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QUARTERLY PROGRESS REPORT
JANUARY, FEBRUARY, MARCH, 1967
REACTOR FUELS AND MATERIALS DEVELOPMENT PROGRAMS
FOR
FUELS AND MATERIALS BRANCH
OF
USAEC DIVISION OF REACTOR DEVELOPMENT AND TECHNOLOGY

JUNE, 1967

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REACTOR FUELS AND MATERIALS DEVELOPMENT PROGRAMS
FOR
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June, 1967

PACIFIC NORTHWEST LABORATORY
RICHLAND, WASHINGTON

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SUMMARY

REACTOR FUELS AND MATERIALS

FAST FUELS OXIDES AND NITRIDES

Studies of the effects of ball-milling time, sintering time, and atmosphere on sintered density of UN-20 wt% PuN were conducted. Increased ball-milling time resulted in higher sintered densities. Sintering at 1800 °C for 6 hr resulted in higher densities and larger grain size than sintering at lower temperatures or for shorter times. Relative to sintering in pure argon, neither a nitrogen partial pressure nor helium yielded a significant improvement; a hydrogen partial pressure had a drastic detrimental effect.

A series of out-of-reactor high-temperature experiments to evaluate hypostoichiometric mixed-oxide fuels, helium and sodium bonded in stainless-

steel cladding was started. The program is comprised of three parts: Preparation of helium and sodium-bonded test capsules, thermal testing, and metallographic and analytical study of the specimens.

Radial plutonium-concentration profile measurements by isotopic dilution mass spectrometry for UN-20 wt% PuN irradiated to 13×10^{20} f/cc at 65 kW/ft showed that gross plutonium migration occurred during irradiation.

Stoichiometric PuO_2 was etched at room temperature using a mixture of 40 ml HF(52%) and 10 ml HNO_3 . Surface staining of etched UN-20 wt% PuN was reduced by replacing the alcohol rinse with a water rinse.

NUCLEAR CERAMICS

The thermal diffusivity of $(\text{U}_{0.8}, \text{Pu}_{0.2})\text{O}_{2.00}$ and $(\text{U}_{0.8}, \text{Pu}_{0.2})\text{O}_{1.92}$ was measured to 1200 °C using a laser heat-pulse apparatus. The thermal diffusivity of $(\text{U}_{0.8}, \text{Pu}_{0.2})\text{O}_{1.92}$ was approximately one-half that of $(\text{U}_{0.8}, \text{Pu}_{0.2})\text{O}_{2.00}$ at 100 °C and about

two-thirds that of $(\text{U}_{0.8}, \text{Pu}_{0.2})\text{O}_{2.00}$ at 1200 °C. The calculated thermal conductivity for $(\text{U}_{0.8}, \text{Pu}_{0.2})\text{O}_{2.00}$ from 100 to 1200 °C was the same as the measured thermal conductivity for $\text{UO}_{2.00}$.

Samples of PuN were melted under nitrogen pressures from 1 to 70 atmospheres in the temperature range 2500 to 2800 °C. The measured congruent melting point for PuN is 2730 ± 30 °C at a nitrogen pressure of 40 atmospheres. The decomposition pressure for PuN according to the equation $\text{PuN}_{(s)} \rightarrow \text{Pu}_{(l)} + 1/2 \text{N}_{2(g)}$ increases from one atmosphere at 2570 ± 30 °C to 40 atmospheres at the congruent melting point.

Sintered ($\text{U}_{0.8}, \text{Pu}_{0.2}$)N shows stability considerably greater than that of PuN but less than that of UN.

As part of a continuing study to determine solubility limits of oxygen in PuN and UN-PuN solid solutions, PuN samples were synthesized in nitrogen atmospheres containing 30, 100, and 300 ppm oxygen. Chemical and x-ray diffraction analyses showed that PuO_2 is definitely present in the samples containing 100 ppm and 300 ppm.

An apparatus to evaporate and condense isothermal sections of the Pu-O-N ternary diagram is essentially complete.

The high-temperature intrinsic electrical conductivity of UO_2 is being studied. The results for single-crystal and polycrystalline UO_2 above 1400 °K were analyzed using a least squares, polynomial equation. It was concluded that until more data are

available for many UO_2 specimens, the best expression of conductivity above 1400 °K is

$$\sigma = 3.569 \times 10^3 e^{-1.15/kT} (\text{ohm-cm})^{-1}$$

The absorption spectra for single-crystal and polycrystalline ThO_2 were determined from 0.247 to 13 μm . Complex changes in the ultraviolet and visible spectra resulted when the ThO_2 was heated in hydrogen or air. The absorption in the infrared is the same for both polycrystalline and single-crystal ThO_2 and is independent of the annealing conditions. The characteristic absorption edge is 5.02 eV.

The thermal diffusivity of a sintered UN-20 wt% PuN sample was measured from 195 to 1575 °C using a laser heat-pulse apparatus. The thermal diffusivity increased with temperature from a value of $0.0326 \text{ cm}^2/\text{sec}$ at 195 °C to a value of $0.0440 \text{ cm}^2/\text{sec}$ at ~ 1100 °C. From 1100 °C to the highest measurement temperature, 1575 °C, the thermal diffusivity was almost constant. The calculated thermal conductivity increased from $0.0204 \text{ cal/sec/cm/}^\circ\text{C}$ at 195 °C to $0.0305 \text{ cal/sec/cm/}^\circ\text{C}$ over the same temperature range.

A study to determine the relationships between microstructure and fabrication history of mixed UO_2 - PuO_2 fuels has been started. Two specimens were examined by optical and reflection electron microscopy.

NUCLEAR GRAPHITE

An electron-microscope examination of impurity effects on the oxidation of graphite by oxygen has been initiated. Impurities in the graphite appear to play a major role in the structural changes observed. A highly selective oxidation attack, which greatly increased contrast within the samples, was observed when thermal oxidation followed a microwave oxidation treatment.

Surface-area measurements have been made on several types of graphites prior to their irradiation in GETR. The surface area of each of these samples will be compared with that obtained after neutron irradiation. It was shown that in making accurate BET surface-area measurements, pressures should be chosen so as to be in the range where a monolayer is absorbed on the graphite sample. The surface-area apparatus has been modified for use with krypton as well as nitrogen as the absorbate.

Measurements of the rate of oxidation of boronated graphite by 0.5% oxygen in helium have been extended to include the oxidation of "black" boronated graphite containing nominally 5% boron as B_4C . At temperatures up to 680 °C, the activation energy for oxidation is about 38 kcal/mole.

Irradiation data are summarized for CSF and Nc-8 graphites after an exposure of 2.4×10^{22} nvt ($E > 0.18$ MeV) at 800 °C. The respective volume changes are +33 and +11.7 percent. The behavior of parallel orientations of both graphites suggests an approach

to "turnaround" observed earlier in transverse orientations.

A reactor-grade graphite, TSGBF, experienced transverse and parallel growths of +34.8 and 8 percent, respectively, in irradiations at 1000 °C after 8.7×10^{21} nvt ($E > 0.18$ MeV). Volume expansion is 97%. Two experimental graphites show greatly improved behavior for the exposure levels attained.

The high-temperature graphite irradiation capsule, GEH-13-13, has completed half its irradiation goal for four cycles. Seven of the original twelve thermocouples are operating, indicating capsule temperatures ranging from 800 to 1250 °C.

Pyrolytic graphites graphitized at 2200 and 3400 °C were irradiated at 600 °C. Transverse expansion rates are 1.62 and 0.49%/10²¹ nvt, respectively, for the two process temperatures. Parallel contraction rates were 0.62 and 0.03%/10²¹ nvt, respectively.

Glassy carbons irradiated to 6.4×10^{20} nvt ($E > 0.18$ MeV) at 600 °C exhibit high contraction rates. Heat treatments of 1000, 2000, and 3000 °C produced material which displayed decreasing contraction rates for increasing heat-treatment temperature. This temperature dependence has also been found in conventional graphites.

Irradiations of pyrolytic and single-crystal graphites have been completed. Of the eight capsules, four were irradiated in the Hanford Snout Facility at 50 °C, three in a

Hanford test hole at 650 °C, and one in the ETR at 1000 °C. All the samples have been returned to Union Carbide Corporation for remeasurement of the elastic properties.

Parallel samples of both EGCR and TSX graphite have survived more than 1.1% radiation-induced strain in the ETR.

Analysis of lattice and bulk thermal expansion of graphite is being extended to temperatures above 1000 °C.

The preirradiation calibration of 24 thermocouples to be irradiated in EBR-II is nearly complete. Goal exposures for the irradiations are 3 and 10×10^{21} nvt (fast) on each thermocouple type. After discharge, the couples will be recalibrated in an NRTS hot cell.

The analysis of previously proposed models of polycrystalline graphite was extended to the case of preferential crystallite orientation. To serve as a check on the results the analysis was carried out by two different methods. The general shape of curves of thermal expansion versus orientation parameter for the modified models without accommodation parallels the average of the experimental observations. Introducing crystallite accommodation lowers the calculated curves to give good agreement with the experimental curve. The two models with accommodation define a region which includes most experimental values of Young's moduli. Thus, these modified models are better representations of polycrystalline graphite than the constant stress or constant strain models.

BASIC SWELLING STUDIES

The first controlled pressure test at 5,000 psi is operating as designed in a reactor. Two other capsules are under irradiation and three more capsules are either complete or are in the final stages of construction.

The postirradiation examination of uranium alloy specimens irradiated from 350 to 525 °C at low pressure to 0.4 - 0.5 at.% BU reveals that U + 4 wt% Mo - 0.1 wt% Si is far more resistant to swelling than dilute uranium alloys containing several hundred parts per million of Fe, Al, Si and C. It was further observed that specimens

of U + 4 Mo - 0.1 Si which had been solution treated prior to irradiation were more resistant than were specimens that had been aged. The alloys containing additions of Fe, Al, Si and C are, in turn, more swelling resistant than are alloys containing only additions of Si and C.

Techniques and equipment have been developed for sealing irradiated uranium specimens in a NaK filled capsule for studying the influence of pressure (to 15,000 psi) on the post-irradiation annealing characteristics of uranium. The pressure bonding

autoclave has been put into operating condition and a test with nonirradiated specimens is currently underway at 15,000 psi and 900 °C.

Nonirradiated control specimens of several uranium alloys were annealed in vacuum at 700 °C (beta phase) for

a month with 15 cycles to 500 °C in order to evaluate the tendencies for cracking and carbide dissolution. Preliminary metallographic examination showed no evidence of either cracking or carbide dissolution.

IRRADIATION DAMAGE TO REACTOR METALS

ALLOY SELECTION

Production of a new program material, Incoloy Alloy 800, is completed. The rod and flat stock will be stored at Battelle-Northwest. The tube blanks will be stored at Atomics International.

Six tensile specimens from the GE-San Jose superheat program, irradiated in the EBR-II, show almost no effects of the irradiation on Incoloy 800 (0.17×10^{20} n/cm²) but substantial changes in strength and ductility for Inconel 625 and Hastelloy X ($2.7 - 2.9 \times 10^{20}$ n/cm²).

IRRADIATION FACILITIES OPERATION

A total of 205 specimens was discharged from the ETR at the conclusion of Cycles 86 and 87. The variety of specimens included tensile, double cantilever beam (DCB), thin foils and single crystals, and corrosion blanks.

Tensile data reports have been recorded, processed, and stored in the Radiation Effects on Metals (REM) computer program for 5009 individual tests.

Thermal aging of an inert atmosphere out-of-reactor capsule, GEH-22-3, con-

taining tensile specimens of AISI 304 and 316 SS is in progress.

The results of melting point tests conducted on a series of irradiated Tempil melt pellets show that the pellets are not suitable as thermal monitors in neutron environments.

IRRADIATION DAMAGE TO STAINLESS STEELS

Annealed AISI 304 SS tensile specimens have been irradiated at 650 °C in a NaK environment to an exposure of 3.5×10^{20} fast fluence. It appears that carbide precipitation in these specimens is inhibited by neutron irradiation but that carbides are partly responsible for the loss of high-temperature ductility. An exposure of 6.0×10^{21} fast fluence has been obtained on 304 SS. This is the highest exposure to date obtained in the ETR G-7 hot water loop. These data have been used to test the reliability of predicting tensile properties, in particular uniform elongation, from lower exposures. It has also been illustrated that the data at this exposure provide an important link for the comparison of fast-to-thermal

irradiations. In this regard, it has been shown that the tensile properties of 304 SS converge at 6.0×10^{21} fast fluence for a test temperature of 750 °C. It has also been shown that the nature of the radiation-induced displacement damage at this exposure is probably different from that observed at lower exposures.

IRRADIATION DAMAGE TO NICKEL-BASE ALLOYS

Electron transmission microscopy of a standard solution treated specimen of Hastelloy X-280 that was irradiated at 540 °F (280 °C) to 1×10^{20} nvt (>1 MeV) and annealed at 600 °C for 2 hr showed zones 1-2 μ in width around matrix and grain boundary precipitates that were denuded of cluster defects. This had not been observed in either the as-irradiated condition or after a 500 °C anneal.

Phase analysis of Inconel 600 confirms that more chromium carbides result from the experimental aging treatments than from the standard solution treatment.

Phase analysis of Inconel X-750 was instituted to illuminate mechanisms of ductility improvement.

IRRADIATION DAMAGE TO SINTERED ALUMINUM PRODUCT

A program to determine the effect of irradiation on Sintered Aluminum Products (SAP) has been initiated. Irradiation at high temperature to a fluence of 1×10^{22} ($E > 1$ MeV) are planned. Test material is on hand. Characterization of material has been initiated.

IN-REACTOR MEASUREMENTS OF MECHANICAL PROPERTIES

In-reactor creep tests conducted on annealed 304 SS are showing a greater reduction of rupture life due to irradiation at temperatures above 700 °C than at temperatures below 700 °C.

An in-reactor creep test conducted on Hastelloy X-280 ruptured in a shorter time than predicted from unirradiated data for this alloy.

Specimens of Zr-2.5 wt% Nb pre-crept in-reactor at 350 and 400 °C and then tested in tension showed no appreciable loss of ductility.

DAMAGE MECHANISMS

This investigation of the influence of neutron radiation damage on two purities of alpha iron has shown that:

1. The major effect is an increase in internal stress which is attributed to small defect clusters.
2. Carbon impurity atoms serve as traps for interstitials and nucleate the majority of the clusters.
3. Defects in irradiated iron produce a small change in activation volume that recovers upon annealing at 350 °C. This is a modification of the basic rate controlling process rather than a new rate process.
4. Activation volumes recover with strain, reflecting the interaction between defects and dislocations and the localized nature of the deformation.

A system for measuring the electrical resistivity of materials has been set up and is presently being checked out and evaluated.

HIGH PRESSURE STUDIES

Calibration of the In-Reactor Diamond High Pressure Cell to 50 kbars has demonstrated that the actual pressure on a weak sample surrounded by a strong washer may deviate by a factor of two or more from that predicted by a simple force/area ratio. The proposed fcc-bcc phase transition in NaCl at 17 kbar was not observed which is in accordance with the more recent findings of high pressure scientists.

A description of the out-of-reactor high pressure-temperature equipment is presented. This equipment will be used in pre- or postirradiation studies of nuclear reactor materials.

IN-FLUX OXIDATION AND HYDRIDING OF TITANIUM AND NIOBIUM

Specimens of titanium, niobium, niobium-1% zirconium, and Zircaloy-2 were exposed 37 days in the ETR G-7 loop in pH-10 NH_4OH at 280 °C. Titanium weight gains were lower than Zircaloy-2 weight gains. Niobium weight gains were variable, but were generally considerably higher than Zircaloy-2. Titanium absorbed hydrogen in-flux, while niobium did not.

PRESSURE-VESSEL DOSIMETRY

The possibility of using fission-track detectors as a fluence-monitoring technique for pressure-vessel surveillance is being investigated. Glass, mica, and plastic samples have been irradiated in test facilities in the Hanford K-Reactor to determine the limiting exposure level at which the detectors become useless due to radiation damage. Plastics were found to be unsuitable for use at expected

pressure-vessel fluences. Fast-neutron irradiation damage limited the use of the micas investigated to fluences less than $\sim 5 \times 10^{18} \text{ n/cm}^2$, $E > 1 \text{ MeV}$, (about 10 yr at the surface of a typical pressure vessel). Above this exposure, optical microscopy methods could not be used successfully.

Mica and glass samples were coated with a thin layer of highly depleted uranium and irradiated. This technique appeared an attractive way to monitor fast neutrons and minimize the tracks formed by thermal-neutron-induced fission of ^{235}U . This coating technique yielded satisfactory results only at fluences less than $\sim 10^{15} \text{ n/cm}^2$ ($E > 1 \text{ MeV}$). Therefore, coating fissionable material on mica and glass is not suitable for pressure-vessel applications.

Natural mica is a good candidate for a detector material within its exposure limits. Fission fragments are registered with 100% efficiency in mica, and processing techniques, including etching and data analysis, have been established. However, extension of the fluence range will require a more radiation resistant material. To determine whether the accuracy of the method will meet pressure-vessel requirements, further investigation is required for detector calibration, determination of the reproducibility of the fission tracks, and effects on nonhomogeneous distribution of the uranium in the material.

INTERCALIBRATION TEST ON COUNTING LABORATORIES

An intercalibration test has been initiated among several counting

laboratories in order to insure that experimenters involved in the Irradiation Effects on Reactor Structural Materials Program have comparable fluence determinations.

