20. The stoichiometric ratio is 3. The other conditions were temperature 750°C, pressure 5 torr, and flow rates of 95 and 5 cm³/min of WF₆ and ReF₆, respectively. The macrostructure of these deposits with the substrate still in place is shown in Fig. 25.1. Gas flow was perpendicular to the view shown. The rhenium content increased from 4 to 7% as the H₂/MF₆ ratio increased from 1 to 20. The uniformity of thickness around the substrate is clearly dependent upon H₂/MF₆ ratio. As the H₂ content of the gas mixture increased, the surface texture of the deposits changed from grainy (like fine sandpaper) to smooth, but the smoother deposits contained many more nodular growths. The edges of the deposit (Fig. 25.1) prepared with the largest amount of hydrogen illustrate nodular growths, which occurred with increasing frequency throughout the deposits with increasing hydrogen content in the gas mixture. Figure 25.1 also shows that the metal recovery, or deposition efficiency, and the deposition rate were maximum for the deposit prepared with a stoichiometric gas mixture. Another series of small deposits prepared with a stoichiometric mixture of gases showed that the deposition rate

1. R. E. McDonald and G. A. Reimann, *Floating-Mandrel Extrusion of Tungsten and Tungsten-Alloy Tubing*, ORNL-4210 (February 1968).

2. J. I. Federer, *Metals and Ceramics Div. Annu. Progr. Rept. June 30, 1970*, ORNL-4570, pp. 118-19.

3. J. I. Federer and A. C. Schaffhauser, "Chemical Vapor Deposition and Characterization of Tungsten-Rhenium Alloys," pp. 74-81 in *IEEE Conference Record of 1970 Thermionic Conversion Specialist Conference, October 26-29, 1970*, The Institute of Electrical and Electronics Engineers, New York, 1970.

H ₂ , cc/min	100	300	500	1000	2000
(WF ₆ + ReF ₆), cc/min	100	100	100	100	100
Recovery, %	15	29	26	23	19
Deposition Rate at Midsection, mil/hr	4.6	8.0	7.2	4.8	4.0

Fig. 25.1. Morphology of nominal W-5% Re deposits produced at 750°C and 5 torr.

continuously increased with increasing total gas flow rate at least up to 1400 cm³/min.

On the basis of information derived from the small deposits, larger sheet-type deposits of nominal W-5% Re alloy having about 55 in.² of surface area were successfully prepared. The material deposited on 2-in.-wide X 16-in.-long resistance-heated molybdenum substrates contained within a water-cooled chamber. The direction of gas flow through the chamber was periodically reversed to minimize the effect of gas depletion and improve thickness uniformity. Deposits having thickness up to 0.090 in. have been prepared with a variation of only about 0.010 in. over 90% of the length. The microstructure was fine grained and contained only a few nodules.

We can now give the optimum conditions for depositing nominal W-5% Re alloys on stationary sheet substrates: temperature 700 to 750°C, pressure 5 to 10 torr, and H₂/(WF₆ + ReF₆) ratio of 3. We obtained a deposition rate of about 0.006 in./hr at an efficiency of about 60% with flow rates of 600, 190, and 10 cm³/min of H₂, WF₆, and ReF₆, respectively.

The effect of gas mixture on the morphology and grain structure of nominal W-25% Re deposits was also studied. As in the above study, the H₂/MF₆ ratio was varied from 1 to 20 while other factors were held constant in the preparation of small deposits. The deposit prepared with a H₂/MF₆ ratio of 1 contained 51% Re, an unexpected result. The rhenium content of the other deposits was in the range 19 to 24%. The

morphology and grain structure were greatly affected by the H_2/MF_6 ratio. The smoothest deposits were obtained at ratios of 3 and 5, at ratios of 1, 10, and 20 the deposits had numerous nodules on the surfaces and rough nodular edges. The microstructure ranged from columnar grains with a small amount of porosity to noncoherent structures with increasing H_2/MF_6 ratio. The results suggested that deposits of best quality would be obtained with a near-stoichiometric gas mixture. This was found to be true in the coating of 0.040-in.-diam wires with a nominal W-25% Re alloy deposit. Coatings prepared with a mixture having a H_2/MF_6 ratio of 3 were mostly smooth, with only a few nodules, whereas coatings prepared with gas mixtures having a ratio of 15 were completely nodular and very porous. In the latter state the coatings have practically no mechanical strength.

EVALUATION OF METHODS FOR JOINING TUNGSTEN AND ITS ALLOYS

N C Cole   G M Slaughter

We have welded tungsten and its alloys using many different methods. Previously, we had gas-tungsten-arc (GTA) welded unalloyed tungsten with and without the addition of filler metals^{4,5}. We have also GTA welded tungsten alloys (W-25% Re, W-25% Re-30% Mo, and W-5% Mo) without the addition of filler metals⁶. Now we have electron-beam (EB) welded (without adding filler metal) sheets of arc-cast and CVD unalloyed tungsten. We have also GTA welded W-25% Re, adding either Mo-50% Re or W-25% Re-30% Mo filler metals.

Arc-cast and CVD unalloyed tungsten sheets were EB welded with varying degrees of success. Transverse cracks were plentiful in EB welds made without a regulated preheat in arc-cast 0.060-in.-thick tungsten. We preheated the workpiece as much as practicable with the torch, but this type of preheat was not sufficient to prevent cracking. However, this same material was GTA welded crack-free by preheating to 175°C with a heating fixture. In some cases, two welding passes were made with no cracking.

The EB welds in CVD 0.075-in.-thick tungsten were free of cracks even when welded without a preheat. The base material contained only 5 ppm F. In the past, we

4 N C Cole and G M Slaughter, *Metals and Ceramics Div Annu Progr Rept June 30 1968* ORNL-4370, pp 73-75

5 N C Cole and G M Slaughter, *Metals and Ceramics Div Annu Progr Rept June 30, 1970*, ORNL-4570, p 120

6 N C Cole, R G Gilliland, and G M Slaughter, "Welding of Tungsten," to be published in *The Welding Journal*

Fig. 25.2. Ductile-to brittle transition curves of welded W-25% Re sheet.

found that 10 ppm F in the base metal caused bubble coalescence in the heat-affected zone, resulting in grain-boundary cracking⁷. Even after welding, the CVD tungsten with 5 ppm F contained no grain-boundary bubble formation detectable by the optical microscope.

Welding W-25% Re with Mo-50% Re and W-25% Re-30% Mo filler metals was generally successful. However, we had cracking problems when welding with the Mo-50% Re filler wire. The Mo-50% Re filler wire appeared to be slightly contaminated, which affected the quality of the welds. However, the welds did not contain porosity because the filler wires and base metals were arc-cast.

The ductile-to-brittle transition temperature (DBTT) curves of these welds are compared in Fig. 25.2 with curves for GTA manually welded W-25% Re in which filler metal was added. The arc-cast W-25% Re sheet base metal tested in the stress-relieved condition was ductile at room temperature. The DBTT of welds in W-25% Re was considerably higher than room temperature. The addition of Mo-50% Re or W-25% Re-30% Mo filler metal to the welds caused the DBTT to be even higher. The welds with no filler metal were tested with either the face or the root of the weld in tension. The bends with the root in tension were more ductile. We achieved a 90° root bend at 350°C but only a 25° face bend at 400°C. Probably the slight notch on

7 N C Cole, *Fuels and Materials Development Program Quart Progr Rept June 30 1968* ORNL-4330, pp 295-301

the face of the weld (due to the weight of the molten metal) contributed to the loss of ductility. Root bends in welds made with either W-25% Re-30% Mo or Mo-50% Re achieved only 60° at 350°C.

BEHAVIOR OF TUNGSTEN ALLOYS UNDER FAST-NEUTRON IRRADIATION

F. W. Wiffin   R. K. Williams
D. A. Dyslin⁸   D. L. McElroy
H. E. McCoy, Jr.

Data from the fast-neutron irradiation damage of other refractory metals, which are reported in Chap. 29 of this report, suggest that voids will form in tungsten for irradiation temperatures between 830 and 1570°C, 0.3 and 0.5 times the absolute melting temperature. Void densities may be as high as 10^{17} voids/cm³, and the accompanying swelling may exceed 1%. Limited data on powder-metallurgy tungsten show high densities of small voids after irradiation to 1.5×10^{20} neutrons/cm² (>1.0 MeV) at 1000 and 1300°C. These effects in tungsten could be detrimental to the performance of thermionic diodes for space power applications and high-temperature thermocouples for fuel center-line temperature measurement in LMFBR experiments. As the void density increases, the intervoid spacing will approach the mean free path of conduction electrons, and a significant increase in resistivity is expected. This behavior could affect the high-current performance of thermionic diodes and produce changes in the thermoelectric power and shunting of thermocouples.

We have designed and constructed a one-pin experiment for EBR-II to test the effect of irradiation temperatures between 1000 and 1500°C on the behavior of tungsten and tungsten alloys at a maximum fluence of 2.8×10^{21} neutrons/cm² (>0.1 MeV). We are irradiating 0.10-in.-diam rod specimens of tungsten

and tungsten-rhenium alloys produced by powder-metallurgy, arc-melting, and CVD techniques. Determination of the high-temperature electrical resistivity of control specimens for this experiment is under way. The data and techniques used for these measurements are presented in Chap. 8 of this report. Laser welding appears to be an excellent method for attaching the necessary instrumentation leads to the irradiated tungsten resistivity specimens. Wires of Pt and Pt-10% Rh laser welded to tungsten rods sustained thermal cycles to 1400°C and static load tests.