FAST NEUTRON MECHANISMS

The possible effects of nonideal effusion conditions on expected neutronic-hydrogen concentration profiles in fast reactor core components have been evaluated for endothermically occluding alloys systems. The formation of surface permeation regions with unfavorable hydrogen diffusivity or solubility characteristics can substantially increase the steady-state concentrations calculated for ideal effusion behavior; however, the magnitude of these concentration increments can be readily predicted using simple permeation tests. The maximum neutronic-hydrogen concentrations calculated for the transient period preceding steady-state effusion behavior approximate those for complete hydrogen retention.

EBR-II IRRADIATIONS

Initial tensile testing of specimens of annealed AISI 304 SS irradiated in EBR-II over the temperature range room temperature to 1600 °F (870 °C) has been completed. Results show that radiation hardening persists to temperatures as high as $0.67 T_m$ after fast reactor irradiation to 1.7×10^{22} nvt. This radiation hardening results in high-temperature ductility loss.

Two subassemblies containing AISI 304, 316, 321, and 348 and various nickel-base alloys have been placed in the EBR-II.

LIQUID METAL CAPSULE IRRADIATIONS

Liquid metal capsule GEH-22-3 was discharged during shutdown of ETR Cycle 87 accumulating a total fast fluence of 1.38×10^{21} .

GEH-22-4 began irradiation in Cycle 87. Design modifications have permitted capsule sodium temperatures of 1400 °F (760 °C) at 50-50 gas mixture control.

EXPERIMENTAL TESTING FACILITIES

The building which will house the testing facilities has been improved sufficiently for office spaces and workshop to be occupied. Renovation of the remainder of the building will begin when a project proposal for that purpose receives final approval. Four test stands from the CANEL equipment pool have been overhauled and will be ready for service shortly. The prototype cell for testing irradiated samples in vacuum or controlled atmosphere is in place and nearly complete. The remotely operable test stands which are to be used in this cell are ready for testing under cell conditions with manipulators. The sodium loop which will provide high temperature flowing sodium for the test program will not be shipped until April; delay is because of late delivery of essential parts. The special creep test apparatus to be used in the sodium loop has been designed and a prototype is being made ready for performance tests. The final unit is approximately half the physical size and half the cost of the original working model. The scoping design package of the section of the sodium loop for testing of irradiated samples is nearly

complete. A special dispenser has been designed for dispensing high-purity liquid sodium without contamination to other enclosed containers.

MODEL GAS LOOP

The model gas loop was operated a total of 3110 hr since installation of the new heater; this includes 920 hr this quarter. Exposure of superalloys and refractory metal corrosion specimens at two locations in the loop is continuing. No major maintenance problems were encountered during the quarter.

A study of a method to upgrade the temperature under which the vertical specimens can be evaluated was made.

TEST ASSEMBLY EVALUATION

Exposure of a prototype ATR test assembly in the model gas loop demon-

strated that the present design performs satisfactorily. Surface contamination of Mo, Cr, Mn, Fe, and O was found on the assembly after exposure at 940 °C. Contamination resulted in significant strengthening of Nb and modest strengthening of Ta, but good room temperature ductility was retained.

SUPERALLOY AND REFRACTORY METAL CORROSION STUDIES

The niobium, niobium-1 zirconium, and tantalum corrosion samples exposed to ATR Model Loop "clean run" conditions readily pick up impurities from loop atmospheres pure enough to permit evaporation of superalloys. Molybdenum, TZM, and tungsten samples remain comparatively unaffected. Continued exposure of all samples is planned.

ATR GAS LOOP OPERATION AND MAINTENANCE

Examination of test assemblies and corrosion coupons exposed in the Model Gas Loop show evidence of in-leakage of air even though the gas impurity level was maintained at less than 1.0 ppm total impurities. Tests are planned to determine the source and amount of in-leakage. Studies are also being conducted to develop methods of increasing the temperature of specimens to 2500 °F (1370 °C) which will more closely approximate the temperatures anticipated during ATR operation.

Minor weaknesses in the gas chromatographs are being corrected and work is continuing towards achieving maximum sensitivity and assurance that equipment will measure total impurities in the gas to less than 1 ppm. The gas analysis equipment for measuring dew point in the Transfer Facility was inspected and accepted.

Examination of corrosion coupons after 504 hr exposure in the Model Gas Loop is in progress. Hastelloy X-280 and Haynes 25, which incurred weight

loss, show metal loss from grain boundaries. Niobium and tantalum, which incurred weight gains, show surface contamination. In the case of one niobium sample, the surface con-

tamination layer was shown to be Nb-N_{0.9-0.1}.

Review of vendor data has continued and is currently 60% complete.

METALLIC FUELS

The successful irradiation of three Th-2.5 wt% U-1.0 wt% Zr tubular fuel elements continued in the P-7 pressurized water loop in the ETR. The exposures range from 8400 to 17,700 MWd/ton with corresponding fuel volume increases from 0.9 to 3.1%. This is very nearly the calculated theoretical minimum swelling. An interim report, "Irradiation Behavior of Th-U-Zr Metallic Fuel Elements" being written by J. W. Goffard and R. K. Marshall will describe the status of these elements and the results of the post-irradiation studies conducted on an element removed from test after an exposure of 12,000 MWd/ton.

Twenty-seven hollow core uranium fuel elements 0.45 in. diam by 6.25 in. long and coextrusion clad with Zry-2 have been irradiated in the ETR-M3 loop facility to exposures ranging from 280 MWd/ton to a maximum of 3344 MWd/ton. Maximum core temperatures range from 365 to 540 °C. These fuel elements have 0.025 or 0.050 in. thick Zry-2 cladding and central voids of 5, 10, or 20% of the fuel volume.

Interim examination and measurements made in the ETR basin after each

reactor cycle show that all the fuel elements have an accumulated volume decrease, ranging from 0.1% to a maximum of 1.8%, with most falling between 0.5 and 1.0%. The data thus far indicate there is an exposure threshold at which the decrease in volume stops and begins to reverse that is dependent on the cladding thickness and the initial central void volume in the fuel.

Neutron radiographs obtained on eight elements during an interim examination showed that there has been no measurable decrease in the internal void size at exposures up to 2040 MWd/ton.

Visual examination in the reactor basin indicates that although some warping occurs during the early stages of the irradiation of an element it does not appear to continue indefinitely. The general appearance of the cladding remains good except for two elements. These two showed evidence of accelerated corrosion around the weld and on the end cap at one end. The accelerated corrosion is believed caused by excess Zr-Be braze in the weld and some braze left on the end cap after final machining and cleanup.

NONDESTRUCTIVE TESTING RESEARCH

A study of methods to excite multi-parameter eddy current test coils for the purpose of reducing circuit complexity is underway. An R-L electrical circuit model equivalent to a simple eddy current test was derived. The R-L circuit was converted to its R-C dual which will be used for further study.

An investigation of the relationships between electrical properties and operational characteristics of eddy current coils is being conducted. Probe complex impedance was measured as a function of sample conductivity with operating frequency as an independent parameter. Unique characteristics were noted at, and near, the resonant frequency of the probe.

Improvements were made to a thermal wave transducer system being developed

for measurement of thermal properties of materials. A method is being developed for remotely measuring surface thermal impedance values by measuring temperature transients generated on a sample excited by a pulsed, high-intensity, light source. An electrical circuit equivalent of the relationship between steady state thermal impedance and heat and temperature response transients is being designed.

Fabrication of a manipulator for conducting ultrasonic measurements on neutron irradiated steel samples has been completed. The first group of a series of test specimens has been encapsulated and made ready for an April loading in the Experimental Test Reactor, Arco, Idaho.

FAST REACTOR DOSIMETRY AND DAMAGE ANALYSIS

Potential high-temperature fluence monitors composed of a magnesium oxide carrier doped with 1 wt% of iron, nickel, or cobalt oxides have been fabricated and irradiation tested. The monitor containing cobalt was acceptable with a pellet-to-pellet variation in metal content of <1%. The iron and nickel monitors were not acceptable. Development work is continuing.

Dosimetry experiments have been started in the EBR-II. One-dimensional spectral calculations have been carried out and the response of a variety of threshold and (n, γ) monitors has been determined. Initial results suggest that the monitor materials being studied will allow the monitoring of most of the neutrons that cause materials damage in a fast reactor.

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FAST FUELS OXIDES AND NITRIDES

R. E. Nightingale

SINTERING OF URANIUM-PLUTONIUM
MONONITRIDES

E. T. Weber

Sintering is being used to fabricate UN-20 wt% PuN samples with densities in the range 80-90% TD for use in irradiation testing and property measurements. Preliminary examination of the sinterability of this material under various conditions was completed during this quarter. Current and future work on densification is oriented toward scale-up of the sintering process to moderate fuel production volumes and toward more fundamental studies of the sintering process.

Procedures used in the preparation and processing of material were discussed in a previous report.⁽¹⁾ Figure 3.1 shows the influence of ball-milling time on sintered density (as determined by mercury displacement) and diameter shrinkage. The strong influence of surface area on sinterability is also apparent from microstructures of samples ball-milled for different periods, as shown in Figure 3.2. Alpha autoradiographs of polished sections of the sintered pellets (Figure 3.3) indicated increased homogeneity of plutonium in the nitride for milling times up to 12 hr; longer milling times gave no detectable improvement.

Sintering studies in atmospheres of, (1) a nitrogen partial pressure in argon, (2) nitrogen-hydrogen mixtures, and (3) helium were conducted.

The nitrogen was introduced or removed above 1200 °C to prevent the formation of higher nitrides. Table 3.1 shows the results. Relative to sintering in pure argon, neither a nitrogen partial pressure nor helium yielded a significant improvement; a hydrogen partial pressure had a drastic detrimental effect.

The effect of sintering at 1700 °C versus 1800 °C and for 3 hr versus 6 hr in argon is summarized in Table 3.2. Sintering at 1800 °C for 6 hr resulted in higher densities and larger grain size (Figure 3.2) than the other tests.

X-ray diffraction analysis of all the mixed nitrides sintered at 1700-1800 °C indicated single-phase nitride. No regular variation in width or resolution of high-angle diffractometer peaks was apparent. A Guinier camera pattern of typical sintered material also indicated only single-phase nitride. Analyses were made for U/Pu ratio of samples sintered under the various conditions to check the possibility of selective volatilization of the plutonium. The U/Pu ratios for all samples fell in the range 4.00-4.35, which is approximately the range of uncertainty for the analytical procedures.

The sensitivity of the ball-milled nitride powders to oxygen and water vapor in the atmosphere in which it was handled is shown as weight-gain

curves in Figure 3.4. Ball-milled powders contained in a platinum dish were exposed to the nitrogen atmosphere of the glove box in which the powder was handled and compacted. Water vapor and oxygen levels in the atmosphere ranged from 150 to 400 ppm and from 0.05 to 0.2%, respectively. Weight gain for a sample of PuN crushed to -325 mesh was also documented. The

sudden upturn after 17 days probably represents a period of increased atmospheric impurities. As-synthesized (not ball-milled) PuN and UN exposed to the same atmosphere showed no detectable weight change ($<0.01\%$) over a 20-day period; sintered pellets exposed to the air atmosphere of another glove box for 20 days also showed no detectable weight change.

FIGURE 3.1. Sintered Density and Percent Diameter Shrinkage as a Function of Ball-Milled Time, Showing the Increased Sinterability of Five Powders

a. Ball Milled: 8 hr
Sintered: Ar, 1700°C, 3 hr

b. Ball Milled: 16 hr
Sintered: Ar, 1700 °C, 3 hr

c. Ball Milled: 24 hr
Sintered: Ar, 1700 °C, 3 hr

d. Ball Milled: 24 hr
Sintered: Ar, 1700 °C, 6 hr

*FIGURE 3.2. Etched Microstructures of Sintered UN-20 wt% PuN Illustrating Effect of Milling Time and Sintering Conditions.
Note: Larger Grains are Nitride; Dark Areas are Porosity, Small Bright Particles are Oxide*

a. Hand Crushed to -325 Mesh
Sintered: Ar, 1700 °C, 3 hr

b. Ball Milled: 8 hr
Sintered: Ar, 1700 °C, 3 hr

c. Ball Milled: 24 hr
Sintered: Ar, 1700 °C, 3 hr

FIGURE 3.3. Alpha Autoradiographs of Sintered UN-20 wt% PuN Showing Improved Plutonium Homogeneity Resulting from Ball Milling

TABLE 3.1. Effect of Atmosphere on Sintering of UN-20 wt% PuN

Ball Milling Time	Sintering Temperature, °C	Sintering Atmosphere	Average Diameter Shrinkage	Lattice Parameter (Å)
8	1700	Ar	3.7%	4.893
8	1700	90% Ar + 10% N ₂	3.0%	4.893
12	1700	Ar	5.5%	4.892
12	1700	50% N ₂ + 50% H ₂	2.4%	4.888
16	1700	Ar	5.6%	4.892
16	1700	He	6.0%	4.893

TABLE 3.2. Effect of Time and Temperature on Sintering of UN-20 wt% PuN (Argon Atmosphere)

Ball Milling, Time	Temperature, °C	Sintering Time, hr	Average Diameter Shrinkage, %
24	1700	3	6.0
24	1800	3	6.0
24	1700	6	6.0
24	1800	6	7.4
8	1700	3	3.7
8	1800	3	3.7
8	1800	6	5.3

FIGURE 3.4. Weight Change of Ball-Milled (16 hr) UN-20 wt% PuN and -325 Mesh PuN in an Impure Nitrogen Atmosphere

COMPATIBILITY EXPERIMENTS WITH (U_{0.8}Pu_{0.2})O₂ AND STAINLESS STEEL

J. L. Daniel and M. P. Bauleke

A series of out-of-reactor high-temperature experiments to evaluate hypostoichiometric mixed-oxide fuels, helium, and sodium bonded in stainless-steel cladding was started. The program is comprised of three parts: Preparation of helium and sodium-bonded test capsules, thermal testing, and metallographic and analytical study of the specimens.

Encapsulation methods were developed, and four UO₂-25 wt% PuO₂ capsules were fabricated using the following procedure: (1) the sodium inlet and outlet tubes of the pellet-containing capsules were joined in series; (2) all capsules in the series were evacuated and backfilled with sodium in a single operation at 200 °C; and (3) the sodium-filled capsule "string" was heat-soaked at 425 °C for 3 hr under a back-pressure of helium. The resulting capsules were cooled, cut apart from the "strings", weld-sealed, and enclosed in evacuated sealed tubes for thermal testing (Figure 3.5). Low-temperature testing and metallography development are being conducted on these specimens; subsequent test capsules now in preparation include a sodium expansion plenum to permit thermal testing to 800 °C or higher.

Low-temperature testing is underway, using vertical clamshell furnaces fitted with temperature controllers and over-temperature safety cut-off switches and operable from 100 °C to 1000 °C. Two specimens (O/M's of 1.96 and 2.00 and density of approxi-

mately 86% of theoretical) are undergoing a prolonged period of repeated melting and freezing to determine effects on sodium penetration and pellet stability. The internal pressure is estimated to be over 12,000 psi upon melting of the sodium in the closed capsule.

Metallography on these sodium-bonded fuel capsules will be considerably more informative if conducted with the sodium remaining in situ. Since no metallography methods have been reported in the literature for mixed systems of this type, development of suitable techniques has been undertaken, beginning with two of the first test capsules.

IRRADIATION PERFORMANCE OF UN-20 wt% PuN

J. A. Christensen

Radial plutonium-concentration profiles were measured by isotopic dilution mass spectrometry for UN-20 wt% PuN irradiated to 13×10^{20} fission/cm³ 65 kW/ft. As was observed with similar fuels with lower burnup (2.3×10^{20} fission/cm³),⁽¹⁾ gross plutonium migration occurred during irradiation. Total plutonium concentration varied from 16.9 wt% at the fuel periphery to 14.1 wt% at the mid-radius to 7.6 wt% at the inner surface of the nitride region (about the one-third radius in the fuel cross section). A UO₂-PuO₂ annulus which surrounded a large, central, metal nugget highly enriched in fission-product ruthenium existed within the nitride region. The oxide contained 10.4 wt% plutonium; in the metal nugget, 7 wt% of the uranium plus plutonium was plutonium. Results are shown in Figure 3.6.

FIGURE 3.5. Low Temperature Compatibility Capsules
(Upper: Secondary encapsulation tube; Lower: Four
sodium-bonded UO_2 -25 wt% PuO_2 Capsules, before
secondary encapsulation)

FIGURE 3.6. Plutonium Distribution in UN-20 wt% PuN after 13×10^{20} Fission/cm³ at 65 kW/ft

CERAMOGRAPHY OF PuO₂ AND UN-20 wt% PuN

M. P. Bauleke

A method of chemically etching PuO₂ without heating to show grain structure and etch pits in annealed pneumatically-impacted PuO₂ was developed. The specimen in Figure 3.7 was ground on 240 grit paper and 60 μ diamond wheel and final-polished with 0.3 μ alumina in

CCl on a vibratory polisher. It was etched by immersion in a solution consisting of 40 volumes of HF(52%) and 10 volumes of conc. HNO₃ for 60-90 minutes, depending upon degree of etching required. Residual etchant in the sample and resin mount was neutralized by boiling in dilute NaOH for 1 hr, followed by a distilled water

750X

FIGURE 3.7. Microstructure of Annealed Pneumatically Impacted PuO₂. (Center dark area is a pore. Needle marks coming from pore into and across grains are etching artifacts.)

750X

FIGURE 3.8. Typical Microstructure of Argon Sintered UN-20 wt% PuN. (Dark areas are pores.)

rinse and drying. If the etchant is incompletely neutralized, artifacts are created around pores and the microscope lens will be corroded.

An etching procedure for UN-20 wt% PuN was developed to reduce staining by replacing the final alcohol rinse with a water rinse. The procedure used to give the microstructure shown in Figure 3.8 was:

- Swab etch 60-90 seconds with an etchant made of 80 ml H₂O, 20 ml

HNO₃, 3 drops HF and 0.1 gram cerium nitrate;

- Swab rinse in very dilute ammonium hydroxide;
- Final water rinse and dry.

REFERENCE

1. Quarterly Progress Report, April, May, and June, 1966, BNWL-CC-761, Battelle-Northwest, Richland, Washington.

NUCLEAR CERAMICS

R. E. Nightingale

THERMAL DIFFUSIVITY OF $(\text{Pu}, \text{U})\text{O}_{2+x}$

R. L. Gibby

The thermal diffusivity of $(\text{U}_{0.8}, \text{Pu}_{0.2})\text{O}_{2.00}$ and $(\text{U}_{0.8}, \text{Pu}_{0.2})\text{O}_{1.92}$ was measured to 1200 °C using a laser heat-pulse apparatus.⁽¹⁾ As shown in Figure 4.1, the thermal diffusivity of $(\text{U}_{0.8}, \text{Pu}_{0.2})\text{O}_{1.92}$ was approximately one-half that of $(\text{U}_{0.8}, \text{Pu}_{0.2})\text{O}_{2.00}$ at 100 °C and about two-thirds that of $(\text{U}_{0.8}, \text{Pu}_{0.2})\text{O}_{2.00}$ at 1200 °C. The calculated thermal conductivity for $(\text{U}_{0.8}, \text{Pu}_{0.2})\text{O}_{2.00}$ from 100 to 1200 °C was the same as the measured thermal conductivity for $\text{UO}_{2.00}$ within experimental error.

The samples were prepared as follows: Coprecipitated mixed-oxide powder (UO_2 -20 wt% PuO_2) was densified by pneumatic impaction at 1200 °C and 20,000 atms. Small thermal-diffusivity specimens (0.635 cm dia x 0.05 to 0.08 cm) were sliced from chunks of the impacted material. The as-impacted material was characterized as to impurity content, density, plutonium content, oxygen content and lattice parameter (Table 4.1). The microstructure of the impacted oxide (Figure 4.2) shows a flow pattern produced by the impaction process; however, the grain size of the impacted material is too small to be resolved in the photomicrograph.

Hypostoichiometric oxide was prepared by hydrogen reduction of the densified material at 1500 °C. The

oxygen-to-metal ratio (O/M) was reduced from 2.00 to 1.92 by heating for eight hours in ultra-pure hydrogen. X-ray diffraction studies indicated that the reduced material was single phase with a lattice parameter of 5.4808 ± 0.0002 Å, a value which is significantly higher than that of the stoichiometric oxide (Table 4.1).

During the thermal diffusivity measurements the stoichiometric sample was maintained in a flowing argon - 8% hydrogen atmosphere which had been passed over 0°C water. This atmosphere maintains stoichiometry at temperatures to 1400 °C. The hypostoichiometric sample was heated in a flowing atmosphere of dried argon - 8% hydrogen to prevent re-oxidation. To further assure that the oxygen content of the samples had not changed during a run, thermal diffusivity measurements were taken both during heating and cooling. No changes were observed.

The thermal conductivity of the stoichiometric oxide was calculated using the relationship

$$K = \alpha \rho C_p$$

where α is thermal diffusivity, ρ is density, and C_p is heat capacity. Because heat capacity data are not available for UO_2 - PuO_2 solid solutions, heat capacity were calculated by combining UO_2 ⁽²⁾ and PuO_2 ⁽³⁾ heat capacity data. The calculated values were only slightly

Neg 0670989-4

FIGURE 4.1. Thermal Diffusivity-Temperature Relationship of Pneumatically Impacted $(\text{U}_{0.8}\text{Pu}_{0.2})\text{O}_2 + \text{X}$ for Two Oxygen-to-Metal Ratios (O/M)

TABLE 4.1. Properties of Pneumatically Impacted $(\text{U}_{0.8}\text{Pu}_{0.2})\text{O}_2$

Lattice Parameter (X-Ray Diffraction)		5.4553 $\pm$.0003 Å	
Oxygen-to-Metal Ratio (Thermogravimetric)		2.000	
Weight Percent Plutonium (Isotopic Dilution)		17.6%	
Density (Mercury Displacement at 10 μ)		10.57 g/cm ³	
Percent of Theoretical Density (11.08 g/cm ³)		96%	
Chemical Impurities (Spectrochemical)			
Ag	1 ppm	Mg	<5 ppm
Al	50	Mn	5
As	<20	Mo	20
B	10	Na	5
Bi	<1	Ni	23
Ca	2	P	<5
Cd	<1	Pb	<1
Cr	45	Si	320
Cu	10	Sn	14
Fe	68	Ti	<1
Ge	<10	V	<10
K	20	Zn	20
Li	<5

Neg 46144C

(100X)

FIGURE 4.2. Photomicrograph of Pneumatically Impacted $(U_{0.8}, Pu_{0.2})O_2$

higher than for pure UO_2 ; therefore, UO_2 data could have been used without introducing significant errors. The variation of density with temperature was estimated from thermal expansion data.⁽⁴⁾

The calculated thermal conductivity of $(U_{0.8}, Pu_{0.2})O_{2.00}$ is plotted as a function of temperature in Figure 4.3, the UO_2 data of Godfrey et al.⁽⁵⁾ and the $(U_{0.8}, Pu_{0.2})O_2$ data of Schmidt⁽⁶⁾ and Hetlzer et al.⁽⁷⁾ are shown for comparison. These data are obtained using steady-state methods in contrast to the transient method employed in this investigation. Within experimental error, all of the data are equal.

These experiments indicate that a simple substitution of plutonium for uranium in the UO_2 fluorite lattice has a negligible effect on the thermal conduction of UO_2 ; however, anion vacancies produced by hydrogen reduction of the mixed oxide are effective scattering centers, reducing thermal diffusivity by one-half that of stoichiometric oxide at 100 °C and somewhat less at higher temperatures.

MELTING STUDIES ON PLUTONIUM AND URANIUM-PLUTONIUM NITRIDES

E. T. Weber

The relative stability of compositions in the UN-PN pseudobinary are

Neg 671066

FIGURE 4.3. The Calculated Thermal Conductivity of $(U_{0.8}Pu_{0.2})O_{2.00}$ as a Function of Temperature (Other data shown for comparison)

being studied by determination of dissociation pressures and congruent melting points. A congruent melting point for PuN has not been previously reported. Data obtained apply also to the determination of the U-Pu-N phase diagram and should indicate deviations from ideal mixing which occur in the system.

Samples of PuN were melted under nitrogen pressures from 1 to 70 atmospheres in the temperature range 2500 °C to 2800 °C. The measured congruent melting point for PuN is 2730 ± 30 °C at a nitrogen pressure of 40 atmospheres. At higher nitrogen pressures

the scatter in the data points increases but there is an apparent decrease in melting point. The decomposition pressure for PuN according to the equation $PuN_{(s)} \rightarrow Pu_{(l)} + 1/2 N_{2(g)}$ increases from one atmosphere at 2570 ± 30 °C to 40 atmospheres at the congruent melting point.

These data show a significant deviation from those of Olson and Mulford⁽⁸⁾ for PuN, as shown in Figure 4.4. The curve for Olson and Mulford's equation, $\log P_{N_2} \text{ (atm)} = 8.193 - (29.54 + 10^3)/T + 11.28 + 10^{-18} T^5$, is displaced toward higher temperatures at a given nitrogen pressure; i.e., at 20

FIGURE 4.4. Decomposition and Melting Curves of PuN, $(U_{0.8}, Pu_{0.2})N$, and UN Under Nitrogen

atmospheres the difference in the decomposition temperatures is 50 °C. However, our temperature of 2570 °C at one atmosphere N₂ is in good agreement with their value of 2580 °C at the same pressure. As an additional check on the validity of our measurements, samples of arc-cast UN were melted under nitrogen pressures of 2.5 to 6 atmospheres. The melting temperature of 2860 ± 30 °C obtained for UN is in good agreement with the 2850 ± 30 °C value obtained by Olson and Mulford⁽⁹⁾ and Bugl and Bauer.⁽¹⁰⁾

Dissociation behavior of a sample of sintered (U_{0.8},Pu_{0.2})N was determined and is also shown in Figure 4.4. This material shows stability considerably greater than that of PuN but less than that of UN. However, the decomposition of this material may be influenced by the levels of oxygen and carbon impurities present.

The high-pressure filament furnace used in this work is described in a previous report.⁽¹⁾ Temperatures measured by an optical pyrometer on the edge of the tungsten Vee filament were corrected from a calibration obtained with high purity metal and Al₂O₃ standards. Pressures were measured with a Heise gage. An improvement in observation technique was developed to reduce poor sighting characteristics caused by density currents in high-pressure gases at high temperatures. A system of refractory metal heat shields was designed to limit convection and streaming of high-pressure gas in the sight path. Difficulties in obtaining clear sightings have thus been eliminated to a pressure of at least 70 atmospheres. This improvement may have contributed to the differences

between our data and that of Olson and Mulford at higher pressures.

The PuN used for these experiments was typical metal-hydride-derived nitride obtained from a standard synthesis run; the (U_{0.8},Pu_{0.2})N sample was virtually the same as that used for thermal-diffusivity measurements (Table 4.1 of the Thermal Diffusivity of (U_{0.8},Pu_{0.2})N contribution). Oxygen and carbon analyses of the PuN indicated levels of less than 600 and 300 ppm, respectively. Both X-ray and inert-gas-fusion analyses for oxygen and nitrogen indicated no significant change in the lattice parameter of composition as a result of melting under high-pressure nitrogen.

Ceramographic examination of several partially or fully melted samples revealed small, bright second-phase inclusions distributed within grains and along grain boundaries. Figure 4.5 shows this phase in the microstructure of a congruently melted PuN sample. The second phase was observed in both congruently and incongruently melted materials and may therefore indicate a hypostoichiometric composition range for PuN at high temperatures and over a wide range of nitrogen pressures.

Work is continuing on the decomposition behavior across the UN-PuN pseudobinary and on the examination of the high-temperature composition range in PuN and the mixed nitrides.

Pu-O-N PHASE EQUILIBRIA

C. E. McNeilly

As part of a continuing study to determine solubility limits of oxygen in PuN and UN-PuN solid solutions, PuN samples were synthesized in nitrogen

Neg 4727A

500X

FIGURE 4.5. Photomicrograph of Congruently Melted PuN Showing Precipitated Metallic Second Phase

atmospheres containing 30, 100, and 300 ppm oxygen. Chemical and X-ray diffraction analyses showed that PuO_2 is definitely present in the samples containing 100 and 300 ppm oxygen. However, there appears to be an unexpected difference in lattice parameter of the Pu(N,O) phases in the two samples. Additional PuN samples will be prepared in nitrogen containing 10 and 1000 ppm oxygen.

A series of physical mixtures of 1, 2, 5, 10, 20 and 50% PuO_2 in PuN was prepared, and an empirical calibration curve based on the ratio of intensity of the (111) line for

PuO_2 to that of the (111) line for PuN is being prepared. This curve will serve as a standard for determining the actual amount of PuO_2 phase present in nitride samples containing oxygen. The amount of oxygen in solution in the Pu(N,O) phase can then be determined by subtraction of oxygen present as PuO_2 from the total oxygen content. The amount of dissolved oxygen will then be related to the observed lattice parameter for the Pu(N,O) phase in each sample.

An apparatus to evaporate and condense isothermal sections of the Pu-O-N ternary diagram is essentially

complete. Plutonium will be evaporated from a source located at one corner of an equilateral triangle and oxygen and nitrogen will be metered from the other corners. A platinum foil, which can be resistance heated, is located above the three sources. Control of the temperature of the platinum foil should result in deposition of isothermal sections of the Pu-O-N ternary phase diagram. Vacuums of 1×10^{-7} torr with leak rates of $1 \times 10^{-6} \frac{\text{cc}}{\text{sec}}$ can be routinely obtained in the apparatus. Cerium is being used as a stand-in for plutonium, but efforts to evaporate a Ce-O-N section have failed because of the lack of a suitable container from which to evaporate the cerium. Al_2O_3 , BeO, ThO_2 , graphite, and tantalum have been tried but have not been successful. Evaporation from a tungsten heater will be attempted. If this does not work, the apparatus will be modified to permit electron-beam heating of cerium and Plutonium in a water-cooled crucible.

ELECTRICAL CONDUCTIVITY OF URANIUM DIOXIDE

J. L. Bates

The high-temperature intrinsic electrical conductivity of UO_2 is being studied. The results for single-crystal and polycrystalline UO_2 (11, 12, 13) above 1400 °K were analyzed using a least squares, polynomial equation. The purpose of the present study was to compare the linear first-order equation of $\log \sigma$ versus T^{-1} plots with higher order equations to determine the degree of nonlinearity of the intrinsic conduction.

The intrinsic electrical conductivity of solids can be given by

$$\sigma = n \epsilon \mu \quad (1)$$

where n is the intrinsic carrier concentration, ϵ is the electronic charge and μ is the carrier mobility. The electronic charge is constant. The mobility of an electron or hole does not change significantly above the characteristic temperature. (For UO_2 the characteristic temperature is <300 °K.) The carrier concentration based upon the quantum-mechanical treatment of free-electron carriers in a nondegenerate state can be expressed

$$n = \frac{2(2\pi m^* kT)^{3/2}}{h^3} e^{-E_g/2 kT} \quad (2)$$

where m^* is the effective mass and E_g is the energy difference between the valence and conduction bands. This equation also assumes that $m^* = m_+^* = m_-^*$ and $n = (n_+ n_-)^{1/2}$, i.e., the Fermi level lies exactly between the valence and conduction bands. Thus, the equation for conductivity is given by

$$\sigma = \epsilon \mu \frac{2(2\pi m^* kT)^{3/2}}{h^3} e^{-E_g/2 kT} \quad (3)$$

For temperatures where $kT < E_g$, the exponential term is very much more important than $T^{3/2}$. The equation is then approximated by the familiar form

$$\sigma = \sigma_0 e^{-E_g/2 kT} \quad (4)$$

where σ_0 is a constant and E_g is twice the activation energy, E . By plotting $\log \sigma$ as a function of T^{-1} (Figure 4.6), the activation energy may be obtained from the slope of the straight line.

The least-square curve of $\log \sigma$ versus T^{-1} above 1400 °K was determined

Neg 0670767-1

FIGURE 4.6. Electrical Conductivity of Uranium Dioxide.

for each specimen and for the combined data from the three specimens (Table 4.2). The results show no significant difference in the conductivities of single crystal and polycrystalline UO_2 , nor any difference between the ac and dc data. A reasonable linear fit of the data is obtained with the activation energies varying from 1.14 to 1.21 eV. For all data, the electrical conductivity above 1400 °K can be expressed as

$$\sigma = 3.569 \times 10^3 e^{-1.15/kT} \quad (5)$$

Although a reasonable fit of the data is obtained from a linear equation, statistically a better fit of the data is obtained with a third order polynomial. For all data

$$\ln \sigma = 9.646 - 2.087 \times 10^4 T^{-1} + 1.231 \times 10^7 T^{-2} - 6.484 \times 10^9 T^{-3} \quad (6)$$

These results show that the slope of the $\log \sigma$ versus T^{-1} curve above 1900 °K increases slightly with increasing temperature. A plot of $\frac{d(\ln \sigma)}{d(T^{-1})}$ versus temperature is shown

in Figure 4.7. Above 1900 °K, the slope varies linearly with temperature as

$$\frac{d(\ln \sigma)}{d(T^{-1})} = -10.627 \times 10^3 - 1.4013 T \quad (7)$$

Between 1400 and 1900 °K, $\frac{d(\ln \sigma)}{d(T^{-1})}$ varies only slightly with temperature.

From Equation (3), the temperature dependence of σ above 1900 °K can be expressed as

$$\sigma = \sigma'_0 T^{3/2} e^{-E/2kT} \quad (8)$$

or

$$\ln \sigma = \ln \sigma'_0 + 3/2 \ln T - \frac{E'}{2kT} \quad (9)$$

and differentiation gives,

$$\frac{d(\ln \sigma)}{d(T^{-1})} = \frac{E'}{2k} - \frac{3}{2} T \quad (10)$$

This is the same form as Equation (7) obtained from a plot of the data above 1900 °K (Equation 7) where

$$\sigma = 2.104 \times 10^{-2} T^{1.401} e^{-\frac{0.9157 \text{ eV}}{2kT}} \quad (11)$$

TABLE 4.2. Linear Fit of Electrical Conductivity of UO_2 Above 1400 °K
 $\sigma = \sigma_0 e^{-E/kT}$

Specimen	Data Points	($\text{mho}^\circ/\text{cm}$)	Standard* Deviation	Activation Energy (eV)	Standard* Deviation
MR-5	24	5.240×10^3	0.058×10^3	1.212	0.0068
B-40-A	36	4.1414×10^3	0.0120×10^3	1.168	0.0015
B-38-C	133	3.3703×10^3	0.0200×10^3	1.144	0.0010
All Data	193	3.569×10^3	0.0222×10^3	1.151	0.0006

* 95% Confidence Level.