EFFECT OF LOW-PRESSURE GASES ON THE CREEP PROPERTIES OF TUNGSTEN ALLOYS

H. Inouye

The creep properties of W-25% Re were measured in low-pressure oxygen to simulate interaction with oxygen derived from the decomposition of oxides at high temperatures. The results are compared with the creep properties of the alloy in a vacuum of 10^{-7} torr. Between 1650 and 2000°C and stresses of 1000 and 2000 psi, the creep rates were as much as 250 times lower in 10^{-5} torr O₂ than in vacuum; however, rupture strains were only 2 to 7% in the O₂ environment. At 1800°C the creep strength in 10^{-5} torr O₂ was twice that in vacuum. Specimens exposed to oxygen before creep testing in vacuum were also stronger than specimens tested in vacuum. The oxygen content was generally lower in specimens tested in oxygen than in the as-received material. The lower creep rates of W-25% Re in oxygen are attributed to a surface layer of σ -phase resulting from selective volatilization of tungsten oxides.

We are also measuring the creep properties of 0.040-in.-diam tungsten wire in low-pressure CH₄ to simulate the effect of carburization by uranium carbide at thermionic temperatures. Table 25.1 compares the

8. General Engineering Division.

Table 25.1. Comparison of creep properties of tungsten at 1800°C and 2000 psi in vacuum and in CH₄

Pressure of environment (torr)	Time (hr) for strain of			Rupture results		Creep rate (hr ⁻¹)
	0.5%	1%	2%	Life (hr)	Elongation (%)	
1.8×10^{-7} (vacuum)	23	53	117	327	7.0	1.5×10^{-4}
2.6×10^{-6} (CH ₄)	16	30	62	278	6.5	2.0×10^{-4}
5.2×10^{-6} (CH ₄)	22	42	77	163	4.9	3rd stage only
2.6×10^{-5} (CH ₄)	16	36	71	113	3.9	3rd stage only

creep behavior in vacuum and in CH_4 at 1800°C and a stress of 2000 psi, carburization lowers the creep strength. A progressive decrease in the rupture life and ductility with an increase in CH_4 pressure is also noted. Temperature measurements during the test show an increase in the $0.665\text{ }\mu\text{m}$ spectral emissivity of tungsten from 0.43 to about 0.6 after about a 30-hr exposure to CH_4 . This increase is attributed to the formation of W_2C at the surface. After test the specimen showed a silvery metallic surface and no change in weight.

FORMATION OF CREEP CAVITIES IN POWDER-METALLURGY TUNGSTEN

J. O. Stiegler

At elevated temperatures metals lose ductility because grain-boundary cracks form. Details of the nucleation and growth of these cracks in powder-metallurgy tungsten were studied by electron fractography. Creep tests were interrupted, and the specimens were fractured at room temperature to expose any cavities or cracks formed at high temperatures.

After annealing 1 hr at 1600°C the grain boundaries of the tungsten were populated by about 10^7 gas bubbles per square centimeter, averaging approximately $0.2\text{ }\mu\text{m}$ in diameter. The bubbles were distributed nonrandomly and showed large variations in size and distribution. Different grades of tungsten showed different grain-boundary structures.

Under stress at 1600°C these bubbles expanded. At low stresses they grew slowly and maintained equiaxed, crystallographic shapes. At high stresses they grew rapidly in the plane of the grain boundary and formed irregular, flat cavities about $1\text{ }\mu\text{m}$ thick. These cavities grew rapidly in certain directions but always kept blunt ends. No evidence of cavities nucleated by deformation

was obtained, but a few rare cases of possible triple-grain junction cracks were found. Only a slight tendency for rounding of the flat cavities was noted for annealing times as long as 100 hr at 1600°C .

The model most in agreement with these observations is one in which the gas bubbles expand to form the cavities by the stress-directed diffusion of vacancies along the grain boundaries. At low stresses this occurs slowly enough that the cavities can maintain equiaxed shapes by surface diffusion. When the growth rate exceeds some critical value, surface diffusion becomes too slow, and the cavities grow in the plane of the boundary. Their irregular shapes suggest that the average stress does not direct their growth but that local variations in stress, possibly resulting from grain-boundary sliding or deformation within the grains, are responsible. The wedge-like cracks observed with the optical microscope arise when the flat cavities reach a triple-grain junction and are opened into a wedge by sliding on the adjacent grain boundaries. This model reconciles the conflicts in some of the previous models for crack formation.

Since the specimen elongates as the cavities expand, their growth constitutes a creep mechanism. The creep rate from the diffusion-controlled growth of equiaxed cavities is in order-of-magnitude agreement with measured creep rates for materials containing cavities. The creep rate from growth of cavities at the concentrations present in the powder-metallurgy material is about two orders of magnitude faster than Nabarro-Herring diffusional creep in the same material. Some unusual observations made on a powder-metallurgy W-25% Re alloy, which deformed at a faster rate at 1650°C than at 2200°C at a stress of 500 psi, were explained semi-quantitatively by this model of creep due to cavity growth and the observed microstructural features.

26. Uranium Nitride Fuels

J. L. Scott   P. Patriarca

Uranium mononitride is of interest as a fuel material for space-nuclear reactors because of its high thermal conductivity, high melting point of 2800°C , and good irradiation stability. Because space reactors reject heat by radiation, fuel pin cladding temperatures of interest are 1000°C or greater. The objective of our program is to establish the rate of swelling and fission-gas release of UN irradiated in refractory metal cladding at surface temperatures above 1000°C . The program also includes development of fabrication of very high-purity UN, because impurities such as carbon or oxygen may adversely affect performance.

Development of nitride fuels for fast breeders is reported in Chap. 16 of this report, and fundamental studies of nitrides are in Chap. 6 and others.

FABRICATION OF URANIUM MONONITRIDE

V. J. Tennery   R. A. Potter   T. G. Godfrey

We developed the techniques required to isostatically press large annular cylinders of UN so as to produce sintered parts having dimensions within 0.015 in. of nominal. During this process, oxygen contamination of the UN is prevented. The cylinders have the nominal dimensions: OD = 0.63 in., ID = 0.20 in., length = 1.6 in., and the mass ≈ 110 g. The isostatic pressing form is loaded in an inert atmosphere glove box sealed off from the atmosphere, removed from the box, isopressed at 60×10^3 psi, then returned to the box and unloaded. Machining techniques using diamond grinding tools were developed and the cylinders were machined to within ± 0.0005 in. on the diameters and lengths, with a TIR below 0.001 in. A group of the sintered and machined cylinders are shown in Fig. 26.1. Approximately 130 of these cylinders were produced for an irradiation study of UN. The oxygen content of the UN in all this material was below 400 ppm. Techniques were also developed for producing some very small cylinders of UN, which were fully enriched in ^{235}U . The specimens were used in fission gas release studies and were required to be 0.050 in. OD $\times$ 0.030 in. ID $\times$

Fig. 26.1. Sintered and machined annular cylinders of uranium mononitride.

Fig. 26.2. Fission gas release specimens of uranium mononitride. Straight pin length = 1.11 in.

0.26 in. long. The insides of these cylinders were successfully machined by electrostatic discharge methods. Approximately 50 of these specimens were produced. Two of the cylinders are shown beside a straight pin in Fig. 26.2.

IRRADIATION TESTING OF URANIUM NITRIDE

T. N. Washburn

The objective of the ORNL program for irradiation testing of uranium mononitride (UN) is to obtain basic information on fuel swelling, fission-gas release, and compatibility with cladding materials at fuel temperatures from 1000 to 1500°C, cladding outside surface temperatures of 900 to 1400°C, and linear heat ratings of 5 to 10 kW/ft. Detailed descriptions of our capsule design¹ and previous test results²⁻⁴ have been reported.

Examination of Capsule UN-3

D. R. Cuneo⁵

Examination of capsule UN-3 was completed. Partial results of the postirradiation examination have been given previously.⁶ This capsule contained 3-in.-long UN-fueled pins. The top pin cladding was W-25% Re, and the middle and bottom pin cladding was T-111 (Ta-8% W-2% Hf) with a tungsten barrier between the cladding and the UN fuel. The top fuel pin exposure was 1.4 at. % burnup, and the other two pins reached estimated burnups of 1.75 at. %.

Briefly, the findings since last year are summarized below. Details are reported elsewhere.^{7,8}

Electron microprobe analysis of the cladding of the failed middle fuel pin revealed no indications of uranium contamination from the fuel, or of any diffusion from the tungsten liner into the T-111 cladding. However, large concentrations of hafnium

were noted at cracks and voids, both in the T-111 cladding and in the CVD tungsten liner. The mechanism for this concentration of hafnium is not known. Grain size in the failed portion of the cladding was six times that in the unfailed region. A scanning electron micrograph of the failed region of the cladding is shown in Fig. 26.3.

Similarities in dimensional and microstructural changes for the bottom fuel pin showed that with additional time or higher temperature operation, this pin would have failed in a similar mode. These fuel pins were identical in cladding material and uranium enrichment (T-111 with 3-mil tungsten liner, and 12% ²³⁵U). Typical metallographic observations from a transverse section of the bottom fuel pin are seen in Fig. 26.4. The accumulation of fission gas at grain boundaries in the fuel is seen at the higher magnification. Self-shielding in a thermal-neutron flux caused a much higher fission rate near the periphery of the fuel, and accumulation of fission gas at the grain boundaries is sufficient to cause grain pullout in this region during specimen preparation.

The top fuel pin, which operated at 1350°C fuel center temperature and 1300°C cladding outside surface temperature, was clad with W-25% Re and fueled with 20%-enriched UN. Metallographic examination showed no evidence of any general chemical incompatibility between the UN fuel and the cladding. An apparent general intergranular penetration of the cladding by the fuel reached a maximum depth of only 20 μm. Examination of the interface between fuel and cladding also showed that the fuel was in intimate contact with the cladding during irradiation. In several regions grains of fuel separated from the periphery of the fuel pellet during cooling and remained attached to the cladding. No deleterious effects were noted.