Neg 0670701-1

FIGURE 4.7. The Temperature Dependence of $d(\ln\sigma)/d(T^{-1})$ for the Intrinsic Electrical Conductivity of UO_2 Above 1400 °K

This would suggest that above 1900 °K, the $T^{3/2}$ term cannot be neglected. At 2000 °K, kT is approximately 0.2 times the activation energy and kT is not $\ll E'$. It is interesting to note that the power of T from the data (1.401) is very close to the theoretical value of 1.5.

The exact meaning of the 0.916 eV for E' is somewhat obscure since it applies only to the data above 1900 °K. It need not agree with the activation energy obtained from the linear curve (1.15 eV) since the activation energy could be a function of temperature without altering the slope of the $\log \sigma$ versus T^{-1} curve, ($E_g = E' + \alpha T$). It can be shown that the α/k term would

become part of the σ_0 term during differentiation.

Although there is a statistical difference between the first and third order relationships for the conductivity, the linear equation is representative of the data within experimental error. It is concluded that until more data are available for many UO_2 specimens, the best expression of conductivity above 1400 °K is

$$\sigma = 3.569 \times 10^3 e^{-1.15/kT} \quad (5)$$

ABSORPTION SPECTRA OF THORIUM DIOXIDE

J. L. Bates

The absorption spectra for single-crystal and polycrystalline ThO_2 were

determined from 0.247 to 13 μm .^(14,1) Complex changes in the ultraviolet and visible spectra resulted when the ThO_2 was heated in hydrogen or air. The absorption in the infrared is the same for both polycrystalline and single-crystal ThO_2 and is independent of the annealing conditions. The characteristic absorption edge is 5.02 eV.

Samples were prepared as follows: Polycrystalline wafers, 0.007 cm thick and 1.27 cm in diameter, were cut from large, high-density compacts prepared by cold pressing and sintering at 1750 °C in commercial hydrogen. Single-crystal specimens, 0.025 to 0.25 cm thick, were cut from crystal boules which had been grown by arc-fusion. The crystals were annealed in hydrogen for eight hours at 1700 °C

and polished on both surfaces. The results of spectrographic analyses of the ThO_2 samples are given in Table 4.3.

The absorption spectra were measured at room temperature using a Cary Model 14 spectrophotometer (0.2 to 2.65 μm) and a Perkin-Elmer Model 521 spectrophotometer (1.5 to 15 μm). No correction was made for reflection.

The absorption spectra for ThO_2 are shown in Figure 4.8. In the infrared region between 2.0 and 13 μm , the spectrum exhibited broad bands at 2.2 μm (0.56 eV), 2.7 μm (0.46 eV), 4.9 μm (0.25 eV), and 8.5 μm (0.15 eV), with an intense band at 9.8 μm (0.13 eV). Another band was resolved at 11.4 μm (0.11 eV) very close to the edge of a large absorption region beginning at 13 μm .

TABLE 4.3. Spectrographic analysis of Thorium Oxide Specimens

Element	Impurities, ppm		Element	Impurities, ppm	
	B-39 (Crystal)	B-16 (Sintered)		B-39 (Crystal)	B-16 (Sintered)
Ag	< 0.2	---	Mn	< 4.0	1.0
Al	5.0	5.0	Mo	< 2.0	---
B	< 0.5	0.1	Na	---	500.0
Be	0.05	---	Ni	2.0	10.0
Bi	---	10.0	Pb	10.0	0.5
Ca	100.0	---	Si	---	< 10.0
Cd	< 10.0	---	Sn	---	< 0.5
Cr	< 1.0	---	Ti	0.2	---
Cu	4.0	0.2	V	< 1.0	---
Fe	5.0	< 50.0	Y	50.0	---
Mg	50	10.0	Zn	< 20.0	---
			Zr	< 1.0	---

Neg 0670701-2

FIGURE 4.8. Absorption Spectra of Thorium Dioxide from 0.247 to 13 μ Showing Variations in Spectra Resulting from Heat Treatment in Hydrogen (1725 °C) and Air (1000 °C)

Complex changes in the absorption spectra at shorter wavelengths for ThO_2 single crystals were observed after heating in hydrogen or air (Figure 4.8). The hydrogen-annealed crystal exhibited two absorption bands at 0.71 μm (1.75 eV) and 0.403 μm

(3.08 eV), with a shoulder on the absorption edge at approximately 0.306 μm (4.05 eV). Annealing in air for 16 hours at 1000 °C altered the color from light blue to light tan. The bands at 0.710 μm and 0.403 μm were removed. However, the absorption increased significantly

near the absorption edge ($0.247 \mu\text{m}$) resulting in an intense band at approximately $0.306 \mu\text{m}$ (4.05 eV). In the infrared region to $2.0 \mu\text{m}$, no changes in the absorption spectra due to annealing in either hydrogen or air were observed. The crystal was annealed an additional 64 hr in air at 1000°C with no further change in the spectra.

The data suggest another band at approximately $0.26 \mu\text{m}$ ($\sim 4.8 \text{ eV}$). However, because of the high optical density near the edge, resolution of this band was difficult and its existence is questionable.

Weinreich and Danforth⁽¹⁵⁾ have also reported complex changes in the absorption spectra of ThO_2 during heating in air and vacuum. Heating in air at 1000°C reddened the crystal, but the color was removed on heating in vacuum at 1000°C . Subsequent heating at 1800°C in vacuum produced a sharp absorption peak at about $0.400 \mu\text{m}$ observed well with the peak at $0.403 \mu\text{m}$ observed in this study. However, Weinreich and Danforth did not observe the peak at $0.71 \mu\text{m}$, and there was a difference in the apparent color of the crystal after heating in air.

The optical energy gap for ThO_2 is 5.02 eV ($0.247 \mu\text{m}$). This energy was the same for both the hydrogen and air-annealed samples. It is significantly greater than the 3.3 eV reported by Vratny and Kikalas⁽⁷⁶⁾ and the 3.9 eV reported by Weinreich and Danforth.⁽¹⁵⁾ The latter authors reported an apparent shift to a lower energy gap when the specimen was heated in vacuum. The formation of an intense band at $0.306 \mu\text{m}$ (0.405 eV) on annealing in air could cause an apparent shift to shorter wave-

lengths if the optical densities of their samples were so high that this band could not be resolved.

THERMAL DIFFUSIVITY OF $(\text{U}_{0.8}\text{Pu}_{0.2})\text{N}$

R. L. Gibby and E. T. Weber

The thermal diffusivity of a sintered UN-20 wt% PuN sample was measured from 105 to 1575°C using a laser heat-pulse apparatus.⁽¹²⁾ As shown in Figure 4.9, the thermal diffusivity increased with temperature from a value of $0.0326 \text{ cm}^2/\text{sec}$ at 195°C to a value of $0.0440 \text{ cm}^2/\text{sec}$ at approximately 1100°C . From 1100°C to the highest measurement temperature, 1575°C , the thermal diffusivity was almost constant. The calculated thermal conductivity increased from $0.0204 \text{ cal/sec/cm/}^\circ\text{C}$ at 195°C to $0.0305 \text{ cal/sec/cm/}^\circ\text{C}$ over the same temperature range.

The mixed nitride was prepared by sintering nitrides which were synthesized from uranium and plutonium metal through the metal-hydride nitride route. The combined UN and PuN were ball milled for 24 hr, pressed into pellets and sintered for six hours at 1700°C in argon. The characteristics of the material are shown in Table 4.4.

The sintered material was determined by X-ray diffraction to be mainly single-phase nitride. The diffraction patterns indicated that the residual oxide phase was composed chiefly of $(\text{U,Pu})\text{O}_2$ with a barely detectable amount of U_3O_8 also present. The oxide phases were concentrated at nitride grain boundaries as shown in Figure 4.10.

The sample was maintained in a flowing atmosphere of dried argon - 8% H_2 during the experiment to prevent oxidation. Measurements were made both during heating and cooling.

FIGURE 4.9. The Thermal Diffusivity of Sintered $(\text{U}_{0.8}\text{Pu}_{0.2})\text{N}$ as a Function of Temperature.

TABLE 4.4. Properties of UN-20 wt% PuN

Lattice Parameter, a_0	$4.894 \pm .001 \text{ \AA}$
Amount of oxide phase present (from X-ray diffraction)	2 to 4%
Density*	
a. Mercury displacement	12.0 g/cm^3 (85% TD)
b. Calculated from size and weight	11.3 g/cm^3 (80% TD)
Chemical Analysis**(1)	
a. Oxygen	$0.28 \pm 0.07\%$
b. Nitrogen	$5.18 \pm 0.25\%$
c. Carbon	$500 \pm 200 \text{ ppm}$
d. U/Pu	4.28 ± 0.20

* Disagreement between densities is due primarily to dimensional irregularities in samples.

** Oxygen and nitrogen content were measured by inert-gas fusion, the analysis being based on a UN standard with a nitrogen content of $5.40 \pm 0.1 \text{ wt\%}$. (17)

750X

(a) Unetched: Bright Solid Areas are Nitride, Light Gray Inclusions are Oxide, Dark Irregular Areas are Porosity

(b) Etched ($\text{HNO}_3\text{-HF-Ce}(\text{NO}_3)_3\text{-H}_2\text{O}$ Etchant): Larger Grains (Gray and White) are Nitride, Small Bright Well-Defined Particles are Oxide, and Dark Areas are Porosity

FIGURE 4.10. Microstructure of Thermal Diffusivity Sample (UPH-13-2)

Thermal conductivity values were determined for each data point using the relationship

$$K = \alpha \rho C_p \quad (1)$$

where α is thermal diffusivity, ρ is density, and C_p is heat capacity. Since heat capacity data for $(\text{U}_{0.8}, \text{Pu}_{0.2})\text{N}$ have not been determined, UN heat capacity data⁽¹⁸⁾ were used in the calculations. A constant density was assumed for all temperatures because thermal-expansion data were also not available. The calculated thermal conductivities

are plotted against temperature in Figure 4.11. The data were also corrected to 100% TD using the relationship⁽¹⁹⁾

$$k_{\text{TD}} = \frac{k_m [1 + P (x - 1)]}{1 - P} \quad (2)$$

where P is porosity, k_m is measured thermal conductivity and x is a constant which varies with porosity. For a porosity of 0.15 (volume fraction), x is equal to 2.9 and Equation (2) reduces to

$$k_{\text{TD}} = 1.51 k_m \quad (3)$$

FIGURE 4.11. The Thermal Conductivity of $(U_{0.8}Pu_{0.2})N$ as Calculated From Thermal-Diffusivity Data (Data also shown corrected to 100% theoretical density)

Figure 4.11 shows thermal conductivity of UN-20 wt% PuN corrected for porosity.

MICROSTRUCTURE OF MIXED OXIDES

J. L. Daniel and S. J. Mayhan

Since mixed UO_2 - PuO_2 fuels are expected to be used in fast-reactor programs, the relationships between microstructure, density, O/M ratio, and preparation history are important factors in fuel design and performance. In the initial phase of a program undertaken to study these relationships, two specimens of low density UO_2 -20 wt% PuO_2 ,* one mechanically mixed and one coprecipitated, were examined by optical

and reflection electron microscopy. Both materials displayed marked porosity and contained a prominent white phase - as plates in the coprecipitated material and as needles in the mechanically-mixed specimen (Figure 4.12). Electron microprobe analysis showed these areas to be primarily uranium. Reflection electron microscopy confirmed these observations (Figure 4.13).

A concentrated effort is underway to develop a routine technique for preparation of thin oxide specimens for transmission electron microscopy. Several specimens have been adequately thinned, but release from the mount and transfer to supporting grids for microscopy have proven troublesome.

* Specimens provided by NUMEC Co.

Coprecipitated

500X

Mechanically Mixed

500X

FIGURE 4.12. Microstructure of UO_2 -
20 wt% PuO_2 (As-polished)

FIGURE 4.13. Reflection Electron Micrographs of UO_2 - 20 wt% PuO_2 (as polished)

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NUCLEAR GRAPHITE

R. E. Nightingale

ELECTRON MICROSCOPY STUDIES

S. S. Jones

A Preliminary examination has been made of the nature of oxidation attack upon TSX and AGOT-LS graphites by the thermal and microwave-excited reactions with oxygen. Both of these nuclear graphites are manufactured from Continental-Lake Charles coke and #30 coal tar pitch binder. They differ principally in the extent of impurities present. TSX has less than 10 ppm total ash, whereas AGOT-LS has 300-400 ppm ash. The higher impurity content of AGOT-LS appears to be due mostly to the presence of vanadium, titanium, molybdenum, calcium, and boron. This phase of the graphite oxidation study is intended to give information about structural changes and impurity behavior during oxidation. In addition to information obtained by examination of the specimen image, the use of selected-area diffraction was found to be helpful in spite of the complexity of the diffraction patterns.

One specimen of each type of graphite used in this study was given as nearly identical treatment as possible in order to compare the effects of a very aggressive and a mild oxidation attack. Initially, the graphites were oxidized with microwave-excited oxygen in the glowing region of the discharge at a pressure of 100-200 microns. After this relatively strong oxidation treat-

ment, the specimens were examined by transmission electron microscopy. They were then given a rather mild oxidation treatment by a five-minute exposure to oxygen at one millimeter pressure and a temperature of about 600-700 °C. Following further microscopic examination, this procedure was repeated to assess the affect of the two types of oxidation treatment.

In both microwave and thermal oxidation, oxygen was flowing over the specimen. The microwave-excited oxygen attacks graphite in a highly unselective manner while the opposite is true of the thermal treatment. Microscopic examination has revealed some striking difference between effects of these treatments of the two graphite types.

Brief mention has been made previously to some of the changes produced in TSX and AGOT-LS by microwave-excited oxygen. One outstanding feature is the production of lace-like networks which may involve carbon suboxide polymers. These networks were present in both types of microwave-oxidized graphite. However, they occurred far more extensively in AGOT-LS than in TSX and are therefore believed to be related to the presence of impurities. In fact, clusters of impurities were often found either within or close to the lace networks. While the identity of the impurities has not been established, they are rather easily observed as almost

opaque structures with distinctive diffraction patterns, in otherwise translucent areas (Figure 5.1).

Another prominent structural feature, observed in both TSX and AGOT-LS after treatment with microwave-excited oxygen, is the presence of many straight edges and sharp angles. Such features were often found in the form of saw-tooth or stair-step arrangements. Although these formations were found more frequently in the TSX specimen than in the AGOT-LS specimen, it is possible that they may have been due to the difference in the specific coke-binder areas which were selected for observation in the two specimens.

The thermal oxidation step which followed the microwave oxidation treatment produced pronounced changes in both TSX and AGOT-LS specimens. A highly selective oxidation attack was observed and the effect greatly increased contrast within the specimens. More translucent-to-transparent areas were produced and translucent areas which were already present before the treatment exhibited much greater structural detail. In the case of the TSX specimen, the thermal treatment tended to eliminate the straight edges and sharp angles produced by the earlier microwave treatment. The translucent areas bounded by these edges and angles now appeared to have characteristic protrusion of the edge planes of layered graphite structures (Figure 5.2). Where the graphite layer planes were perpendicular to the electron beam, there was considerable evidence of selective oxidation, giving numerous hole penetrations of the layers as well as loose graphite flakes.

While the effect of the thermal oxidation of the AGOT-LS specimen was equally pronounced, the changes produced were somewhat different. Fewer graphite edge planes were found exposed than were observed after the same treatment of the TSX specimen. However, this may have been due to the different selections of coke and binder exposed to view in the two specimens. There appeared to be no new lace networks formed by the thermal treatment, but those networks remaining from the microwave oxidation treatment were not entirely removed. Perhaps the most outstanding change produced in AGOT-LS by this treatment was the creation of many translucent-to-transparent areas with various complex structural characteristics (Figure 5.3). It appears that these areas are very thin graphite layers, located approximately perpendicular to the electron beam, with numerous dense structures distributed in various arrangements. The graphite layers were often found to be penetrated by holes of many sizes, sometimes with hexagonal shapes (Figure 5.4). Such pitting effects may be related to impurities present and were not seen so extensively in TSX as in AGOT-LS. Loose graphite flakes were easily seen in both graphite types.

The more dense structures found on the translucent areas in AGOT-LS after the thermal oxidation treatment appear to be of several different types. The most common type seems to be thick pieces of graphite remaining after large sections of many graphite layers have been oxidized. This type of structure was found much more frequently in AGOT-LS than in TSX and may be another

*FIGURE 5.1 Cluster of Impurities in
AGOT-LS Graphite (Magnification -
90,000X)*

*FIGURE 5.2 Exposed Layer Structure of
TSX Graphite Produced by Thermal Oxida-
tion Reaction (Magnification - ~90,000X)*

*FIGURE 5.3 Typical Area in AGOT-LS
Graphite Produced by Thermal Oxidation
Reaction (Magnification - ~45,000X)*

FIGURE 5.4 Typical Pitting of AGOT-LS Graphite Layers by Thermal Oxidation Reaction (Magnification - 84,000X)

feature characteristic of impure graphite. The other dense structures found in AGOT-LS are probably the impurities. They seem to occur in many shapes, sizes, and arrangements. While they were easily seen in the microwave-oxidized specimen before the thermal oxidation treatment, they were seen in greater contrast after the thermal treatment. Structures have been seen which have sharp rectangular profiles, and cubes as well as other assorted polyhedra have been observed (Figure 5.5). The various shapes found may be connected with crystal structures of the impurities present.

The effect of extended thermal oxidation treatment on TSX and AGOT-LS has been investigated briefly. It is conceivable that this treatment might produce more thin areas in the specimens, suitable for further study, than could be made using the microwave oxidation treatment. Preliminary results do indicate that considerably more translucent areas are produced. The usefulness of these new areas can be determined only after further examination. It has been found that as the thermal treatment is extended from five to thirty minutes the fragility of the specimen is increased considerably. While no quantitative estimate can now be made, it appears that the same thermal oxidation treatment causes greater attack on AGOT-LS than on TSX as observed in kinetic studies.

Selective-area electron diffraction continues to be a useful tool in this investigation. Essentially all of the diffraction patterns which have been obtained are too complex to be interpreted theoretically in detail at this

time. However, it is possible to relate some of the patterns to certain typical structures. These relationships are being investigated in an effort to develop more detailed correlation between structure and diffraction pattern. In addition to the spot, circular, and elliptical graphite patterns which have been mentioned earlier, other useful correlations have been found. For example, straight-line patterns have been observed whenever graphite edge planes are viewed parallel to the electron beam. Also, the lace networks found in various graphite specimens give diffuse, broadband, circular diffraction patterns. The presence of impurities appears to be associated with a random spot diffraction having no obvious element of symmetry. The most recent work involving thermal oxidation has uncovered other unknown structures having still different diffraction patterns. Thus, the long-term study of structure-pattern associations appears to be quite worthwhile as an aid in interpreting the complex phenomena involved in this investigation.

GRAPHITE SURFACE-AREA MEASUREMENTS*

R. E. Woodley

The high temperature irradiation of graphite may result in large dimensional changes. To determine if corresponding changes in total surface area occur that might affect the amount of fission products adsorbed or the rate of gas reactions, surface-area-measurements have been performed on several graphite samples which are presently being

* This work was sponsored in part by the Gas Cooled Projects Branch.

FIGURE 5.5 Polyhedral Structures Observed in AGOT-LS Graphite After Thermal Oxidation Treatment
(Magnification - 84,000X)

irradiated in capsule GEH-13-13 in the ETR.

Because these graphite samples are appreciably smaller than the samples normally employed for surface-area measurements (0.25 in. diameter and 1.75 in. long as compared to 0.426 in. diameter and 4 in. long), it was first necessary to determine the precision with which measurements could be performed with the existing equipment. In this apparatus, nitrogen is used as the adsorbate, whereas krypton is ordinarily used as the adsorbate to determine small surface areas. Two separate measurements were performed on a standard-size sample of TSX graphite, which was then machined to the smaller size sample being irradiated, and two additional measurements made. The specific surface areas obtained were 0.476 and 0.480 m²/g on the standard samples and 0.471 and 0.475 m²/g on the small sample, thereby indicating that accurate measurements could be performed on the small samples using nitrogen adsorption. It was, however, necessary to employ appreciably lower relative pressures for the small samples to ensure that the relative pressure at which a monolayer is adsorbed was bracketed. The monolayer volume and hence the specific surface area obtained in this manner are considered to be more precise. The surface-area apparatus has been modified to include the possibility of using krypton as well as nitrogen as the adsorbate. The use of krypton allows the measurement of relatively small surface areas and will permit even more accurate measurements to be performed on the small graphite samples employed in the irra-

diation capsules. Because the vapor pressure of krypton at liquid nitrogen temperature is only about 2.6 mm Hg and krypton pressures during a surface-area measurement may only range up to a few hundred microns, a special means is needed to measure these low pressures accurately without contributing excessive volume to the system. A thermistor sealed into the vacuum line and used as one arm in a Wheatstone bridge circuit is a sensitive pressure-measuring device. Variations in the gas pressure and hence the thermal conductivity of the gas are readily detected by the thermistor with its large negative temperature coefficient of resistance. The bridge circuit is balanced at pressures <10⁻⁵ mm Hg by means of a potentiometer, and higher pressures are then measured as an off-balance of the bridge. The thermistor gauge has been calibrated and it has been found that the response is about 2 mV/micron for pressures less than about 200 microns. The response then decreases gradually with further increase in pressure to a value of about 0.2 mV/micron at 2000 microns. Surface-area measurements are now being made to assess the accuracy and reproducibility of this technique for measuring the surface area of small graphite samples.

A computer program for calculating surface areas from krypton adsorption data, has been written and tested. The program includes the calculation of krypton vapor pressure from nitrogen vapor-pressure data and the correction necessitated by thermal transpiration of krypton.

OXIDATION OF BORONATED GRAPHITE

R. E. Woodley

During the manufacture of the boronated graphite employed as a neutron shield in the Fermi Reactor, the graphite located in the center of the graphitizing furnace acquired a shiny grey appearance, whereas the remainder of the material had the usual dull black coloration characteristic of ordinary nuclear graphite. The differences between these "black" and "grey" boronated graphites is that there is microscopic evidence that the B_4C melted during manufacture of the "grey" material resulting in extensive recrystallization of the graphite. Melting of the B_4C did not occur in the case of the "black" material. In addition, the "black" boronated graphite has a specific surface area about 3 times that of the "grey".

Measurements of the oxidation rate initially performed on the "grey" boronated graphite have now been extended to include the oxidation by 0.5% O_2 in helium of "black" boronated graphite containing nominally 5% boron as B_4C . In general, it has been found that the initial oxidation rate of the "black" material is faster than that of the "grey" material because of the higher surface area. The actual ratio of the rates varies with temperature, however, because the two materials exhibit different activation energies. As previously reported, the activation energy for the "grey" material is about 32 kcal/mole, at temperatures between 580 and 780 °C. At temperatures up to about 680 °C, the activation energy observed for the "black" material is about 38 kcal/mole, the difference be-

ing attributed to the greater ease with which the oxidant can penetrate the "black" boronated graphite.

Three separate series of rate measurements at a temperature of about 730 °C have yielded rates which are greater when calculated from weight measurements than when calculated from the gas flow rate and the concentration of gaseous products, although the reverse should be true because of the formation of B_2O_3 in the sample. By leaching the samples of "black" boronated graphite following their oxidation, only about 1 mg of B_2O_3 is removed compared with 5 to 9 mg removed from the "grey" material. Therefore, the rates as calculated by the two different methods should at least be approximately equal. Because at present no reason for this discrepancy is known, future work will concentrate on this problem.

The removal of the B_2O_3 causes a rate increase in the "black" boronated graphite, but not to the extent observed in the case of the "grey" material. The rate subsequently decreases until it apparently attains a value which it would have obtained had the B_2O_3 not been removed.

The other interesting feature of the oxidation rate at 730 °C is the presence of a small initial hump in the rate-versus-time curves, indicating the occurrence of a fast initial reaction which subsequently decreases and is then overshadowed by the normal rate. It has been found that this hump can be removed by leaching the sample in boiling water before the oxidation test. This treatment results in a weight loss to the sample of only

about 0.1 mg but nevertheless removes the material, perhaps machining dust, which reacts rapidly with oxygen. By graphically integrating the area under the hump to obtain the weight lost by the sample during the fast reaction, a value of very nearly 0.1 mg was found, in excellent agreement with the leaching result.

IRRADIATION OF NUCLEAR GRAPHITE

J. H. Cox, Jr.

Additional data have been obtained on two reactor-grade graphites, CSF and NC-8, at temperatures in the range 400 to 800 °C. At the maximum exposure of 2.4×10^{22} nvt ($E < 0.18$ MeV), NC-8 graphite irradiated at 800 °C displays length changes of +19.8 and -7.5%

in the transverse and parallel directions, respectively. The corresponding volume change is +33%. CSF graphite, at the same temperature and exposure, displays net length changes of +10.1 and -7.8% in the transverse and parallel directions, respectively. The CSF volume change is +11.7%. A photograph of the samples is shown in Figure 5.6.

The contraction rate of both NC-8 and CSF decreased in the parallel orientation for the last exposure, indicating an approach to "turnaround" for the parallel orientation similar to that experienced in the transverse orientation at a lower exposure (see Figure 5.7).

Neg 0670590-1

FIGURE 5.6 Dimensional Changes in Irradiated CSF Graphite

FIGURE 5.7. Dimensional Changes in Irradiated CSF and NC-8 Graphites

NC-8 DIMENSIONAL CHANGE
TRANSVERSE ORIENTATION

NC-8 DIMENSIONAL CHANGE
PARALLEL ORIENTATION

Figure 5.7. (Contd)

The fifteenth capsule in this program, H-3-15, is scheduled for insertion in the GETR during March. Capsule H-3-14 was removed from the reactor prematurely because of an apparent slow water leak. Post-irradiation examination and weight measurements on all samples indicate the capsule was removed before any sample damage had taken place. Only two weeks irradiation time was lost because the GETR was shut down for an extended outage to replace the primary heat exchanger.

IRRADIATION OF "DIMENSIONALLY STABLE" GRAPHITE

J. H. Cox, Jr.

Irradiation tests of dimensionally-stable" graphites have a dual objective:

- obtain engineering data for reactor design; and,
- obtain basic data to determine the variables that influence the dimensional behavior of graphite under irradiation.

The samples are irradiated at various temperatures in the range 600 to 1000 °C. Maximum exposures range to 9×10^{21} nvt ($E > 0.18$ MeV).

Samples of a reactor-grade material, TSGBF, included in this series at 1000 °C are shown in Figure 5.8. These samples experienced an expansion of 34.8% in the transverse orientation and an expansion of 8% in the parallel orientation at 8.7×10^{21} nvt ($E > 0.18$ MeV). The corresponding volume change is +97%. Both orientations went through a linear contraction before "turnaround" and the current expansion.

Two of the improved grades display dimensional stability superior to any

reactor grades at the present exposure level. These are compared to a reactor grade, NC-8, in Figure 5.9. The transverse orientation shows a large improvement and the parallel orientation a slight improvement.

HIGH-TEMPERATURE GRAPHITE IRRADIATIONS IN THE ETR

A. L. Pitner

The high-temperature graphite irradiation in the ETR is progressing satisfactorily and the capsule GEH-13-13 has now completed two cycles of operation. It is scheduled for discharge after two more reactor cycles, with a maximum neutron exposure of 3×10^{21} nvt ($E > 0.18$ MeV).

Five of the twelve thermocouples monitoring capsule temperatures have failed. Of the five stranded W 5% Re - W 26% Re type two have failed, of

FIGURE 5.8 Dimensional Changes in Irradiated TS6BF Graphite

FIGURE 5.9 Dimensional Changes of Improved Graphites

the seven conventional Geminol thermocouples three have failed. All but one thermocouple operated for an entire cycle and established the temperature profile of the capsule. Consequently, temperatures at positions of failed thermocouples can be inferred from the temperatures of operating thermocouples. Sample temperatures for the first two cycles ranged from 800 °C to 1250 °C.

HANFORD GRAPHITE IRRADIATIONS

J. H. Cox, Jr.

Pyrolytic Graphite

Pyrolytic graphites heat-treated at 2200 and 3400 °C have been irradiated in a Hanford Reactor at approximately 600 °C. The 2200 °C material expanded at a rate of 1.62% per 10^{21} nvt ($E > 0.18$ MeV) and contracted at a rate of 0.622% per 10^{21} nvt for the

transverse and parallel orientation respectively, over the exposure range 0.19 to 2.0×10^{21} nvt. The 3400 °C material expanded at a rate of 0.491% per 10^{21} nvt and contracted at a rate of 0.033% per 10^{21} nvt for the transverse and parallel orientations respectively, over the exposure range 0.23 to 0.58×10^{21} nvt. For all materials tested a higher processing temperature resulted in less contraction.

Glassy Carbon

Several samples of glassy carbon pipe and rods, manufactured by Tokai Electrode Mfg. Co., Ltd., have been irradiated to a total exposure of 6.4×10^{20} nvt ($E > 0.18$ MeV) at approximately 600 °C. Samples from all three heat treatments, 1000, 2000, and 3000 °C, exhibit high contraction rates. However, as in conventional nuclear graphites, the contraction rate decreases with an increase in processing temperature. The length-change data are given in the following tabulation:

Radiation-Induced Length Changes of Glassy Carbon

Sample	Process Temperature,	Length change, %	
	<u>°C</u>	<u>Length</u>	<u>Diameter</u>
<u>Pipe</u>			
GC 10	1000	-4.99	-4.32
GC 20	2000	-2.16	-1.99
GC 30	3000	-1.68	-1.58
<u>Rod</u>			
GC 10	1000	-4.45	
GC 20	2000	-2.94	
GC 30	3000	-1.66	

IRRADIATION OF PYROLYTIC AND SINGLE-CRYSTAL GRAPHITE

A. L. Pitner

Irradiations were completed on pyrolytic and single-crystal graphite from Union Carbide Corporation. The irradiations are part of a study to determine the effects of neutron irradiation on the elastic properties of these graphites. All specimens have been returned to UCC for analysis and the exposure calculations for each capsule are being completed.

Of the eight capsules irradiated, four were irradiated in the Hanford Snout Facility at 50 °C to nominal exposures of 2.5, 20, and 50×10^{17} nvt ($E > 0.18$ MeV); three were irradiated in a Hanford test hole at 650 °C to nominal exposures of 3, 5, and 10×10^{19} nvt ($E > 0.18$ MeV); and one capsule was irradiated at 1000 °C in the ETR to an exposure of about 1×10^{20} nvt ($E > 0.18$ MeV).

A report is being prepared describing the irradiation techniques and conditions of each capsule.

STRAIN-TO-FRACTURE

W. C. Morgan

Two parallel samples, one NC-8 and one TSX graphite, have sustained more than 1.1% total strain in the ETR. These samples were irradiated at approximately 900 °C at a strain rate of 0.06% per 10^{20} nvt.

The capsule, GEH-13-60, which was irradiated in the ETR during Cycle 85, suffered three separate mishaps.

- The lead tube was incorrectly bent prior to insertion in the reactor, but was rebent and the capsule installed.
- Midway in the cycle, the gas supply line broke and the capsule was depressurized for about 5 hr.
- During discharge the capsule lead tube became caught on some piping in the discharge canal and broke when excessive force was used to free it.

The break in the lead tube allowed canal water, which was contaminated by a previous rupture of a fuel element containing NaK, to saturate the samples.

Since these samples represented about \$80,000 in irradiation costs, they were returned to PNL, leached in distilled water to remove the contaminants, dried, and remeasured. The samples do not appear to have suffered any appreciable oxidation during the 5 hr when the gas supply was off, nor to have been adversely affected by the other events. Therefore, they will be inserted in future capsules for additional irradiation.

GRAPHITE STRUCTURE

W. C. Morgan

The analysis of thermal expansion and lattice expansion coefficients is continuing and is being extended to temperatures above 1000 °C. A high-temperature furnace has been adapted to obtain thermal expansion data to 2400 °C. The preliminary data indicate an increase in the accommodation coefficients at the higher temperature, thus implying that internal stresses are influencing the thermal expansion coefficients.

THERMOCOUPLE IRRADIATIONS IN EBR-II

A. L. Pitner

Preparations are continuing for the irradiation of thermocouples in EBR-II. Initially, two pins containing 12 thermocouples each will be irradiated to fast exposures of about 3 and 10×10^{21} nvt. The pin loadings are identical, so the results should define the irradiation behavior of each thermocouple type as a function of exposure. Thermocouple types to be included in the first irradiations are chromel-alumel, Geminol, W 5% Re - W 26% Re, W - W 26% Re, and Pt-Pt 10% Rh.

Pre-irradiation calibration of the thermocouples against a Pt-Pt 10% Rh standard is nearly complete. After encapsulation and irradiation, the couples will again be calibrated against a Pt-Pt 10% Rh standard in an NRTS hot cell.

AVERAGING TECHNIQUES IN POLYCRYSTALLINE GRAPHITE

O. D. Slagle

In the previous quarterly report⁽¹⁾ the problems involved in calculating Young's modulus and coefficients of thermal expansion for polycrystalline graphite were described. A modified constant-stress model and a modified constant-strain model were introduced in an attempt to derive a consistent model for polycrystalline graphite. These models, when applied to an isotropic graphite, gave significantly better results than the limiting models of constant stress or constant strain.

A more detailed analysis of these models includes preferential crystallite orientation, assuming a crystallite distribution function as described

previously⁽²⁾. In terms of the acute angle, ϕ , which a crystallite c axis makes with the reference direction, the relative density of crystallites is written as

$$I(\phi) = A + B \cos^6 \phi + C \sin^6 \phi$$

By varying A, B, and C a range of orientations can be studied. The degree of crystallite alignment is denoted by an orientation parameter R which represents the effective fraction of crystallites aligned to contribute their a -axis thermal expansions to the reference direction⁽³⁾.

Values of the thermal expansion coefficients and Young's Moduli for the proposed modified models were found by dividing the crystallite distribution into distinct intervals of crystallite orientation having nearly the same Young's modulus, E, and expansion coefficient, α . Two methods were used. One divided the angle ϕ into N equal intervals and characterized each interval by values of α and E at the midpoint. The alternative method divided the distribution function into N equal intervals of thermal expansion coefficient. Buessem⁽⁴⁾ used this latter method in his analysis of some anisotropic ceramics.