Capsule Fabrication

E. J. Manthos

Three new irradiation test capsules were fabricated: one (UN-5) sponsored by the AEC and two (UN-4 and UN-6) by NASA. Capsules UN-4 and UN-5 contain two types of UN pellets — solid 85%-dense cylinders and annular 95%-dense cylinders. The inner diameter of the annular pellets was sized such that both types of pellets gave the same fuel smear density. The six fuel pins in these two capsules have T-111 (Ta-8% W-2% Hf) cladding. Capsule UN-6 contains UO₂ pellets with T-111 cladding on one fuel pin and Nb-1% Zr on two. Capsule UN-6 serves to investigate the backup or derated design being considered for advanced space reactors. The control cladding temperature of each

1. V. A. DeCarlo, F. R. McQuilkin, R. L. Senn, K. R. Thoms, and S. C. Weaver, *Design of a Capsule for Irradiation Testing of Uranium Nitride Fuel*, ORNL-TM-2363 (February 1969).

2. T. N. Washburn, D. R. Cuneo, and E. L. Long, Jr., "Irradiation Performance of Uranium Nitride at 1500°C," *Amer. Ceram. Soc. Bull.* **50**, 427 (1971).

3. T. N. Washburn, K. R. Thoms, S. C. Weaver, D. R. Cuneo, and E. L. Long, Jr., "Examination of UN-Fueled Pins Irradiated at 1400°C Cladding Temperature," *Trans. Amer. Nucl. Soc.* **13**, 101 (1970).

4. S. C. Weaver, K. R. Thoms, and V. A. DeCarlo, "Irradiation Testing of UN in ORR," *Trans. Amer. Nucl. Soc.* **12**, 547 (1969).

5. On loan from the Reactor Chemistry Division.

6. T. N. Washburn, S. C. Weaver, K. R. Thoms, D. R. Cuneo, and E. L. Long, Jr., *Metals and Ceramics Div. Annu. Progr. Rept. June 30, 1970*, ORNL-4570, pp. 116-117.

7. D. R. Cuneo and E. L. Long, Jr., *Fuels and Materials Development Program Quart. Progr. Rept. June 30, 1970*, ORNL-4600, pp. 177-80.

8. D. R. Cuneo and E. L. Long, Jr., *Fuels and Materials Development Program Quart. Progr. Rept. Sept. 30, 1970*, ORNL-4630, pp. 180-85.

R-54109

Fig. 26.3. Scanning electron micrograph of T-111 cladding of the failed middle fuel pin of capsule UN-3. (a) Grain size in region near failure is about 6 times that of other sections. (b) Smaller grain size of region away from failure.

R-52345

Fig. 26.4. Transverse section of bottom fuel pin of capsule UN-3.

capsule test is 1000°C, with the UO₂ fuel central temperature restricted to 1550°C. Thus, the UO₂ fuel will operate at 6.5 kW/ft maximum, while the UN will operate at 9 to 10 kW/ft.

Capsule Operation

B. Fleischer   K. R. Thoms⁹

Capsule UN-4 and UN-5 have operated satisfactorily since their insertion in the ORR, their thermal history has been presented graphically.¹⁰ A detailed thermal analysis has been made using the calorimeter and the cladding thermocouples. We have detected and rationalized temperature penetrations and have a reasonable explanation for our operation at higher heat ratings than anticipated for maintenance of 1000°C cladding temperature. The need for a higher heat rating is apparently caused by reduced thermal resistance between the fuel elements and the ORR coolant. The low thermal resistance is a result of the NaK capsule being slightly off center with respect to the primary container. This condition requires UN-4 and UN-5 to operate at 15% higher heat ratings than anticipated.

The thermal perturbations are also related to the position of the NaK capsule with respect to the primary container. Sporadic thermal cycles as great as 80°C and lasting about 12 sec are apparently caused by shifting of

the NaK capsule with respect to the container. Calculations show that as little as 0.001 in. movement would cause a 40°C change in temperature at design power level. As a result of these findings we have reduced the dimensional tolerances for UN-6 to reduce the perturbations and achieve the desired cladding temperature at the designed power level.

Proposed UN Tests in EBR-II

B. Fleischer   M. K. Preston¹¹

A proposal for testing of UN—refractory metal fuel elements in EBR-II was prepared and submitted to the AEC. The proposal, described in more detail in the periodic reports,^{12,13} provides for testing of Nb—1% Zr, T-111, and W—25% Re cladding at 1000°C using 95%-dense annular fuel pellets. These materials would be tested over a range of burnup from 0.75 to 5.5% FIMA and heat ratings from 4 to 11.5 kW/ft. Data from these tests are considered essential for future engineering development of fuel elements for space nuclear systems.

⁹ Reactor Division

¹⁰ B. Fleischer and K. R. Thoms, *Fuels and Materials Development Program Quart. Progr. Rept. March 31, 1971*, ORNL-TM-3416, pp. 176–80.

¹¹ On loan from General Engineering Division

¹² B. Fleischer, T. N. Washburn, and M. K. Preston, *Fuels and Materials Development Program Quart. Progr. Rept. Dec. 31, 1970*, ORNL-TM-3300, pp. 220–22.

¹³ B. Fleischer, T. N. Washburn, and M. K. Preston, *Fuels and Materials Development Program Quart. Progr. Rept. March 31, 1971*, ORNL-TM-3416, pp. 179–81.

Part IV. General Fuels and Materials Research

27. Fuel Element Fabrication Development

G. M. Adamson, Jr.   W. R. Martin

The objective of this program is twofold, to improve fuel element fabrication technology for research and test reactors, and to advance the knowledge concerning those factors that limit irradiation performance of HFIR and ATR fuel elements. Two recent reports describe postirradiation examination¹ and manufacturing development² of HFIR fuel plates.

IRRADIATION EXPERIMENT ON THE SWELLING BEHAVIOR OF ALUMINUM-BASE DISPERSION FUELS

M. M. Martin

The goal of this experiment is to determine factors that may influence the performance of aluminum-clad UAl_x and U_3O_8 dispersions in the ATR and HFIR at fission densities up to 2.5×10^{21} fissions/cm³. Material variables included are (1) initial void content of the fuel dispersions (i.e., type of fuel dispersoid, dispersoid concentration, and fabrication procedure); (2) void stability in the absence of significant burnup; (3) fuel dispersoid particle size; and (4) dimensional stability of aluminum-clad Al-24 wt % α - Al_2O_3 dispersion, which may be substituted for the aluminum in the filler section of HFIR inner and outer annulus fuel plates. Two grades of U_3O_8 , burned and high-fired, and arc-cast UAl_x were used at dispersoid concentrations that correspond to current HFIR and ATR loadings and 25% increases in these loadings. Table 27.1 lists the

pertinent attributes of the unirradiated plates and their exposure in HFIR.

All components for the capsule were fabricated with strict quality assurance. Final assembly, testing, and installation in HFIR were accomplished without difficulty. It was irradiated in the beryllium reflector from January 11, 1971, to May 13, 1971. Our miniature fuel elements were free of obstruction and appeared to be in good physical condition with no evidence of failure. Detailed examination is under way.

HFIR FUEL ELEMENT SUPPORT

W. R. Martin   G. M. Adamson, Jr.

HFIR Fuel Element Manufacture

R. W. Knight

Assistance to Texas Instruments, Inc. has continued throughout the past year. To date, 107 fuel assemblies have been delivered. None has met all the specifications, but all have been accepted on waiver and will be operated at full power. The most troublesome factor for all assemblies was welding. The welding machine had two malfunctions, which caused burnthrough that had to be repaired by broaching. One lot of No. 3 sideplate stock (13 pieces) was sent to salvage because internal stresses in it created excessive out-of-roundness in the outer assembly. The fuel plate yields for plates in groups are presented in Table 27.2. The major cause of fuel plate rejection is bond defects. These FY 1971 results show a 2.5% improvement in yield over the FY 1970 total. The net yield of plates for FY 1971 was 97.8%.

During the year, 29 approval requests were submitted and processed: Of these, seven were for waivers on 165

1. A. E. Richt, R. W. Knight, and G. M. Adamson, Jr., *Postirradiation Examination and Evaluation of the Performance of HFIR Fuel Plates*, ORNL-4714 (in press).

2. R. W. Knight and T. L. Sherman, *Development of Manufacturing Procedures for HFIR Fuel Plates to ORNL Specifications*, ORNL-4713 (in press).

Table 27.1. Miniature test fuel plates irradiated in HFIR for 11,613 MWd

Reference plate number	Core composition ^a (wt %)	²³⁵ U Loading		Fuel particle size distribution		Irradiation conditions		Peak ²³⁵ U Burnup (fissions/cm ³)
		Enrichment in fuel particle (wt %)	Volumetric core composition (g/cm ³)	Upper range (μm)	<44 μm (wt %)	Center-line temperature (°C)		
						Maximum	End of life	
								× 10 ²¹
11 ^b	53 arc-cast UAl _x	0.2	0.00	44–149	21	49	49	0.0
21	54 arc-cast UAl _x	0.2	0.00	44–149	21	49	49	0.0
31 ^c	55 arc-cast UAl _x	0.2	0.00	44–149	21	49	49	0.0
12	47 high-fired U ₃ O ₈	93.2	1.41	44–88	10	89	71	2.5
22	50 burned U ₃ O ₈	93.2	1.43	44–88	11	85	68	2.5
32 ^{b,d}	51 arc cast UAl _x	93.1	1.31	44–149	24	80	63	2.2
01–02 ^e	47 high-fired U ₃ O ₈	93.2	1.40	44–88	10	89,93	72,74	2.2–2.6
13	40 high-fired U ₃ O ₈	93.2	1.14	44–88	10	84	63	2.2
23	42 burned U ₃ O ₈	93.2	1.15	44–88	11	83	62	2.2
33	54 arc-cast UAl _x	0.2	0.00	None	100	51	49	0.0
14	53 arc-cast UAl _x	93.1	1.32	44–149	24	92	69	2.6
24 ^b	52 arc-cast UAl _x	93.1	1.31	44–149	24	90	68	2.5
34	53 arc-cast UAl _x	93.2	1.32	44–53	97	88	67	2.5
03–04 ^e	44 high-fired U ₃ O ₈	93.2	1.29	44–88	10	94,94	71,72	2.5–2.6
15	63 arc-cast UAl _x	93.1	1.67	44–149	24	98	78	3.0
25	64 arc-cast UAl _x	93.1	1.69	44–149	24	96	76	3.0
35	63 arc-cast UAl _x	93.2	1.66	44–53	97	94	74	2.9
16	40 high-fired U ₃ O ₈	0.2	0.00	44–105	9	58	51	0.0
26	40 high-fired U ₃ O ₈	0.2	0.00	44–88	39	57	51	0.0
36	24 α-Al ₂ O ₃			44–88	55	54	51	0.0
05–06 ^e	51 high-fired U ₃ O ₈	93.2	1.58	44–88	10	101,99	80,78	2.6–3.0

^aCladding and matrix materials are aluminum alloys 6061 and 101, respectively.

^bPlates hot rolled to final gage to lower fabrication void content.

^cPlates cold rolled an additional 20% in thickness to increase fabrication void content.

^dPlate hot pressed after hot rolling operation to decrease fabrication void content.

^eInstrumented plates. Temperatures at other plates are calculated.

fuel plates; 110 were approved. The other 22 requests submitted and approved dealt with revisions to manufacturing practices, procurement and disposal of materials and equipment, and occasional special and experimental manufacturing tasks.

Modifications and Improvement to HFIR Fuel Plates

R. W. Knight

The reduced incidence of nonbonds in fuel plates shown in Table 27.2 can be attributed to the switch from commercial to reagent grade nitric acid, since no other production change directly affected fuel plate assembly. The cost of the higher priced acid was offset by less consumption and improved yields.

Six inner and six outer annulus fuel plates containing the cheaper burned grade of U₃O₈ were used in the HFIR in fuel element assembly 100. This fuel assembly operated normally in the reactor. Assessment of the fuel plates in the hot cell will start in January 1972. The void volume of the fuel section of the core in the as-rolled plate increased an average of 3.9 and 2.6% for the outer and inner fuel plates, respectively.

Work is continuing to increase the void volume of the fuel core filler section with the addition of Al₂O₃. One miniature plate has been irradiated in HFIR. Void volume produced by this method was stable during irradiation. Dummy fuel plates are being made at Texas Instruments, Inc. to establish manufacturing parameters and assess nonbond results. Data for homogeneity

Table 27.2. HFIR fuel plates rejected during manufacture^a

Reasons for rejections	FY 1971		FY 1970		All production to date	
	Number rejected	Percent	Number rejected	Percent	Number rejected	Percent
Compacts	6	0.06	2	0.02	287	0.42
Surface	21	0.23	27	0.30	2009	2.93
Bond defects	134	1.45	354	3.96	3581	5.22
Core location	31	0.33	57	0.64	628	0.91
Homogeneity	122	1.32	84	0.94	1399	2.04
Dimensions	0	0.00	48	0.54	142	0.21
Form	0	0.00	1	0.01	36	0.05
Miscellaneous	0	0.00	6	0.07	236	0.34
Total	314	3.39	579	6.48	8318	12.12
Accepted on waiver	110	1.19	159	1.78	2626	3.83
Net rejected	204	2.20	420	4.70	5692	8.29

^aNumber manufactured: 9264 in FY 1971, 8934 in FY 1970, 68,638 total.

standards have been evaluated and are reported in a later section of this chapter.

Thermal Conductivity of U₃O₈-Aluminum Fuel Plate Cores

R. S. Graves

The thermal conductivity and electrical resistivity of U₃O₈-Al cermet were measured from 7 to 127°C in a guarded longitudinal heat flow apparatus for the HFIR project. Four samples were machined from fuel plate material fabricated by the picture-frame technique using two forms of U₃O₈. Oxide volume fractions of 0.12 and 0.18 were obtained using 13.5 and 19.5% burned U₃O₈ (density 7.6 g/cm³) and 12.5 and 18.1% high-fired U₃O₈ (density 8.2 g/cm³). The resistivity values, which reflect the volume fraction of electrically nonconducting material (oxide and voids), indicate larger void volume fractions for the burned U₃O₈ samples. For this temperature range the thermal conductivity values for a given cermet are independent of temperature to within 2%, as expected from previous results on 101 aluminum.³ The thermal conductivity values decrease with increasing volume fraction of electrically nonconducting material and fall within 3.5% of the values expected for aluminum containing voids. The thermal conductivity of the burned U₃O₈ sample was less than that of the high-fired by 2.5% at 0.12

volume fraction and 7.5% at 0.18 volume fraction. Both results are consistent with the higher void volume of the burned U₃O₈ samples.

Establishment of X-Ray Attenuation Standards for Burned U₃O₈ and High-Loaded, High-Fired U₃O₈ Plates

B. E. Foster S. D. Snyder

One inner- and one outer-annulus plate containing high-fired U₃O₈ at the standard HFIR fuel loading, one inner plate with 1.35 times that loading, one outer plate with 1.25 times that loading, and four similar plates loaded with burned U₃O₈ were fabricated by the Texas Instruments, Inc. We made x-ray attenuation scans of these plates, and the appropriate places were analyzed for uranium content. We plotted the weight of uranium in 0.078-in.-diam right-circular cylinders through the fuel plate as a function of x-ray attenuation at the normal energy conditions of 50 kVcp, 2.5 mA. As with past data we observed a bias for the inner-annulus plate containing high-fired U₃O₈ at the standard HFIR loading when compared with our original calibration data. However, a considerable reduction in point scatter allowed us to see that the bias was very uniform. The reduction in point scatter is attributed to the use of improved control of sample machining and location and more precise chemical analysis obtained from more stable transistorized coulometers.

We used a least-squares polynomial fit of the uranium content as a function of attenuation in computer programs to derive in tabular form our calibrations for

3. D. L. McElroy, R. S. Graves, and J. P. Moore, *Metals and Ceramics Div. Annu. Progr. Rept. June 30, 1970*, ORNL-4570, pp. 134-35.

both the inner- and outer-annulus high-fired U_3O_8 and burned U_3O_8 plates. Contrary to past practice, we find that each type plate has its own calibration; a continuous calibration cannot cover both the inner and outer annulus for a particular type of oxide. We tested the high-fired U_3O_8 calibrations by determining from attenuation scan data the content of uranium in one inner and one outer plate fabricated with production techniques and containing a standard loading. Agreement with the quoted uranium content of these plates is within 0.5%.

After establishing and confirming the proper x-ray energy and calibration curve, we determined equivalent thicknesses of aluminum for the fabrication of contoured attenuation standards for fuel plates containing the standard loading of burned oxide as well as increased loadings for both high-fired and burned oxide fuels.

DEFORMATION BEHAVIOR OF FUEL CORES DURING ROLLING

J. H. Erwin   R. G. Donnelly

In our effort to eliminate nonuniform deformation (dogboning) from fuel cores roll bonded within cladding materials somewhat weaker than the fuel core, we fabricated a limited number of simulated plates. These plates represent the completion of this effort to solve the dogboning problem. Before the billets were assembled, each end of the cores was relieved at midthickness by milling a 60 or 90° included angle the full width of the core. For the 60° relief, cores were machined to depths of 0.114, 0.146, and 0.200 in., the equivalent of 3, 5, and 10% of the longitudinal area of the 0.272-in.-thick $\times$ 1.800-in.-long cores. For the 90° relief, cores were machined to depths of 0.087, 0.110, and 0.130 in., the equivalent of 3, 5, and 7.5% of the longitudinal area. The simulated cores were aluminum alloys, either 6061 or 2219, and the cladding was alloy 8001. We rolled the billets at 490°C, one group at reductions according to HFIR schedule on a 12-in.-diam mill and another group at reductions 1.5 times the HFIR schedule on a 20-in.-diam mill. We removed billets from the rolling schedule at thicknesses of about 0.200, 0.100, 0.063, and 0.050 in. to observe the cross section.

Visual examination of these simulated cores revealed the following.

1. For the range of variables examined, we found no influence of size of rolling mill or reduction rate.
2. Shaping of the core with radii within the range from 0 to 1 in. reduced the dogboning significantly when the ratio of fuel core to cladding strength was 2.0. But at strength ratios of near 3, the core shaping was ineffective in reducing dogboning.
3. A V-shape core was effective in reducing the dogboning of plates containing the very strong cores, but extensive fishtails were produced that would be objectionable.

EXAMINATION OF A FAILED ATR FUEL PLATE

A. E. Richt   J. L. Miller, Jr.

A substantial effort was made to assist the AEC and Idaho Nuclear Corporation (INC) in analyzing the localized failures in a few ATR fuel elements. A number of fuel plates in the ATR had released small amounts of fission products to the reactor coolant. The failures were small protuberances that looked like pimples on the surfaces of the fuel plates. The pimples are generally located near the corners of the fuel core and are open to the coolant water.

We examined one metallographic sample, which contained a single, longitudinal cross section through a pimple near the upper (i.e., coolant inlet) end of a fuel plate. The microstructure of that cross section was studied, and it was chemically analyzed with the electron microprobe.

Since the failures might have been caused by the accidental contamination of the fuel cores with some foreign material, we analyzed the material within the cavity with the electron microprobe. A spectral scan of this material revealed significant amounts of only Al and U; however, since we cannot presently detect the elements with lower atomic numbers, this material may also have contained O, H, N, and C. Scans across this material, however, revealed that the Al and U concentrations varied inversely in a rather periodic manner. We interpreted this as an indication that the material within the cavity consisted of oxidized or hydrolyzed fuel material (i.e., corrosion products of the Al-UAl_x fuel dispersion) and that no organic foreign materials were present to account for the failure.

Metallographic examination of the specimen also indicated that the failures might have been a result of corrosion. Many small pits were in the cladding near the blistered area. A deeper pit was found a short distance away from the blistered area. This pit completely penetrated the 6061 alloy cladding, which is nominally 0.015 in. thick.