The effect of the method of evaluation on the values of $\bar{E}$ and $\bar{\alpha}$ was determined. In the method of dividing ϕ into N equal intervals, a value of N = 50 was sufficient. However, in the method using equal intervals of α , even for N as large as 200 there was no sign of convergence. Plotting $\bar{E}$ and $\bar{\alpha}$ for N = 50, 100 and 200 versus 1/N, suggested a straight line extrapolation to N = ∞ through the points for 100

and 200. This gives values of $\bar{E}$ and $\bar{\alpha}$ in good agreement with the previous method. To check these results, the two crystallite averaging methods were extended to the constant stress and strain models. Good agreement was found.

Thermal expansion coefficients calculated from the modified models are compared with the experimental values⁽³⁾ and the predicted values of the constant stress model in Figure 5.10. Both of the modified models predict closely the observed deviation from the constant stress value. There is a comparatively larger deviation with increasing R with a maximum deviation in the region of R = 0.8.

Consistent with experimental observations,^(3,5) the modified models predict a thermal expansion coefficient greater than the constant stress model at low values of R. A c-axis accommodation mechanism would have difficulty explaining this negative accommodation. Such a prediction by the modified models reflects the influence of the constant strain approximation. This is in accord with our contention that the constant stress model itself is a poor reference state for predicting the effect of porosity, internal stresses and cracking.

Introducing accommodation lowers the expansion coefficients to give good agreement with the experimental values. As mentioned previously, if accommodation is taken into account, the modified constant stress model is identical to the constant stress model. The modified constant strain model with accommodation nearly fits the experimental curve, and in addition,

FIGURE 5.10 Thermal Expansion Versus Orientation Parameter

the experimental values fall within the limits imposed by the modified models. These limits are considerably narrower than the limits defined by the constant stress and constant strain models.

In Figure 5.11 calculated Young's moduli for the modified models are compared with the experimental values (6,7,8) and the predicted values of the constant stress model. With the introduction of accommodation these models predict the low values of elastic moduli observed. Furthermore, they predict a steeper dependence of Young's moduli on orientation parameter than the constant stress model which is in better

agreement with the experimental data. Young's moduli lie between the values predicted by the constant stress and constant strain models but are lower than the average of the two limiting approximations.

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Young's Modulus Versus Orientation Parameter

FIGURE 5.11 Young's Modulus Versus Orientation Parameter

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BASIC SWELLING STUDIES

R. D. Leggett

When fissionable metals are irradiated, the ordered metallic structure is perturbed in a number of ways. High energy neutrons and fission fragments collide with metal atoms, knocking them out of their structural positions. The resultant defects, vacancies, interstitials, dislocation loops, etc., can adversely affect metallic properties. Similarly, the fission products generated, some of which are noble gases, may be incompatible with the structure and so precipitate or coalesce as second phase inclusions or gas pores. Furthermore, the high localized temperatures associated with the fission event can cause anisotropic fissionable metals such as uranium to drastically change shape in accordance with the crystallography of the specimens.

These effects and their interactions are being studied with regard to the influence of irradiation variables such as the specimen temperature, burnup, burnup rate, and external pressure, and with regard to the influence of metallurgical variables such as composition, structure, and geometry. The data thus far obtained on this program have established that, contrary to previous beliefs, swelling at low burnup in alpha uranium is due to mechanical processes associated with the irradiation "growth" phenomena and with fission event induced defects rather than with

the agglomeration and growth of fission gas pores. This is manifested as a maximum in the swelling-temperature curve in the 400 to 600 °C range. Swelling continues to decrease above 600 °C up to about 700 °C. Above 700 °C, fission gas swelling begins to occur. A few tenths of a percent alloying addition or an applied external pressure have been found to be effective in overcoming this "mechanical" type of swelling. Efforts are continuing to better define the basic mechanisms involved and the inter-relationship between burnup, temperature, pressure and metallurgical state. Fundamental information developed by this program will provide a basis for engineering exploitation of the many beneficial attributes of metal fuels for use in reactor applications.

IRRADIATION PROGRAM

C. R. Hann

The high pressure control system has been installed and tested to meet reactor safety requirements. The system supplies helium gas stored in bottles at 10,000 psi to irradiation capsules controlled at 5,000 psi. This system is controlling our first controlled pressure test at 5,000 psi (capsule P-10) which is operating as designed in a reactor.

The status of capsules on which work is now actively in progress is summarized in Table 6.1.

Each capsule in the series P-10 through P-15 contains twelve specimens as indicated in Table 6.2. Specimens contained in capsules 35, 36 and P-9 are described under "Postirradiation Examination".

Capsule P-16 contains the twelve specimens described in Table 6.3.

Several capsules listed above contain Ni, Fe, Mo, and Re foils; Mo and Re length change rods; and Mo and Fe tensile rods for purposes of another program.

TABLE 6.1 *Capsule Status*

<u>Capsule Number</u>	<u>Control Temperature, °C</u>	<u>Pressure, psi</u>	<u>at.% Burnup (Goal)</u>	<u>Comments</u>
35	525	~30	0.5	Discharged
36	450	~30	0.38	Discharged
P-9	450	1,000	0.5-1.0	Discharged
P-10	450	5,000	0.2-0.8	Under irradiation
P-11	550	5,000	0.2-0.8	Construction complete
P-12	625	5,000	0.2-0.8	Under construction
P-13	700	5,000	0.2-0.8	Under construction
P-14	700	500	0.2-0.8	Ready for charging
P-15	700	1,000	0.2-0.8	Under irradiation
P-16	625	1,000	0.35-0.70	Under irradiation

TABLE 6.2 *Specimen Arrangement*

<u>Specimen Number</u>	<u>Composition (Additions in ppm)</u>	<u>Heat Treatment*</u>	<u>% ²³⁵U</u>
A-1	U+109 Fe-30 Al-36 Si-53C	AE	2.88%
A-2	U+109 Fe-30 Al-36 Si-53C	BQ	2.88%
B-1	U+140 Fe-25 Al-95 Si-400C	AE	0.72%
B-2	U+140 Fe-25 Al-95 Si-400C	BQ	0.72%
C-1	U+64 Fe-<5 Al-25 Si-6C	AE	0.72%
C-2	U+64 Fe-<5 Al-25 Si-6C	BQ	0.72%
D-1	U+407 Fe-645 Al-95 Si-500C	AE	0.72%
D-2	U+407 Fe-645 Al-95 Si-500C	BQ	0.72%
E-1	U+393 Fe-807 Al-32 Si-402C	AE	1.47%
E-2	U+393 Fe-807 Al-32 Si-402C	BQ	1.47%
F-1	U+98 Fe-11 Al-34 Si-56C	AE	1.44%
F-2	U+98 Fe-11 Al-34 Si-56C	BQ	1.44%

* Note: AE: As Extruded
BQ: 730 °C - 15 min - Oil Quench

TABLE 6.3 P-16 Specimens

Specimen Number	Composition (Additions in ppm)	Heat Treatment*	% ^{235}U
A-1	U+98 Fe-11 Al-34 Si-56C	AE	1.44%
A-2	U+98 Fe-11 Al-34 Si-56C	BQ	1.44%
B-1	U+98 Fe-11 Al-34 Si-56C	AE	1.44%
B-2	U+98 Fe-11 Al-34 Si-56C	BQ	1.44%
C-1	U+407 Fe-645 Al-95 Si-500C	AE	0.72%
C-2	U+407 Al-645 Al-95 Si-500C	BQ	0.72%
D-1	U+393 Fe-807 Al-32 Si-402C	AE	1.47%
D-2	U+393 Fe-807 Al-32 Si-402C	BQ	1.47%
E-1	U+407 Fe-645 Al-95 Si-500C	AE	0.72%
E-2	U+407 Fe-645 Al-95 Si-500C	BQ	0.72%
F-1	U+393 Fe-807 Al-32 Si-402C	AE	1.47%
F-2	U+393 Fe-807 Al-32 Si-402C	BQ	1.47%

* Note: AE: As Extruded
BQ: 730 °C - 15 min - Oil Quench

These capsules will provide data to evaluate the effects of temperature (both alpha and beta phase), pressure, burnup, burnup rate, and minor alloying additives on the irradiation behavior of uranium.

POSTIRRADIATION EXAMINATION OF URANIUM AND URANIUM ALLOYS

R. D. Leggett and B. Mastel

Uranium specimens were recovered from capsules P-9 (450 °C, 1000 psi, 1.0% B.U.), 35 (525 °C, 30 psi, 0.5% B.U.) and 36 (450 °C, 30 psi, 0.38% B.U.). The damage sustained by the specimens in P-9 was so extensive that no postirradiation measurements were possible. Figure 6.1 depicts the gross deformation and swelling that occurred in these specimens. In some cases the specimens could not be removed from the holder or the perforated tantalum foil used to position the specimens. The capsule is designed so

that the specimen can increase in volume by 50% before positive contact is made between the sample and the holder and foil. However, the sample can only increase in length or change its shape by about 10% before it becomes physically restrained. It would appear from Figure 6.1 that appreciably more than 50% volume increase occurred in most of the specimens in P-9. "Irradiation growth" caused most of the specimens to buckle after they had elongated sufficiently to be restrained by the holder. This capsule and specimen design are not compatible at this extremely high burnup in this temperature range because of the large changes in shape and dimensions. Hence, future evaluations of the effects of pressure on swelling in this temperature range will be done at lower burnup.

The specimens from capsules 35 and 36 were all successfully recovered and

1.47% ^{235}U
1.0% Burnup
405 °C

U+400Fe-800Al-30Si-400C
As-Extruded
(D-9777)

U+400Fe-800Al-30Si-400C
730 °C-15 min-OQ
(D-9778)

0.72% ^{235}U
0.49% Burnup
420 °C

U+64Fe-5Al-25Si-6C
As-Extruded
(D-9783)

U+54Fe-10Al-34Si-480C
As-Extruded
(D-9784)

1.44% ^{235}U
0.98% Burnup
450 °C

U+98Fe-11Al-34Si-56C
As-Extruded
(D-9787)

U+98Fe-11Al-34Si-56C
730 °C-15min-OQ
(D-9788)

1.47% ^{235}U
1.0% Burnup
445 °C

a) 800 °C-2hr-FC plus
730 °C-15min-OQ
b) 800 °C-2hr-FC

U+400Fe-800Al-30Si-400C
(D-9789)

1 1/2X

FIGURE 6.1. Uranium Specimens Irradiated in Capsule P-9
Controlled at 450 °C and 1000 psi

their immersion densities determined. Selected specimens are being processed through metallography. The optical microscope examinations are essentially complete and the electron microscope examinations are about 10% done. The irradiation conditions and the observed swelling are summarized in Table 6.4. The macro-appearance of the specimens as viewed in two positions are indicated in Figures 6.2 and 6.3. (The missing corners evident in these pictures are identifying notches placed in the specimens prior to irradiation.)

The intent of capsules 35 and 36 was to compare the behavior of several promising alloys irradiated under identical conditions of specimen geometry and reactor environment. Included in these capsules were specimens of high purity, high carbon uranium (U + Fe - Al - Si), a composition commonly referred to as British adjusted uranium; U + Fe - Si alloy already under study in this program; Sicral F-1 (similar in composition to U + Fe - Al - Si); U + 1.1 Mo alloys prepared at the Centre D'Etudes Nucleaires de Saclay, France;* and specimens of U + 4 Mo - 0.1 Si and U + 0.1 Al prepared at Atomics International.**

It is obvious from Table 6.4 and Figures 6.2 and 6.3 that the U + 4 Mo - 0.1 Si alloy specimens were far superior to the other specimens. Only about 2% swelling per at.% burnup was observed in this material at

450 °C and only 5 - 15% per at.% burnup at 525 °C. The specimens that had been solution treated prior to irradiation swelled somewhat less than did the aged specimens. This difference in preirradiation heat treatment resulted in different preirradiation microstructures which persisted during the irradiation.

The U + Fe - Al - Si, Sicral F-1 and U + 1.1 Mo alloy specimens behaved similarly during irradiation. Below 350 °C very little swelling occurred although the specimens became severely distorted. As the irradiation temperature was increased to about 450 °C swelling values ("R") of about 100% per at.% burnup were observed. Above 500 °C the observed swelling decreased to "R" = 35 to 50 reflecting the fact that relative to pure uranium or the U + Fe - Si alloy these materials are resistant to the aligned type of tearing typical of uranium irradiated in the 500 - 600 °C temperature range.

The optical and electron metallographic analyses now being conducted on selected specimens from capsules 35 and 36 will be described next quarter.

HIGH PRESSURE, POSTIRRADIATION ANNEALING

G. L. Kulcinski, C. R. Hann, and R. A. Thiede

The purposes of this study are to determine the effect of hydrostatic pressure on: (1) the swelling behavior of irradiated uranium, (2) the healing of irradiation produced microtears in irradiated uranium and (3) diffusion of fission gases in uranium and Zr-2 cladding.

* Courtesy of Dr. J. Lehman, Centre D'Etudes Nucleaires de Saclay, France.

** Courtesy of Dr. C. Weber, Atomics International

TABLE 6.4 Irradiation Conditions and Swelling in Uranium Specimens Recovered From Capsules 35 and 36

Specimen Number	Material*	Heat Treatment (1)	at.% Burnup	Irradiated Temperature, °C**	Initial Density, ρ_i	As Irradiated Density, ρ_f	% Swelling $\frac{\rho_i - \rho_f}{\rho_f} \times 100$	"R" ***
35 A-1	U+Fe-Si	As Extruded	0.5	470	18.94	9.27	105	210
A-2	HiPHiC	As Extruded	0.5	470	18.95	12.74	49	98
B-1	U+Fe-Al-Si	1000-24h-WQ+525-24h	0.5	510	18.85	16.07	17	35
B-2	U+4Mo-0.1 Si	Aged	0.45	510	18.08	17.00	6.4	14
C-1	U+Fe-Al-Si	1000-24h-WQ+640-4d	0.5	510	18.85	15.64	21	42
C-2	U+4Mo-0.1 Si	Solution Treated	0.45	510	17.89	17.47	2.4	6
D-1	Sicral F-1	720 to 750-WQ+570-1h	0.5	525	18.90	16.30	16	33
D-2	U+1.1Mo	+800 at 20°/min	0.5	525	18.71	14.63	28	56
E-1	U+Fe-Al-Si	730-15m-OQ	0.5	485	18.83	12.37	53	106
E-2	U+0.1Al	Aged	0.5	485	18.81	14.38	31	62
36 A-1	U+Fe-Si	As Extruded	0.38	(275-340)	18.97	16.65	14	37
A-2	HiPHiC	As Extruded	0.38	(275-340)	18.99	17.71	7	19
B-1	U+Fe-Al-Si	730-15mWQ+525-24h	0.38	(350-400)	18.87	16.47	15	39
B-2	Sicral F-1	800-2h-FC+730-15m-OQ	0.38	(350-400)	18.92	17.34	6	16
C-1	U+Fe-Al-Si	1000-24h-WQ+640-4d	0.38	(435-450)	18.87	15.35	23	61
C-2	U+Mo-0.1 Si	Solution Treated	0.34	(435-450)	17.92	17.81	0.6	2
D-1	Sicral F-1	720 to 750-WQ+570-1h	0.38	(430-480)	18.91	14.10	34	91
D-2	U+1.1Mo	+800 at 20°/min	0.38	(430-480)	18.74	13.79	36	96
E-1	U+Fe-Al-Si	730-15 m-OQ	0.38	(400-450)	18.86	14.50	30	80
E-2	U+0.1Al	Aged	0.38	(400-450)	18.85	14.15	33	88

* Addition to Uranium (ppm unless noted)
Compositions (ppm)

U+Fe-Si: 140 Fe - 25 Al - 95 Si - 400 °C

U+Fe-Al-Si: 407 Fe - 645 Al - 85 Si - 500 C

HiPHiC - High Purity, High Carbon: 54 Fe - 10 Al - 34 Si - 480 C

Sicral F-1: 325 Fe - 700 Al - 74 Si - 240 C

U+4Mo-0.1Si: 4 wt% Mo-0.1 wt% Si

U+1.1Mo: 1.1 wt% Mo

U+0.1Al: 0.1 wt% Al

**Low Pressure (~ 30 psi), NaK capsule irradiations.

*** R = $\frac{\% \text{ Swelling}}{\text{at.\% Burnup}}$

(1) Temperatures are in °C, times are in minutes, hours or days.