28. Joining Research on Nuclear Materials

G. M. Slaughter

The purpose of this program is to gain needed fundamental and practical information on the welding of structural materials used to manufacture critical components for the nuclear industry. The quality of the welds can be affected by chemical composition, melting practice used in making the base metal or filler wire, and welding techniques. Research is centered on the weldability of alloys that are candidate materials for the construction of vessels, intermediate heat exchangers, steam generators, and core components for liquid-metal fast breeder reactor plants. Stainless steels and Incoloy 800 are emphasized because of their immediate applicability.

DUCTILITY OF INCONEL 600 BASE METAL AT INTERMEDIATE TEMPERATURES

W. J. Werner   D. A. Canonico

Tensile studies were conducted on specially melted Inconel 600 alloys at intermediate temperatures (400 to 1000°C) in an argon atmosphere at a strain rate of 0.002/min. The investigation was similar to that conducted previously¹ in Incoloy 800. The compositions of the alloys ranged from a pure ternary Ni-Cr-Fe alloy to an alloy that contained nominal amounts of C, Si, and Cu and larger amounts of P, S, and Mn. Compositions containing these elements individually were also investigated.

In all instances, the alloys lost ductility above 500°C. The ductility is shown as a function of test temperature in Fig. 28.1. Since recovery was not observed, these alloys behaved like the Incoloy 800 compositions without titanium.

Figure 28.1 also shows the dependence of the yield and ultimate strengths on temperature. The results fell within the indicated ranges, and, as expected, the more complicated alloys generally were stronger.

1. W. J. Werner, *An Investigation of the Effect of Certain Minor Elements on the Elevated Temperature Ductility of Incoloy 800* (thesis), ORNL-4504 (March 1970).

Fig. 28.1. The effect of test temperature on the strength and ductility of experimental Incoloy 600 alloys.

STUDIES ON INCOLOY 800 WELD METAL

D. A. Canonico

Experimental alloys of basic Incoloy 800 composition (Fe-31.5% Ni-21.5% Cr) were drawn to wire and used as filler metals for welding commercial Incoloy 800 sheet and plate. Included in this series of weldments were (1) the commercial Inconel filler metal (82T) that is recommended for joining Incoloy 800 and dissimilar

Table 28.1. Chemical composition of commercially obtained filler metals

Filler metal designation	Form	Chemical composition (wt %)									
		C	Mn	Fe	S	Si	Cu	Ni	Cr	Mo	Others
82T	Wire	0.02	3.00	1.00	0.007	0.20	0.04	Bal	20		Ti-0.55
Y32A1	Flux-coated	0.10	5.65	Bal	0.007	0.47	0.26	40.26	21.16	2.67	
5409	Wire	0.09	4.78	Bal	0.005	0.68	0.32	41.29	20.76	2.62	

materials, (2) two new commercially developed filler metals approaching the Incoloy 800 composition, (3) a filler metal that had been prepared from electroslog remelted Incoloy 800, and (4) 21 experimental filler metals from heats previously studied in our hot ductility tests. These welds were made on fully restrained, $\frac{1}{2}$ -in.-thick commercial Incoloy 800 plates with the gas tungsten-arc process.

The strongest and most ductile welds were those made with the commercial Inconel and modified Incoloy filler metals. However, a number of the experimental Incoloy 800 alloys were nearly of the same high quality. The ORNL alloy with a medium carbon content (nominally 0.04%) was the strongest and most ductile. The high-sulfur and low-carbon alloys cracked during welding. Filler metals with equally high sulfur and titanium did not crack. This is further evidence of the beneficial effect of titanium. The analyses of the Inconel 82T and the new Incoloy 800-type commercial filler metals are given in Table 28.1.

The commercial filler metal, 82T, although recommended for joining Incoloy 800, has reported sensitivity toward hot cracking. We obtained some fissured Inconel 600 welds from industry and have performed electron-beam microprobe analyses on them. The fissures appear to be enriched in niobium. These results, as well as those obtained in our hot ductility study, have given us reason to question the generally recognized effects of various elements on the weldability of nickel-rich materials. For instance, niobium is reputed to be beneficial, titanium variable, phosphorus detrimental, and manganese of no consequence. This study has shown that niobium may be detrimental, titanium is beneficial (because it counteracts the effects of sulfur), manganese can be detrimental for a given sulfur level, and phosphorus at low levels may be beneficial.

WELDABILITY OF AUSTENITIC STAINLESS STEELS

A. J. Moorhead   D. A. Canonico

Our studies have continued to center on the effect of chemical composition on the amount and morphology

of the ferritic phases usually present in stainless steel weld metal. Additional investigations on stainless steel welds are presented in Chap. 17. We have concentrated on the prediction of the amount of ferrite present and its measurement. The amount of ferrite was determined with both the Magne-Gage and the Quantitative Television Microscope (QTM). The ferrite content is normally predicted from the Schaeffler diagram.² In general, the amount of ferrite measured by the two techniques correlated well. However, these measurements agreed rather poorly with predictions by the Schaeffler diagram. Although the diagram was developed for as-deposited weld metal and not for cast or homogenized ingots, better correlation for ingots was expected, since the quenching rate for these drop-cast ingots is not greatly different than that for high-heat-input welds. The ferrite content of the as-cast bars was about 1.5 to 3 times that predicted from the Schaeffler diagram.

We measured the ferrite content of autogeneous welds made on coupons from drop castings of experimental compositions. The procedures used in making these welds, by both the gas tungsten-arc and electron-beam processes, were described earlier.³ After etching cross sections with boiling Murakami's reagent, a series of measurements of ferrite content were taken along the weld center line, using the QTM. The averages of these readings on four compositions, along with the ferrite content predicted from the Schaeffler diagram for stainless steel weld metal, are given in Table 28.2. Two important observations can be made from this table. First, although the Schaeffler diagram predicts that the manganese-bearing heat (No. 5409) should be strongly austenitic, weld metal of this composition had from 3% (electron-beam weld) to 8.5% (tungsten-arc weld) ferrite. This anomaly was further substantiated by a Magne-Gage measurement of over 9% ferrite in the drop-cast ingot. Another manganese-bearing heat of similar composition had about 7% ferrite in the as-cast

2. A. L. Schaeffler, *Welding J.* 26, 601-s-20-s (1947).

3. A. J. Moorhead and D. A. Canonico, *Fuels and Materials Development Program Quart. Progr. Rept. Dec. 31, 1970*, ORNL-TM-3300, pp. 297-303.

Table 28.2. Ferrite content (measured with the QTM) of autogeneous welds in experimental stainless steel alloys

Heat	Composition (wt %)			Ferrite content (%)		
	(bal Fe)			Schaeffler diagram	EB weld	GTA weld
	Cr	Ni	Mn			
5409	18.3	11.9	4.8	0	2.9	8.5
5410	18.3	9.8		7	0.25	3.3
5416	22.2	13.5		7	1.5	7.0
5422	24.1	18.8		0	0	0

ingot. It is also interesting to note that a ternary alloy having the same Fe, Cr, and Ni contents of heat 5409 (i.e., Fe-18.3% Cr-11.9% Ni) would be expected to contain about 2% ferrite in the weld metal. This

indicates that, although manganese in small amounts may act as an austenitizer, in greater amounts it may have no effect or, in fact, become a ferrite former.

The second noteworthy feature of Table 28.2 is the effect of weld energy input on the ferrite content of the weld metal. The energy input of the electron-beam weld was 1700 J/in. and of the GTA weld 4500 J/in. By comparing the ferrite content of the welds made on a single heat, the large effect of energy input can be seen. For example, welds having the composition of heat 5410 (which has Ni and Cr equivalents on the Schaeffler diagram comparable to those of type 304) may or may not contain enough ferrite to prevent hot cracking, depending on the process used. This effect is illustrated dramatically in Fig. 28.2.

Fig. 28.2. Gas tungsten-arc (left) and electron-beam (right) welds on heat 5410 (Fe-18.3% Cr-9.8% Ni) etched with Murakami's reagent to reveal ferrite. The bottom photomicrographs show the fusion lines of the welds.

29. Mechanical Properties of Irradiated Metals and Alloys

J. R. Weir, Jr.   H. E. McCoy, Jr.

Neutron irradiation alters the properties of metals by atomic displacements and by transmutation. Atomic displacements can cause the formation of various defects including dislocations and voids. These can cause marked changes in the mechanical properties as well as swelling. Various transmutation products can be formed in structural alloys, but helium and hydrogen are the most common. In aluminum-base alloys the production of silicon is important. These transmutation products not only directly change the mechanical properties but can have second-order effects by their effect on the defect structure.

The materials problems associated with different reactor concepts due to neutron irradiation vary widely, depending on the neutron spectrum and the structural materials. The LMFBR has a high fast flux in the core, and the stainless steel cladding will experience property changes due to atomic displacements and due to helium produced by transmutations. This work was discussed in Chap. 15, but further work in this chapter is related to LMFBR systems. Some work has been done on pure nickel in an effort to better understand the mechanisms of void formation. Work has also been done on molybdenum and vanadium alloys as potential cladding materials and tantalum for control applications in LMFBR's. This required that we develop the capability of remotely thinning samples for transmission electron microscopy. Niobium and molybdenum are candidate structural materials for controlled thermonuclear reactor applications that involve large fast-neutron fluxes.

Aluminum alloys are in use in numerous reactors, but the HFIR probably exposes them to the most severe conditions of temperature and thermal and fast neutron fluxes. The failure of parts of HFIR has raised the general question of the behavior of aluminum alloys under such service conditions.

The molten-salt reactor exposes Hastelloy N (Ni-base alloy) to high thermal neutron fluxes, and the main effect of irradiation remains the production of helium. This problem will be discussed in Chap. 34.

VOID FORMATION IN IRRADIATED NICKEL 270 (Ref. 1)

J. O. Stiegler   E. E. Bloom

To supplement our work on radiation damage in stainless steels we are conducting additional experiments on a relatively pure face-centered cubic metal, nickel. Specimens of Nickel 270 (99.98% nominal purity) were irradiated in EBR-II to fluences ranging from 1×10^{18} to 1.5×10^{22} neutrons/cm² (>0.1 MeV) at temperatures between 375 and 525°C. Voids were observed in all specimens in concentrations of 1 to 3×10^{14} /cm³, independent of irradiation temperature and fluence. At low fluences the voids existed in clusters, and the reported concentration is an average value over a volume encompassing several clusters. At higher fluences the voids appeared to be distributed homogeneously, but the average concentration did not increase. We contend that the concentration did not increase because the voids that were nucleated in the regions between the clusters were compensated for by merger of closely spaced voids within the clusters. At an irradiation temperature of 470°C and a fluence of 1.5×10^{22} neutrons/cm² no voids smaller than 250 Å in diameter were found, suggesting that at this point nucleation had truly ceased. In this specimen voids as large as 1300 Å in diameter were found, in contrast to the apparent maximum limiting size of less than 300 Å for stainless steel irradiated at the same temperature.²

Although void concentrations did not decrease with increasing irradiation temperature, void shapes were strongly influenced by temperature. At 385°C the voids were cubic, at 470°C they appeared to be truncated octahedra, and at 525°C about one-third of them were elongated along $\langle 110 \rangle$ directions. In the latter case the

1. Summary of a paper to be published in *Radiation Effects*.
2. E. E. Bloom, *An Investigation of Fast Neutron Radiation Damage in an Austenitic Stainless Steel*, ORNL-4580 (August 1970).

maximum length-to-width ratio was about 5. No measurable changes in total void volume were detected over this temperature range at a fluence of 1.4×10^{20} neutrons/cm².

In addition to the voids the specimens contained complex dislocation structures. At low fluences patches of perfect dislocation loops were observed. As the fluence increased these apparently evolved into a loose dislocation structure, with small loops located adjacent to the dislocation lines. This structure coarsened with increasing irradiation temperature. At very high fluences only a system of dislocation lines was observed, many of which appeared to thread the voids.

The heterogeneous void distributions observed at low fluences and the lack of dependence of void concentration on irradiation temperature suggest that many of the voids were nucleated on sites existing in the material before irradiation. Gas bubbles have been observed to form in this material by high temperature annealing treatments alone, and finely dispersed bubbles were suggested as the preexisting nuclei. The eventual formation of voids in the regions between clusters indicates an additional nucleation mechanism that is initiated or augmented by the irradiation.

The sizes and concentrations of voids found were compared with results of two other investigations. A difference of nearly two orders of magnitude in void concentration was found for irradiation at 475 to 500°C at a fluence of about 10^{20} neutrons/cm². It was suggested that impurities were responsible for these differences, although spectral effects may be important.³

PREPARATION OF TRANSMISSION ELECTRON MICROSCOPY SPECIMENS IN A HOT CELL BY REMOTE TECHNIQUES⁴

C. K. H. DuBose   T. L. Chandler⁵

With a semiautomatic technique developed at Oak Ridge National Laboratory,⁶⁻⁸ specimens for transmission electron microscopy have been prepared routinely from $\frac{1}{8} \times \frac{1}{8} \times 0.020$ in. pieces reading up to 10 R/hr. The specimen is first dimpled with an electrolytic jet and then polished uniformly in a standard electrolytic cell until a hole forms in the dimpled region. The region adjacent to the hole is usually sufficiently transparent to electrons to provide a usable specimen. Better specimens are produced near smaller holes, and a light beam and photocell detector halt the polishing automatically as soon as a hole forms.

Tantalum from all irradiations and some stainless steels irradiated in HFIR have activities over an order of

magnitude higher than the limit cited above for preparation of specimens in the laboratory. The need to examine such materials has led to the development of techniques for the complete preparation of specimens for transmission electron microscopy in a hot cell. While the ORNL technique does produce excellent specimens, it is a two-step process that requires complicated handling and precise manipulation and alignment of specimens. In the interest of simplicity, speed, and economy, we modified the commercial electropolishing unit for hot-cell operation. This provides a one-step process in which the specimen is mounted in a special holder and immersed in an electrolyte that is agitated by a pair of submerged jets. The light source, electronic system, photo detector, and power supply from the ORNL system were substituted for those supplied with the commercial unit.

A jig was designed to support the specimen holder during loading and unloading. A light was built into the jig to allow confirmation that a hole had formed and to locate its position. The jig also allows different specimen holders to be aligned with the retaining ring that locates their position in the polishing unit.

The specimens are loaded into specimen holders in the hot cell and are transferred to the electron microscope in a shielded container. They are removed from the container and inserted in the microscope with special tongs that keep the operator at least 3 ft from the specimen. Once the specimen is in the microscope stage, the microscope itself provides shielding for the operator. Slight contamination of the microscope-specimen exchange mechanism has occurred, but the specimen stage and microscope column have been clean.

Specimens of tantalum and stainless steel reading up to 100 R/hr at 5 in. have been successfully prepared and examined by this technique. Specimen quality is appreciably lower than in specimens prepared in the

3. J. O. Stiegler, "Void Formation in Neutron Irradiated Metals," paper presented at the International Conference on Radiation-Induced Voids in Metals, Albany, N.Y., June 9-11, 1971; to be published in the proceedings.

4. Summary of a paper to be submitted for publication.

5. Operations Division.

6. C. K. H. DuBose and J. O. Stiegler, *Semiautomatic Preparation of Specimens for Transmission Electron Microscopy*, ORNL-4066 (February 1967).

7. C. K. H. DuBose and C. Jones, *Techniques for the Preparation of Transmission Electron Microscopy Specimens from Tubing*, ORNL-TM-2408 (January 1969).

8. C. K. H. DuBose and C. Jones, "The Preparation of Transmission Electron Microscopy Specimens from Tubing," *Metallography* 2, 31-39 (1969).

laboratory. Usable areas are obtained in about 50% of the specimens, and about 25% of the specimens are judged good. The low yield may occur because the technique is not well suited to the relatively thick starting material used in these studies. The speed and simplicity of the technique make this sacrifice worthwhile.

IRRADIATION DAMAGE TO BODY-CENTERED CUBIC METALS

F. W. Wiffen

The Effect of Neutron Irradiation on the Strength Properties and Failure Mode of Molybdenum Alloys⁹

Recrystallized samples of arc-cast Mo and Mo-0.5% Ti and powder-metallurgy Mo-50% Re irradiated near 425°C to fluences between 1.5 and 3.5×10^{22} neutrons/cm² (>0.1 MeV) in EBR-II were tensile tested at a variety of strain rates and temperatures. Irradiation increased the yield and ultimate tensile strengths and reduced the work-hardening ability and ductility. In all three materials and for all available test conditions, the ultimate tensile strength occurred within 0.2% plastic elongation. The Mo and the Mo-0.5% Ti behaved similarly, with both showing a strain-rate-dependent ductile-brittle transition temperature (DBTT) of 400 to 550°C, compared with less than 20°C for unirradiated controls. Tests of the irradiated Mo and Mo-0.5% Ti above the DBTT showed elongation limited by the inability to work harden. Elongations less than 10% accumulated in the neck region before specimen failure. The Mo-50% Re was brittle to the highest temperature tested, 800°C, for a strain rate of 0.02/min. Transmission electron microscopy of the as-irradiated Mo showed a very high density of small dislocation loops, more than 10^{17} loops/cm³, with most of the loops arranged in linear arrays. Scanning electron microscopy of fracture surfaces showed failures below the DBTT to be predominantly cleavage with only a small component of grain-boundary separation. Failures above the DBTT showed the dimples characteristic of ductile fracture and were no different than fractures in unirradiated control specimens.

Voids and the Microstructure of Neutron-Irradiated Niobium⁹

Specimens of niobium irradiated in EBR-II at 425, 600, and 800°C to a fluence of 2.5×10^{22} neu-

trons/cm² (>0.1 MeV) were examined by transmission electron microscopy. Irradiation-produced voids were present for all three irradiation temperatures. The void populations were quite similar for the two lower irradiation temperatures, with densities near 2×10^{17} voids/cm³ and average and maximum void diameters of 70 and 130 Å, respectively. The associated volume increases were between 3 and 5%. The void formation at 425°C is very significant because this temperature is only 0.26 of the melting temperature, T_m , and is a clear violation of the common assumption that voids do not form at irradiation temperatures below about $0.30T_m$. At 800°C the void density was 2.4×10^{15} /cm³, the average diameter 185 Å, and the maximum 275 Å. The associated swelling is about 0.9%. The void distribution in the specimen irradiated at 800°C shows a strong ordering tendency, with the voids clearly showing a preference to be arranged on {110} planes. Tilting experiments establish that the ordered arrangement is three dimensional, with the voids on the points of an irregular bcc superlattice that is parallel with the metal lattice and has a lattice parameter of about 670 Å. The ordering is locally incomplete and is also broken by areas of random void arrangement. The defect structure seen in diffraction contrast consists of loops and dislocation segments in all specimens. The density of these defects decreases with increasing irradiation temperature.

The Effect of Alloying and Purity on the Formation and Ordering of Voids in BCC Metals¹⁰

The void populations in Mo, Nb, V, and one alloy of each of these were compared by electron microscopy. All three of the systems responded differently to the alloying. The void concentrations and sizes in the Mo and Mo-0.5% Ti irradiated at 790°C were identical within the measurement limits. After irradiation at 585°C the Mo-0.5% Ti contained more voids, but the sizes were nearly identical. Alloying niobium with 1% Zr reduced the void concentration after irradiation at 790°C by more than an order of magnitude, but this was compensated by an increase in void size. High void concentrations were observed in vanadium irradiated at 385 to 600°C, but samples of V-20% Ti irradiated in the range 475 to 600°C had no detectable voids. They contained high densities of irradiation-produced dislocations in networks and tangles. Voids in Mo, Mo-0.5% Ti, Nb, and Ta were ordered on a bcc

9. Summary of paper presented at the 1971 Spring Meeting of the Metallurgical Society of AIME, Atlanta, May 17-20, 1971.

10. Abstract of paper presented at the 1971 International Conference on Radiation-Induced Voids in Metals, Albany, N.Y., June 9-11; to be published in the proceedings.

superlattice parallel to the metal bcc lattice. Void ordering was not observable in the Nb-1% Zr or in vanadium.