FIGURE 6.2. Macro-appearance of Uranium Alloy Specimens
Recovered from Capsule 35 (525 °C, 30 psi, 0.5% Burnup)

Side View

End View

A-1 (U+140Fe-25Al-95Si-400C)
As-Extruded
D-9742-9743

A-2 (U+54Fe-10Al-34Si-480C)
As-Extruded
D-9743-9746

B-1 (U+407Fe-645Al-85Si-500C)
730 °C-15min-WQ+525 °C-24hr
D-9748-9749

B-2 (U+325Fe-700Al-74Si-240C)
800 °C-2hr+730 °C-15min-OQ
D-9751-9752

C-1 (U+407Fe-645Al-85Si-500C)
1000 °C-24hr-WQ+640 °C-4day
D-9754-9755

C-2 (U+4wt%Mo-0.1wt%Si)
Solution Treated
D-9757-9758

D-1 (U+325Fe-700Al-74Si-240C)
720-750 °C-WQ+570 °C-1hr
D-9760-9761

D-2 (U+1.1wt%Mo)
↓800 °C at 20°/min
D-9763-9764

E-1 (U+407Fe-645Al-85Si-500C)
730 °C-15min-OQ
D-9766-9767

E-2 (U+0.1wt%Al)
Aged
D-9769-9770

1 1/2X

FIGURE 6.3. Macro-appearance of Uranium Specimens Recovered from Capsule 36 (450 °C, 30 psi, 0.38% Burnup)

High Pressure Autoclave

In the last nine months, the pressure bonding autoclave has been repaired and put into satisfactory operating service. The autoclave is to be used for studying metallurgical changes in uranium at pressures up to 15,000 psi while at 900 °C. The autoclave is a cold wall vessel with an internal 3" x 20" heater. The unit was originally tested at the factory to 15,000 psi and 815 °C. After installation cooling fluid (ethylene glycol and water) leaked into the vessel requiring complete disassembly of the vessel to repair the shorted power electrodes. The moisture in the autoclave plus arcing at the electrodes necessitated extensive cleaning and refinishing of machined sealing surfaces.

The original insulating material between the furnace and the autoclave walls was sand with stainless steel baffles every 2 in. It was decided to replace the sand with "Micro-quartz" because of its superior insulating value. Sand was originally chosen by the manufacturer because it left less void volume to be filled with helium.

Because of the damage to the leads and insulation of the original 4 zone, 10 kW heater, it was decided to use new "Hevi Duty" high temperature heating elements, which were furnished in half cylindrical sections. These were mounted on a furnace liner made of 3-in. tubing with a closed bottom. Because of the location of the leads it was not possible to put the original baffles back in place. This revised heater had a total wattage of about 4 kW. Tests in pressurized helium showed this arrangement had inadequate heating capacity, particu-

larly on the bottom of the three zones, at pressure above 6000 or 7000 psi.

A change was made back to the original 10 kW heater, which was repaired. Baffles were installed every 2 in. and "Micro-quartz" was tamped solidly in between. This heater has been tested up to 15,000 psi at a temperature of 900 °C. Total power to hold temperature is about 2.8 kW. The original power requirement during the factory test was 3.6 kW (with sand insulation). The baffles apparently are more important than the quality of the insulation in high pressure helium.

Difficulty was experienced initially with failure of some of the thermocouples in the 4 kW heater. These thermocouples were standard 1/8 in. O.D. magnesium oxide insulated, stainless steel sheathed swaged thermocouples. Two of eight failed by opening up and at least one other gave doubtful readings. When the 10 kW heater was reassembled, 10 new 1/16 in. O.D. sheathed thermocouples were installed. These thermocouples were made from reactor grade material and fabricated to the same standards as used for in-reactor capsule tests. No failure of these thermocouples has been noted and they all appear to yield fairly consistent readings.

The performance of the autoclave now appears to be completely satisfactory for the study of the effects of pressure on the postirradiation annealing characteristics of irradiated uranium.

Postirradiation Annealing Capsule

Preliminary checkouts of the high pressure equipment, capsule design, sample loading and handling procedures, and NaK filling equipment are complete.

Non-irradiated control specimens of uranium with various metallurgical histories were remotely loaded into the specimen capsule and a cap containing an opening for NaK filling was welded in place. The capsule was then loaded into a lead cask and transferred to an inert atmosphere NaK filling facility. The capsule was filled with eutectic NaK, seal welded and transported to the autoclave facility. The capsule was then removed from the lead cask and placed in the autoclave using procedures designed to give a minimum exposure of radiation to personnel. After sealing the autoclave, the pressure was raised to 15,000 psi and the temperature was increased to 900 °C. A 96 hr test is now in progress.

The techniques and equipment that are employed appear to be satisfactory to handle radioactive specimens provided adequate materials compatibility is found. Of special interest in this test is the compatibility of NaK, U, Ta, 304 SS, and Zry-2 under these severe conditions. The lack of data above 700 °C makes such a test mandatory before radioactive samples are used.

EFFECTS OF PHASE TRANSFORMATIONS

C. R. Hann

Metallography conducted on uranium samples irradiated in the beta phase

(capsule 33 and 34) revealed grain boundary cracking and dissolution of the carbides. Since capsules 33 and 34 were controlled at 700 °C while the reactor was up and at 500 °C while the reactor was down, the grain boundary cracking and carbide dissolution might be due in part or entirely to thermal effects rather than irradiation effects.

Unirradiated control specimens for several alloys (see Table 6.5) have been annealed in vacuum for one month at 700 °C and thermally cycled to 500 °C fifteen times which exceeds the number of in-reactor thermal cycles.

Thermal cycles were made by pushing a tantalum boat containing the samples from a 700 °C zone to a 500 °C zone. The samples were cooled from 700 °C to room temperature by pushing the tantalum boat into a cold zone of the horizontal tube furnace.

Although the specimens were quite oxidized after the one month anneal, very little distortion was observed. The oxide was quite tenacious and required considerable time to remove by electropolishing.

No significant density changes were observed and optical metallography did not reveal any apparent dissolution of carbides or grain boundary cracking. Thus the appearance of these features in the irradiated specimens was not due to thermal effects alone.

TABLE 6.5 Uranium Alloys Annealed One Month at 700 °C.

Sample	Composition ⁽¹⁾	Heat Treatment	Pretest ⁽²⁾ Density g/cm ³	Post test Density g/cm ³
1	U + 64 Fe-<5 Al- 25 Si-6C	As Extruded	19.02 + 0.04 - 0.03	19.01 ± 0.01
2	U + 140 Fe-25 Al- 95 Si-400C	BQ ⁽³⁾ + 640 °C-4 days	18.97 + 0.01 - 0.01	18.98 ± 0.01
3	U + 325 Fe-700 Al- 74 Si-240C	720 to 750 °C-WQ + 570 °C-1 hr	18.91 + 0.01 - 0.01	18.91 ± 0.01
4	U + 393 Fe-807 Al- 32 Si-402C	As Extruded	18.88 + 0.03 - 0.03	18.89 ± 0.01
5	U + 407 Fe-645 Al- 85 Si-500C	BQ ⁽³⁾ + 640 °C-4 days	18.86 + 0.02 - 0.03	18.91 ± 0.01
6	U + 54 Fe-10 Al- 34 Si-480C	As Extruded	18.96 + 0.03 - 0.06	19.00 ± 0.01
7	U + wt% Mo + 0.1 wt% Si ⁽⁵⁾	Aged	18.58 + 0.27 - 0.50	18.16 ± 0.01

(1) Additions in ppm unless noted

(2) Average densities of identical materials with the same or similar heat treatments.

(3) Beta Quench: 730 °C-15 min - Oil Quench

(4) Sample prepared at Saclay, France

(5) Sample prepared at Atomic International Laboratory

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IRRADIATION DAMAGE TO REACTOR METALS

A. L. Bement

ALLOY SELECTION

K. R. Wheeler

The purpose of this program is to study, on a limited basis, materials which are potentially useful for reactor application. From such cursory examination, the more promising alloys can be selected for study in depth. In addition, program alloys are procured, warehoused at BNW, and disbursed to the various sites participating in the Irradiation Effects on Reactor Structural Materials Program.

Production of a new program material Incoloy alloy 800 heat No. HH7531A is completed. The heat, fabricated at Huntington Alloy Products Division of INCO, has the following chemistry:

Element	% Composition	Element	% Composition
C	0.03	Mn	1.05
Fe	46.48	S	0.007
Si	0.26	Cu	0.16
Ni	32.44	Cr	19.25

Element	% Composition	Element	% Composition
Al	0.10	Ti	0.20
Co	0.11	Mo	0.12
P	0.011	B	0.0002

All material passed the acidified copper sulphate test for intergranular attack according to the procedures of ASTM-A-393. Each individual piece was visually surface checked and ultrasonically inspected. The tubing was subjected to a 1000 psi internal hydrostatic test. According to the various methods used for inspection, the material was of good quality. Physical properties reported by Huntington Alloy are given in Table 7.1.

Five additional sheets of Incoloy 800 of this program heat are being cold rolled to 0.083 thickness. After final annealing, this material will be shipped to Battelle-Northwest to complete the order. Material from Heat No. HH7531A was distributed as follows:

Shape	Size (In.)	Quantity (Pcs.)	Location
Sheet	0.109 x 12 x 48	4	Battelle-Northwest
Sheet	0.109 x 12 x 48	1	Atomics International
Plate	1 x 24 x 48	3	Battelle-Northwest
Plate	2.5 x 12 x 48	5	Battelle-Northwest
Rod	0.625 x 60	200	Battelle-Northwest
Tube Blanks	1.5 ODx 0.125 wall	12 (376 lb)	Atomics International
Tube Blanks	1.5 ODx 0.125 wall	6 (187 lb)	Superior Tube

TABLE 7.1. As Fabricated Mechanical Properties of Incoloy 800, Heat No. HH7531A

Shape (Thickness or Dia)	Condition	ASTM Grain Size	0.2 Y.S. psi x 10 ³	U.T.S. psi x 10 ³	% Elong.
Sheet (0.109)	Solution Annealed	5.5	40.0	76.5	43.0
Plate (1.00)	Hot Rolled, Annealed	4.5	35.5	75.5	48.0
Plate (2.50)	Hot Rolled, Annealed	5	29.0*	73.5*	50.0
Rod (0.625 ϕ)	Hot Fin, Annealed	7	33.5	80.0	57.0
Tube Blanks (1.50 OD x 0.125 wall)	Cold Drawn Annealed	4.5	36.0	79.0	44.0

* Specified strength values are 30,000 and 75,000 psi for 0.2% Y.S. and U.T.S., respectively. The low readings for the 2 1/2 in. plate are attributed by Huntington Alloy to the low (0.3% combined Al + Ti content of this heat of material. Standard material combined (Al + Ti) content is ~0.6%.

In keeping with the major function of Alloy Selection, specimens of 10 alloys residual from the GE-San Jose superheat fuel-clad-materials investigations are undergoing tensile properties evaluations at BNW. The following alloys and numbers of specimens are involved: (a) (irradiated in the GETR): 16 Incoloy 825, 16 Incoloy 801, 6 In 102, 10 Inconel 718, 4 Incoloy 804, 10 Hastelloy F, and 4 Rene-62; (b) (irradiated in the EBR II): 2 Incoloy 800, 4 Inconel 625, and 4 Hastelloy-X. A similar group of specimens are being creep tested at GE-NMPO.

Tensile results of specimens irradiated in the EBR-II for 200 hours and tested at 1300 °F (704 °C) at a strain rate of 0.02 in/min are given in Table 7.2

At the level of fast fluence reported by GE for the Incoloy 800, the uniform elongation appears not to be affected by the fast neutron

radiation. Necking strain, however, has been reduced approximately 70% by the irradiation. Much greater reductions in total elongation are observed⁽¹⁾ at fluence levels of 2×10^{21} n/cm², the elongation being of the order of 7%.

Inconel 625 and Hastelloy X are known⁽²⁾ to possess a degree of microstructural instability when aged at elevated temperature. The results of this series of tests conducted at BNW confirm the observations by GE investigators⁽²⁾ that fast neutron spectra cause large reductions in ductility at relatively low fast fluence. The Inconel 625 seems particularly sensitive to elevated temperature aging and to radiation damage. One would expect this, however, from its higher alloying content and the increased number of competing reactions occurring within its structure.

TABLE 7.2. Effect of a Fast Neutron Spectra^(a) ($E > 0.05$ MeV) 200 hr Irradiation on the 1300 °F (704 °C) Tensile Properties of Three Superalloys

Specimen Number	Material	Fluence, n/cm ²	Irradiation Temperature, °F	0.2% YS psi x 1000	UTS psi x 1000	% U.E. ^(b)	% T.E. ^(c)	% R.A. ^(d)
--	Incoloy 800	Control	--	26.7	35.3	11.1	45.5	--
L-6	Incoloy 800	0.17 x 10 ²⁰	<1000	24.6	34.3	12.5	22.6	33.3
L-45	Incoloy 800	0.17 x 10 ²⁰	<1000	22.5	34.5	12.3	26.5*	35.4
--	Inconel 625	Control	1000	58.3	85.0	16.4	20.8	--
V-18	Inconel 625	2.7 x 10 ²⁰	1000	91.9	103.8	3.1	3.6*	19.35
V-29	Inconel 625	2.9 x 10 ²⁰	1000	96.6	105	1.7	2.4*	20.00
--	Hastelloy X	Control	1000	26.3	60	26.4	34.9	--
X-2	Hastelloy X	2.7 x 10 ²⁰	1000	39.3	60.6	10.5	11.7	26.6
X-17	Hastelloy X	2.9 x 10 ²⁰	1000	52.7	69.0	8.34	10.88*	20.0

(a) EBR II, thermal neutron flux negligible

(b) Uniform elongation

(c) Total elongation

(d) Reduction of area

* Fractured at gage length marker

IRRADIATION FACILITIES OPERATION

R. E. Robbins and R. W. Barker

The purpose of this phase of the program is to provide for the timely accomplishment of irradiation, testing, and subsequent processing of the data obtained from a variety of reactor structural materials. Irradiations will be performed in aqueous, gaseous, and molten metal environments. Elevated temperature irradiations and tests will be emphasized. Special testing techniques, applicable to either irradiated or unirradiated specimens, will be developed.

Facilities Operation

The experiments discharged from the various Engineering Test Reactor (ETR) core positions for Cycles 86 and 87 are given in Table 7.3 along with the estimated neutron fluxes and exposures. Several ambient temperature capsules were discharged from core positions in

the ETR at the completion of Cycles 86 and 87.

The operating histories of the ETR and G-7 hot water loop for Cycles 85 and 86 are given in Table 7.4. Loop operation was normal for these cycles. The history for the out-of-reactor loop is given in Table 7.5.

An inert (helium) atmosphere, out-of-reactor capsule has been assembled and charged into its initial thermal cycle. This capsule contains annealed AISI 304 and 316 SS tensile specimens and will duplicate the thermal history of sodium capsule GEH-22-3, which was discharged at the conclusion of ETR Cycle 86 having received an exposure of 1.3×10^{21} fast fluence ($E > 1$ MeV) at a specimen temperature of 1100 °F (593 °C). Temperature of the sodium capsule was monitored at four locations with four Chromel-Alumel thermocouples. The inert atmosphere capsule will be aged

TABLE 7.3. Summary of Experiments Discharged at the Conclusion of ETR Cycles 86 and 87

Experiment Designation	Number of Specimens	Type of Specimens	Estimated Flux, $\text{nv}^{(a)}$	Estimated fluence, n/cm^2 $^{(a)}$
<u>CYCLE 86</u>				
GEH-20-251(b)	6	304 SS Miniature Tensile	6.0×10^{13}	2.0×10^{20}
252(b)	6	304 SS Miniature Tensile	10.6×10^{13}	3.8×10^{20}
253(c)	2	A302-B Steel DCB	7.5×10^{13}	2.7×10^{20}
254(c)	2	A302-B Steel DCB	5.5×10^{13}	2.0×10^{20}
257(b)	6	348 SS Miniature Tensile	10.4×10^{13}	1.9×10^{20}
258(b)	6	348 SS Miniature Tensile	7.5×10^{13}	1.4×10^{20}
GEH-14-677	34	Mo, Ni, Re Crystals and Foil	2.7×10^{12}	2.3×10^{19}
679	15	Fe Crystals and Wire	2.7×10^{12}	2.3×10^{19}
686	4	Fe Crystals and 6 Fe Foil	10.4×10^{13}	2.9×10^{20}
<u>CYCLE 87</u>				
GEH-20-243	36	Zr-2 Corrosion Blanks	10.0×10^{13}	7.2×10^{20}
248	6	Hastelloy-X Tensile	10.0×10^{13}	5.7×10^{20}
250	6	304 SS Tensile	10.0×10^{13}	5.7×10^{20}
260	18	25-20 SS Tensile	$25.0 \times 10^{13(d)}$	$5.0 \times 10^{20(d)}$
261(b)	6	304 SS Miniature Tensile	10.6×10^{13}	1.9×10^{20}
262(b)	6	304 SS Miniature Tensile	6.0×10^{13}	1.1×10^{20}
263	6	Inconel-X Tensile	7.5×10^{13}	1.4×10^{20}
274(c)	2	A542 Steel DCB	7.5×10^{13}	1.3×10^{20}
275(c)	2	A542 Steel DCB	5.5×10^{13}	1.0×10^{20}
GEH-14-684	36	Mo and Re Crystals and Foil	3.6×10^{13}	2.0×10^{20}

(a) Neutrons with energies greater than 1 MeV.

(b) Indicates elevated temperature capsule experiment.

(c) Indicates double length quadrant.

(d) Indicates thermal neutron flux.

NOTE: Total specimens discharged, Cycles 86 and 87 = 205

Total specimens discharged, ETR G-7 Loop, Cycles 86 and 87 = 116

Total specimens discharged, ETR G-7 Loop, to date = 3,124

at 1100 °F (593 °C) through four simulated ETR cycles totaling 99.9 days, as outlined in the following schedule.

ETR Cycle	Effective Days	Number of Mid-Cycle Shutdowns	Total Days
83	26.7	0	26.7
84	22.3	0	49.0
85	29.0	4	69.0
86	30.9	0	99.9

The capsule and specimen array are shown in Figure 7.1.