EFFECTS OF IRRADIATION ON ALUMINUM ALLOYS

R. T. King K. Farrell A. Jostsons¹¹

General Effects of Neutron Irradiation on Aluminum and Aluminum Alloys

Because of concern over the safety of critical components of water-cooled test and isotope-production reactors, which are made of aluminum alloys, neutron damage to these materials is under study. The types of irradiation damage found are:

1. The formation of voids and dislocation loops, which condense from vacancies and interstitial atoms produced by atomic displacements. The distribution and extent of this damage has been shown to be very sensitive to irradiation temperature,^{12,13} neutron fluence,¹⁴ the presence of hydrogen and helium,^{12,15} and gross chemical composition and microstructure.^{15,16} We recently obtained evidence that some precipitates may retard void formation to very high fluences.^{16,17} Voids and dislocations are sources of irradiation strengthening.

2. The formation of silicon precipitate particles. Silicon is generated by the thermal-neutron-induced

$^{27}\text{Al}(n,\gamma)^{28}\text{Al}$ reaction followed by a β^- decay to silicon;¹⁸ the size range and distribution of the silicon particles are strongly temperature sensitive. Irradiation-induced strengthening of alloys at temperatures above the range for void formation can be explained on the basis of the dispersed silicon phase. Increases in both the yield strength and resistance to creep deformation are observed.

3. The formation of helium by $^{27}\text{Al}(n,\alpha)$ reactions and other (n,α) reactions. Most of the helium present after irradiation to high neutron fluences comes from the former source, although there are small contributions from certain alloying elements. Thermal neutron reactions with lithium and boron, which are usually present as tramp impurities, probably produce a heterogeneous helium distribution. Helium reduces the tensile ductility of solid-solution aluminum alloys above about 200°C, and probably plays a role in premature intergranular failure at lower temperatures and slow strain rates.¹⁹

4. The formation of hydrogen by $^{27}\text{Al}(n,p)$ reactions. The amount of hydrogen gas produced that remains in aluminum during irradiation is uncertain, and its effects on mechanical properties are not known. Satisfactory chemical analyses for hydrogen in irradiated aluminum have not been achieved, and it is not known whether some hydrogen from the coolant enters the aluminum. Hydrogen and/or helium may play some role in determining the eventual forms assumed by displacement damage.^{12,20}

Effects of Elevated-Temperature Irradiation on 8001 Aluminum Alloy

Irradiation effects are being studied in 8001 aluminum alloy because it is the target cladding material that failed in service in the High Flux Isotope Reactor. Metallographic investigation of the failed tube showed radial cracking that occurred after no measurable circumferential strain. Portions of a failed target rod irradiated to over 1×10^{22} neutrons/cm² (>0.8 MeV) were found, by transmission electron microscopy, to contain many heterogeneously distributed transmutation-induced silicon particles and voids. The voids

11. On attachment from Australian Atomic Energy Commission Research Establishment.

12. K. Farrell, A. Wolfenden, and R. T. King, "The Effects of Irradiation Temperature and Preinjected Gases on Voids in Aluminum," *Radiation Effects* 8, 107-14 (1971).

13. R. T. King, A. Jostsons, and K. Farrell, "Effects of Elevated-Temperature Neutron Irradiation on Aluminum," presented at the American Nuclear Society Spring Meeting, Boston, Mass. (June 1971).

14. N. H. Packan, *Voids in Neutron Irradiated Aluminum*, ORNL-TM-3019 (January 1971).

15. K. Farrell, J. T. Houston, A. Wolfenden, R. T. King, and A. Jostsons, "Effects of Structural Imperfections on Voids in Aluminum," paper presented at the International Conference on Radiation-Induced Voids in Metals, Albany, N.Y., June 9-11, 1971; to be published in the proceedings.

16. J. O. Stiegler, K. Farrell, C. K. H. DuBose, and R. T. King, "High-Fluence Neutron-Irradiation Damage in Aluminum," pp. 215-32 in *Radiation Damage in Reactor Materials Vol. II* (Proceedings of a Symposium, Vienna, 2-6 June 1969), International Atomic Energy Agency, Vienna, 1969.

17. R. T. King, K. Farrell, and A. Jostsons, "The Effect of High Fast Neutron Fluence on the 6061 Aluminum Alloy," presented at the 1971 Spring Meeting of the Metallurgical Society of AIME, Atlanta; to be published.

18. K. Farrell, J. O. Stiegler, and R. E. Gehlbach, "Transmutation-Produced Silicon Precipitates in Irradiated Aluminum," *Metallography* 3, 275-84 (1970).

19. R. T. King, *Cyclotron Simulation of Neutron-Transmutation Produced Gases in Reactor Cladding and Structural Materials*, ORNL-TM-3299 (April 1971).

20. A. Wolfenden, "Effects of Preinjected Hydrogen on the Electron Displacement Damage in 1100 Aluminum," Chap. 5, this report.

tended to form at two preferred sites, alongside stringers of inclusions and near some grain boundaries. Work is now under way to establish whether these voids are involved in the failure of the target rods. Postirradiation tensile tests on 1100 aluminum specimens containing walls of voids near grain boundaries have shown that the voids probably play an important role in premature intergranular failure. Creep tests have been made on 8001 alloy specimens that had been irradiated between 125 and 175°C to a fluence of 1.6×10^{22} neutrons/cm² (>0.8 MeV). These specimens did not contain voids but were hardened by the silicon particles. The specimens all deformed several percent before failing, but changes of about 30°C in the irradiation temperature had a greater effect on strength than doubling the neutron fluence, other conditions being constant.

We feel that voids were not observed in the 8001 alloy creep specimens either because the specimens had been irradiated at a higher temperature than the cladding or because the hoop stresses present in the cladding may have affected void formation. The role of stress during irradiation is not yet known.

Irradiation Effects in 6061 Aluminum Alloy and Its Utility for In-Reactor Service

Because of its high strength, the Mg₂Si precipitation-hardened 6061 aluminum alloy has been selected for numerous reactor components. It has now been examined after irradiation. One component, the High Flux Isotope Reactor target basket, was examined and found not to contain voids at fluences below about $3 \times$

10^{22} neutrons/cm² after irradiation at 60°C; above this fluence voids formed. Only 1.1% swelling was measured after irradiation to 5.4×10^{22} neutrons/cm² (>0.8 MeV). This is very much less than the swelling in 1100 aluminum or alloy 8001 at similar fluences. Of this 1.1% swelling, about half was attributable to void formation and half to precipitation of transmutation-produced silicon.

When voids do form in the slightly overaged 6061 alloy, they usually develop around the coarser Mg₂Si particles and around large inclusions. These features are believed to be incoherent with the matrix and are surrounded by regions that are free of smaller Mg₂Si particles of unproven coherency. Such observations suggest that the optimum structure for minimization of void formation is one containing a finely divided, coherent Mg₂Si precipitate. This structure must be stable during irradiation. In this respect, we found that the original structure in age-hardened 6061 alloy is intact even after irradiation at 150°C to high fast neutron fluences.

Irradiation at temperatures and fluences that did not cause void formation slightly increased the creep strength of the 6061 alloy while decreasing its ductility to the 2 to 5% range. The transmutation-induced silicon probably increased the strength of the alloy.

The resistance of the 6061 alloy to void formation, its high strength, and its stability under irradiation make it preferable to the solid solution alloys for most high neutron fluence applications. Although the postirradiation ductilities of the latter alloys are the greater, the 6061 alloy probably has sufficient ductility for most reactor applications, but more work is needed to study the influence of transmutation-produced gases on ductility at higher neutron fluences.

30. Nondestructive Test Development

W O Harms   R W McClung

This program is designed to develop new and improved methods of examining reactor materials and components. To achieve this we study the pertinent physical phenomena, develop instrumentation and other equipment, devise application techniques, and design and fabricate reference standards. Among the subjects being actively pursued are electromagnetics (with major emphasis on eddy currents), ultrasonics, and penetrating radiation.

ELECTROMAGNETIC INSPECTION METHODS (EDDY CURRENTS)

C V Dodd   C C Lu¹
W A Simpson, Jr   W E Deeds²
C C Cheng³

Our broad program on research and development of electromagnetic inspection methods includes (1) theoretical analysis of basic eddy-current problems, (2) programming the analytical equations for numerical solutions on a digital computer, (3) application of the computer programs to general eddy-current problems, (4) application of the computer programs to specific eddy-current inspection problems, (5) experimental verification of solutions to these problems, and (6) instrument design and construction.

Theoretical Analysis

We developed solutions for multiple planar conductors as described in the following abstract ⁴

A general theory is presented for the axially symmetric, time-harmonic eddy currents produced by a probe coil of rectangular cross section in linear, isotropic, homogeneous, conducting media bounded by an arbitrary number of parallel

plane boundaries. First, the Green's function in each medium is calculated by a matrix method, which greatly simplifies the procedure. Then the vector potential and other quantities of interest are calculated from the Green's functions. The general results are specified to three cases: a probe coil above an arbitrary number of parallel-plane conductors, a probe coil between two three-layer conductors, and a probe coil above a three-layer conductor. We have written computer programs that numerically calculate electromagnetic properties if one specifies the location and physical properties of the coil and conductors.

We have extended the above solutions for multiple planar conductors to the cases of a coil coaxial to and encircling or encircled by cylindrical conductors.

Development of Computer Programs

We published many of our new programs in a report with the following abstract ⁵

This report contains computer programs for solving some eddy-current problems frequently encountered in nondestructive testing. Operating instructions and examples are given for each program. These programs are written in BASIC language and may be used on a time-sharing computer. Various eddy-current tests can be quickly and accurately designed by utilizing these programs.

We wrote additional programs to calculate the impedance of a probe-type coil near multiple planar conductors and to calculate the magnitude and phase of a reflection-type coil above multiple conductors. We also wrote a program to calculate the conductivity and lift-off for a given coil above a conductor if the normalized impedance of the coil is given. We improved our relaxation calculations to include the effect of velocity of the conductor past the coil.

Computer Studies of General Eddy-Current Problems

We are using our computer calculations to determine the optimum parameters for measuring specimen thickness, cladding thickness, and electrical conductivity and

5 W A Simpson, C V Dodd, J W Luquire, and W G Spoeri, *Computer Programs for Some Eddy Current Problems* - 1970, ORNL-TM-3295 (June 1971)

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1 Mathematics Division
2 Consultant, University of Tennessee, Knoxville
3 Consultant, Northwestern College, Orange City, Iowa
4 C C Cheng, C V Dodd, and W E Deeds, "General Analysis of Probe Coils Near Stratified Conductors," to be published in *International Journal of Nondestructive Testing*

for detecting defects.⁶ A number of curves were prepared that show that the eddy-current signal produced by a defect varies as a function of test parameters for various arrangements of the coil and conductor, with special emphasis on differential encircling coils. From these curves the optimum parameters can be selected for a particular test. We determined that there is an optimum value of $\omega\mu\sigma\bar{r}^2$ (Fig. 30.1) to produce maximum sensitivity (phase shift) for measuring the thickness of one conductor clad on another. The figure shows the variation with coil radius of the optimum value of $\omega\mu\sigma\bar{r}^2$ for maximum sensitivity and the phase shift for a 10% change in cladding thickness at that optimum value. This graph demonstrates the optimum value for maximum phase shift. Figure 30.2 shows both the optimum coil radius and the phase shift at the 10% variation in cladding thickness at this optimum plotted against the ratio of conductivities of the base and cladding materials. From this graph we can select the optimum coil size for a given conductivity ratio and cladding thickness and then determine the sensitivity at this optimum. Similarly, we determined the optimum parameters for conductivity measurements.

Computer Studies of Specific Eddy-Current Problems

We applied our computer programs to design specific eddy-current tests. These studies include the design of systems to (1) detect sodium voids in irradiation capsules, (2) detect small surface cracks in aluminum-clad control rods, (3) measure the electrical conductivity of pellets of actinide oxide in an aluminum matrix, (4) measure the level of a liquid metal in a processing system, and (5) measure rapid temperature changes by detecting changes in the permeability of iron caused by the changes in temperature.

Experimental Verification of Computer Calculation

We confirmed some of our computer calculations experimentally. These include the measurement of normalized coil impedance of encircling coils as a function of cladding thickness,⁷ the variation in coil impedance with defects for encircling coils, and phase shift vs thickness for reflection coils.

6. C. V. Dodd, W. E. Deeds, and W. G. Spoeri, "Optimizing Defect Detection in Eddy-Current Testing," *Mater. Evaluation* 29, 59-63 (1971).

7. F. D. Mundt, *Eddy-Current Measurements with a Coil Encircling a Two-Conductor Rod*, MS Thesis and Y-1787 (April 1971).

Fig. 30.1. Optimum $\omega\mu\sigma_1\bar{r}^2$ for maximum sensitivity and phase shift due to a 10% cladding thickness change plotted against normalized cladding thickness (divided by coil mean radius).

Fig. 30.2. Optimum value of cladding thickness divided by coil mean radius and phase shift for a 10% change in cladding thickness as functions of the ratio of conductivities of the cladding and base materials.

Instrument Design and Construction

The stability of the modular phase-sensitive eddy-current instrument has been improved at the higher frequencies. The instrument drifts typically $0.03^\circ/24$ hr at 1 MHz. Tuned frequency amplifiers have been constructed for frequencies from 1 kHz to 2 MHz in a 1, 2, 5 sequence.

ULTRASONIC INSPECTION METHODS

H. L. Whaley K. V. Cook Laszlo Adler²

Frequency Analysis

We improved our theoretical models⁸ and experimental techniques for characterization of flaws by ultrasonic frequency analysis. The basis of our approach is extraction and evaluation of data from the spectral analysis of a broadbanded ultrasonic pulse that has interacted with a discontinuity. The conceptual procedure reported previously,⁹ outlining the steps necessary to characterize a randomly oriented natural flaw in a material, was tested in practice.¹⁰ The sample was a thick block of steel in which flat-bottomed holes of various sizes were drilled at different angles with respect to the surface. Size determination by spectral analysis was demonstrated to be far superior to that by the conventional amplitude technique. To determine both size and orientation, a computer program was devised to solve the transcendental equations involved. Progress was also made in the very difficult problem of characterization of irregularly shaped reflectors (discontinuities) with random orientation. Two separate electronic gates were used simultaneously, allowing any two selected portions of the reflected pulse to be fed to the spectrum analyzer. We determined that thin foils of brass may be used to easily make reflectors of any desired shape, size, and surface contour, thus greatly expanding the availability of samples. A two-transducer method for reflector characterization was also developed. The basic equations are similar to those developed for the one-transducer case. This approach appears to offer a number of important practical advantages and may simplify mechanical motions necessary to obtain the spectral information.

Optical Visualization of Ultrasound

The equipment for acousto-optic imaging has been relocated in a new laboratory space. The design of the optical layout was improved to provide for an imaging system of more general capabilities including, in addition to schlieren, Bragg diffraction and volume holo-

graphy. The working area in which the ultrasonic tank containing the specimen is located is now completely disconnected from the optics so that large samples can be moved in and out without loss of optical alignment. Also, all the optical components and supporting structures have been firmly secured so that the system as a whole remains in excellent alignment under normal use. The sensitivity of the new system was maximized by using two light sources and a variety of samples interacting with the propagation of the ultrasound. A new optical table was constructed employing simplified and inexpensive optical benches and component carriers. This table will be employed to set up prototype optical systems for evaluating ideas that cannot conveniently be tested with the large permanent system.

PENETRATING RADIATION INSPECTION METHODS

B. E. Foster S. D. Snyder

Radiation Scattering

Studies were continued on the use of scattered and fluorescent radiation for measuring the thickness of coatings or claddings on reactor components. In addition to the previously reported measurements of the thickness of Al clad to U, we examined several other combinations of materials such as W on Mo, Mo on type 304L stainless steel, and W on type 304L stainless steel.¹¹

With the ¹⁴⁷Pm isotopic radiation source presently being used, the monitoring time required to accumulate a sufficient number of counts for a valid measurement is about 25 min. This lengthy counting time is tolerable during the initial development work, but for most practical applications the technique should be capable of scanning a specimen with a short dwell time on any given area. Toward this end we have begun studies using one of our mechanical scanning systems that incorporates a commercial x-ray unit as the radiation source.¹²

Closed-Circuit Television for Radiographic Evaluation

We are investigating the use of a closed-circuit television system as a rapid densitometer for reading

8. Laszlo Adler and H. L. Whaley, "Interface Effects in a Multifrequency Ultrasonic Pulse Echo and Its Application to Flaw Characterization," to be published in *Journal of the Acoustical Society of America*.

9. K. V. Cook, H. L. Whaley, Jr., and L. Adler, *Metals and Ceramics Div. Annu. Progr. Rept. June 30, 1970*, pp. 150-51.

10. H. L. Whaley, K. V. Cook, and L. Adler, *Fuels and Materials Development Program Quart. Progr. Rept. Dec. 31, 1970*, ORNL-TM-3300, pp. 306-10.

11. B. E. Foster and S. D. Snyder, *Fuels and Materials Development Program Quart. Progr. Rept. Sept. 30, 1970*, ORNL-4630, pp. 275-77.

12. B. E. Foster and S. D. Snyder, *Fuels and Materials Development Program Quart. Progr. Rept. March 31, 1971*, ORNL-TM-3416, p. 236.

radiographs. The preliminary equipment consists of a film viewer as a source of illumination, an RCA 525-line closed-circuit television system with a scan rate of 9623 in/sec, and an oscilloscope to delay and display any one of the 525 active lines of video. The radiograph is viewed by a zoom lens with a 20- to 80-mm focal length or a microscope lens with magnification of up to 20X.

A calibration curve was made for a range of film densities from 0.4 to 3.4 density units without changing the intensity of film illumination. The sensitivity to a given change in density is about 0.005 density unit. This system is capable of double-pulse operation, which allows selection and magnification of specific areas of interest.¹³

We still have problems with noise and jitter,¹⁴ with most of the noise problems related to repetition rate. The sampling oscilloscopes are excellent for fast pulses of 1 GHz but have excessive noise or jitter at 60 Hz, which is the framing rate of the TV system.

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13 B. E. Foster and S. D. Snyder, *Fuels and Materials Development Program Quart. Progr. Rept. Sept. 30, 1970*, ORNL-4630, pp. 277-78.

14 B. E. Foster and S. D. Snyder, *Fuels and Materials Development Program Quart. Progr. Rept. Dec. 31, 1970*, ORNL-TM-3300, pp. 311-12.

Preliminary evaluation of a newly procured sampling unit with low-impedance cables and probe shows good system stability. The new sampling unit reduces but does not eliminate the jitter. With this system we have been able to measure the wire diameter or spacing on a radiograph of a 400-mesh screen with an accuracy better than 3 μm . The wire spacing was 33 μm and wire diameter 29 μm . The total magnification (optical and electronic) achieved for this measurement was slightly greater than 2600X, yielding an x-y recorder readout of $3\frac{1}{2}$ in. for the 33- μm spacing between the wires.

Shield for ^{252}Cf Neutron Source

We completed the conceptual design of a facility to use 10 mg of ^{252}Cf as a neutron source for both attenuation studies and radiography.¹⁵ The facility was designed to be located and operated within the Nondestructive Testing Laboratory without radiation hazard to personnel.

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15 B. E. Foster and S. D. Snyder, *Fuels and Materials Development Program Quart. Progr. Rept. March 31, 1971*, ORNL-TM-3416, p. 237.

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