A series of irradiated Tempil melt pellets has been examined and tested to determine the effect of irradiation on their melting points. The previously observed⁽³⁾ structural instability of the pellets has been attributed to irradiation effects, since pellets exposed to only the thermal environment for long times exhibited no porosity. Examination of pellets irradiated at temperatures

TABLE 7.4. Summary of Operating History for ETR and G-7 Hot Water Loop - ETR Cycles 85 and 86.

<u>Operating History</u>		<u>ETR Cycle Number</u>	
		<u>85</u>	<u>86</u>
1. <u>Reactor History</u>			
Start up ^(a)		11-17-66	12-26-66
End of Cycle		12-15-66	1-30-67
Megawatt Days		3,500	5,403
Effective Days at 175 MW		20.0	30.9
Number of Scrams ^(b)		N.A.	4
Number of Shutdowns		4	1
2. <u>G-7 Hot Water Loop History</u>			
Maximum Temperature		520 °F	540 °F
Effective Days above 200 °F		20.8	31.7
Effective Days at Oper. Temp.		18.7	29.8
Operating Efficiency ^(c)		104%	102.5%
Temperature Efficiency ^(d)		89.7%	93.9%

(a) *Includes flux runs at low power*

(b) *Power drops below half of full power (175 MW) with immediate recovery*

(c) *Effective days of loop operation above 200 °F (95 °C) with respect to effective days of reactor operation at 175 MW.*

(d) *Effective days of loop operation between 500 and 550 °F (260 and 290 °C) with respect to days of operation above 200 °F (95 °C).*

TABLE 7.5. Summary of Operating History and Discharge Schedule for Out-of-Reactor Loop, ETR Cycles 85 and 86

<u>Loop History</u>		<u>Cycle Number</u>	
<u>1. Time at Temperature, hr</u>		<u>85</u>	<u>86</u>
200 °C (392 °F)		32.1	21.0
218 °C (424 °F)		4.0	8.3
246 °C (475 °F)		15.6	17.3
282 °C (540 °F)		<u>448.3</u>	<u>714.2</u>
Total Time, hr		500.0	760.8

2. Specimen Discharge

(None after Cycle 85 or 86)

FIGURE 7.1. View of Capsule and Contents of GEH-22-3 Inert Atmosphere Out-of-Reactor Capsule

above their melting points is hindered due to pellet decomposition. It is extremely difficult to determine whether or not a pellet has melted while in the reactor.

The results of the melting point tests, outlined in Table 7.6, illustrate the variations in melting points between the irradiated and unirradiated pellets. It should be noted that the observed differences are not uniform but depend upon the particular temperature being considered.

The above results indicate that Tempil melt pellets are not suitable as thermal monitors in neutron environments.

Data Processing

Two hundred and twenty-four tensile data reports have been added to the

Radiation Effects on Metals (REM) computer program during the quarter, raising the accumulative total to 5009. Conversion of the program language from FORTRAN II to FORTRAN IV for use with the UNIVAC 1107 is still in progress.

IRRADIATION DAMAGE TO STAINLESS STEELS

R. E. Robins, J. J. Holmes,
J. L. Brimhall, B. Mastel

The purpose of this program is to determine the combined effects of neutron irradiation and environment on stainless steels. Irradiation-induced mechanical property changes will be determined as a function of fast and thermal neutron fluence, temperature and environment of irradiation and postirradiation test temperatures and environments.

TABLE 7.6. Melting Points of Several Irradiated and Unirradiated Tempil Melt Pellets

	Melting Points (°F)	
	Unirradiated	Irradiated
	750	877
	810	877
	920	990
	960	960
	980	1010
		Vendors
		750
		800
		900
		950
		977

Emphasis will be placed on tensile and creep investigations and on studies of the mechanisms of irradiation-induced property changes.

Annealed AISI 304 SS tensile specimens have been irradiated at 650 °C in a NaK environment to an exposure of 3.5×10^{20} fast fluence and tested at temperatures to 750 °C. As shown in Figure 7.2, the effect of increasing test temperature is to reduce the strength and ductility of 304 SS to values below the original room temperature values. At a test temperature of 750 °C, the strengths of the irradiated material approach those of the unirradiated, as-fabricated material; but the irradiated ductilities remain below the unirradiated values. Transmission electron microscopy, shown in Figures 7.3 to 7.6, has been performed on unstressed sections of tensile specimens tested at room temperature, 300, 500, and 750 °C in order to observe any microstructural changes at these temperatures. A fine carbide precipitate, probably an $M_{23}C_6$ type, was observed in the matrix and grain boundaries of specimens tested at room temperature and 300 °C. At 500

and 750 °C test temperatures, carbides about 270 and 700 Å, respectively, in size were found in grain boundaries and associated with dislocations in the matrix. It appears that carbide precipitation could be partly responsible for the loss of ductility at the higher test temperatures. No helium agglomeration could be observed.

The question arises as to why carbides greater than about 300 Å but less than 700 Å in size were not observed in the 304 SS specimen tested at room temperature due to the 650 °C irradiation temperature. It appears that under the conditions described neutron irradiation may be inhibiting carbide precipitation in these specimens. Similar observations have been made by Meakin and Greenfield⁽⁴⁾ for neutron irradiated molybdenum. However, additional investigations will be made in order to clarify this point.

The effect of test temperature on the strength and ductility of annealed AISI 304 SS irradiated at 290 °C is shown in Figure 7.7. These tensile specimens received an exposure of 6.0×10^{21} fast fluence which is the highest obtained to date in the ETR G-7

FIGURE 7.2. The Effect of Test Temperature on the Strength and Ductility of AISI 304 SS Irradiated in the ETR. (Irradiated at 650 °C to 3.51×10^{20} nvt)

*FIGURE 7.3. AISI 304 SS Irradiated
at 650 °C to 3.5×10^{20} Fast Fluence;
Room Temperature Test. (Note: Distance
between markers is 1 μ .)*

FIGURE 7.4. AISI 304 SS Irradiated at 650 °C to 3.5×10^{20} Fast Fluence; 300 °C Test. (Note: Distance between markers is 1 μ .)

*FIGURE 7.5. AISI 304 SS Irradiated
at 650 °C to 3.5×10^{20} Fast Fluence;
500 °C Test. (Note: Distance between
markers is 1 μ .)*

*FIGURE 7.6. AISI 304 SS Irradiated
at 650 °C to 3.5×10^{20} Fast Fluence;
750 °C Test. (Note: Distance between
markers is 1 μ .)*

FIGURE 7.7. The Effect of Test Temperature on the Strength and Ductility of Irradiated AISI 304 SS. (Irradiated at 290 °C to 6.0×10^{21} Fast Fluence)

hot water loop for 304 SS. The tensile data plotted in Figure 7.7 are of significant importance for several reasons. Although the control data are not shown, radiation hardening of the yield stress was observed at test temperatures above one-half of the melting point. Another reason is that a direct comparison of these data with that obtained by extrapolation from lower exposures can be made in order to test the reliability of analytical models of irradiation effects on tensile properties. The data should provide an important link for the comparison of fast-to-

thermal irradiations since exposures of the order of 6.0×10^{21} fast fluence represent relatively short-term irradiations in a fast reactor. A better understanding of the mechanisms of radiation-induced property changes in 304 SS will be obtained by comparing the nature of displacement type damage produced by the 6.0×10^{21} fast fluence exposure with that produced at lower exposures.

One of the significant features about the tensile data obtained for 304 SS at an exposure of 6.0×10^{21} fast fluence is illustrated in Figure 7.8. The uniform ductility follows a

FIGURE 7.8. The Effect of Test Temperature on the Ductility of AISI 304 SS. (Irradiated at 290 °C in the annealed condition, all transverse specimens)

general trend in the development of a recovery peak as the exposure increases to 1.0×10^{21} fast fluence. The ductility recovery peak is probably due to the annealing out of displacement type damage. The ductility behavior at 6.0×10^{21} fast fluence is different from what might be predicted from ductility values at 1.0×10^{21} fast fluence. Probably the most important difference is the removal of the recovery peak in the 400 to 700 °C test temperature range. The behavior of the ductility at this exposure indicates the presence of some type displacement defect, probably different from that responsible for the ductility behavior up to 1.0×10^{21} fast fluence, which is stable at test temperatures above one-half the melting point. This explanation is substantiated by the fact that the yield strength of 304 SS continues to increase with exposure at all temperatures. For example, at 650 °C the yield strengths at 1.0 and 6.0×10^{21} fast fluence are 20,000 and 38,000 psi, respectively. However, transmission electron microscopy will be performed in order to observe the damage state that exists at the higher exposure.

It is interesting to note that the strength and ductility of annealed AISI SS converges at an exposure of 6.0×10^{21} fast fluence as shown in Figures 7.9 and 7.10. These plots were constructed from irradiation data obtained in the ETR and EBR-II for a variety of irradiation temperatures and illustrate the way in which data at 6.0×10^{21} fast fluence can be used to relate fast-to-thermal irradiation studies. It can be seen

that, independent of irradiation temperature, the yield and tensile strengths continue to increase; but the ductility changes very little beyond the exposure of 6.0×10^{21} fast fluence. The increase in strength is probably due to irradiation hardening which suggests the presence of some type of defect, other than the normal defect clusters observed at low exposures and irradiation temperatures below half the melting point, which is stable at the 750 °C test temperature. For exposures less than 6.0×10^{21} fast fluence, the strength of 304 SS is a function only of exposure as long as the irradiation temperature is 290 °C or above. This does not appear to be the case for uniform ductility since only a scatter band could be delineated.

It is worth mentioning that, at test temperatures below 750 °C, the tensile data do not converge at a particular exposure. The reason for this behavior is not clear, but it may be that the unstable form of the displacement damage is not fully annealed out at the lower test temperatures.

IRRADIATION DAMAGE TO NICKEL-BASE ALLOYS

I. S. Levy

The requirements for corrosion resistance and high temperature strength place nickel-base alloys among the more promising materials for advanced nuclear reactor applications. When these alloys are irradiated at service temperatures, however, they generally suffer embrittlement and reduction in rupture life. The purpose of this program is to determine the effect of modified microstructures upon the irradiation

FIGURE 7.9. Strength of Annealed AISI 304 SS at 750 °C.

FIGURE 7.10. Ductility of Annealed AISI 304 SS at 750 °C

stability of nickel-base alloys. These structural modifications are made by preirradiation thermal or thermo-mechanical treatments and are evaluated by tensile and stress-rupture tests and microstructural examinations.

Solid-Solution Hardened Alloys

Hastelloy X-280

Tensile and stress-rupture tests upon specimens irradiated at 540 °F (280 °C) to 1×10^{20} nvt (>1 MeV) have shown that certain experimental preirradiation treatments can improve postirradiation mechanical properties^(5,6). In order to elucidate the mechanisms for these improvements, extensive micro-structural examinations have been undertaken using optical, replica, and transmission microscopy.^(7, 8, 9, 10, 3)

In previous reports, it was shown that tensile strain at 1350 °F (732 °C) produces a uniform dispersion of a very fine (≤ 400 Å) precipitate within the matrix of unirradiated standard solution-treated material.⁽⁹⁾ Irradiation of this solution-treated material at 540 °F (280 °C) to 1×10^{20} nvt (>1 MeV) produced small point defect clusters 60-120 Å in diam. with a density of $\sim 2 \times 10^{16}/\text{cm}^3$.⁽¹⁰⁾ These defects annealed out of the matrix during the pretest soak at 1350 °F (732 °C);⁽⁸⁾ but tensile strain produced a change in the morphology and positioning of the strain-induced precipitate (relative to that observed in the unirradiated material) in that it was now larger, had a different etching character and was concentrated within 1 to 2 μ of grain boundaries.⁽¹⁰⁾

Ductility of the irradiated material was about 1/5 of that of the unirradiated material.

Annealing studies were initiated to investigate the mechanisms, in this standard-treated material, linking cluster defect breakup at high temperature to the resultant heavy precipitation around grain boundaries during tensile testing. Annealing at 935 °F (500 °C) for 2 hours of specimens irradiated at 540 °F (280 °C) produced only a very slight growth of the cluster defects with no change in density. As in the as-irradiated condition, the defects were uniformly dispersed throughout the matrix and around precipitates, twins, and grain boundaries. This quarter, annealing was performed at 1113 °F (600 °C) for 2 hours. An appreciable decrease in cluster density was observed; cluster size increased only slightly. But more significantly, denuding of the defects was observed to have occurred within 1 to 2 μ of precipitate particles in the matrix or in grain boundaries. No denuding occurred at twin boundaries. An example of this effect is shown in Figure 7.11. Since stress fields associated with non-coherency are short range, it is not felt that this is the driving force for the denuding around matrix and grain boundary precipitates. Rather, the driving force is considered to be a chemical gradient caused by the difference between the composition of the precipitates and that of the surrounding matrix and defects. As the annealing temperature is raised sufficiently to allow breakup of the cluster defects, this driving force

1μ

Neg 4667A

15,000X

FIGURE 7.11. Cluster Defect Denuding Around Grain Boundary Precipitates in Irradiated Hastelloy X-280 after 600 C/2 hr anneal.

results in preferential diffusion of the constituent interstitials to these particles. It is now felt, therefore, that the precipitate found around grain boundaries of irradiated standard-treated material strained at 1350 °F (736 °C) can be explained by (1) this driving force for diffusion of irradiation-induced interstitials towards grain boundary precipitates, (2) the addition of excess vacancies due to the breakup of the irradiation defects, and (3) pipe diffusion towards grain boundaries during the tensile straining. This precipitation, nucleating as it does on dislocations piled up at grain boundaries, results in a hardening of the grain boundary area, causing the observed loss of ductility.

Inconel 600

It was previously reported⁽¹⁰⁾ that, for material irradiated at 540 °F (280 °C) to 1×10^{20} nvt (>1 MeV) and tested at 1350 °F (732 °C), improvements in postirradiation tensile ductility could be achieved with no reductions in strength through the use of experimental preirradiation aging treatments. Microstructural examination of unirradiated specimens had suggested a possible mechanism for these improvements, namely, that carbides formed at the grain boundaries during the preirradiation treatment depleted the area adjacent to the boundaries of solid solution hardeners, such as chromium, making that area more ductile and better able to resist crack propagation. Unirradiated ductility data appeared to support this suggestion in that non-uniform elongation increases of up to 300% were observed for some treat-

ments, an effect considered to be a manifestation of a more ductile grain boundary area.⁽³⁾ Phase analyses conducted during the past quarter add further weight to this hypothesis in that while the standard treated material had the M_7C_3 phase (a chromium-rich phase) in only rare amount, the experimental treatments had it in abundant amounts.

Stress-rupture tests at 1350 °F (732 °C) and the 1000 hour rupture stress of 9800 psi were completed during the past quarter on specimens given preirradiation treatments and irradiated at 540 °F (180 °C) to 1×10^{20} nvt (>1 MeV). Preliminary examination of the data indicates that some treatments can improve postirradiation rupture life. The tests on the unirradiated control specimens are in progress.

Precipitation-Hardened Alloys

Inconel X-750

The ductility improvement found for certain experimental treatments after irradiation at 540 °F (280 °C) to 1×10^{20} nvt (>1 MeV) was correlated with microstructural observations using replica microscopy.⁽¹⁰⁾ The correlation was that treatments that had the best postirradiation (and unirradiated) ductility had retained more grain boundary carbides and a larger denuded zone around the grain boundary after tensile testing at 1350 °F (732 °C). Phase analysis was instituted during the past quarter to illuminate this area of investigation.

Stress-rupture tests at 1350 °F (732 °C) and the 1000 hour rupture stress of 37,500 psi were initiated

on specimens irradiated at 540 °F to 1×10^{20} nvt (>1MeV) and their controls during the past quarter.

IRRADIATION DAMAGE TO SINTERED ALUMINUM PRODUCT

A. J. Lovell

A program to determine the effect of irradiation on Sintered Aluminum Products (SAP) is being initiated. The objective of the program is to provide sufficient irradiation effects data to allow an adequate and safe design using SAP in an irradiation environment. The few irradiation program efforts in the past on SAP material have shown, in general, little effect of displacement damage or mechanical properties at relatively low exposures. Some low temperature irradiations have shown slight increases in strength and reduction in ductility over a range of test temperature to 400 °C. Emphasis should now be placed on higher neutron fluences, higher irradiation temperatures and higher test temperatures.

The program has been outlined to provide high temperature irradiations (300 to 450 °C) of SAP to fluence levels of 1×10^{22} ($E \geq 1$ MeV). The primary emphasis is being placed on postirradiation creep-rupture data.

The irradiations will be carried out in the G-7 loop in ETR and in instrumented capsules placed in the ETR core.

The SAP specimens irradiated in the G-7 loop will be placed in helium-filled sheath capsules to protect the SAP from the loop water. The gas gap between the sheath container and the SAP specimen will be made such that the specimens will be heated by gamma heating to 300 and 400 °C during irradiation.

The instrumented capsules being designed by Atomics International will be operated at 455 °C. The temperature will be controlled by the binary gas method.

The irradiations will be conducted under existing irradiation agreements between Battelle-Northwest and Idaho Nuclear Corporation. The shielded capsule will be under GEH-20 and the AI designed instrumented capsules under GEH-14. The irradiations should be initiated by June or July 1967.

The SAP 895 (10.5% Al_2O_3) and SAP 930 (7% Al_2O_2) material to be used on the program is on hand. Characterization of the 0.4 in. diam extruded rod stock is in progress. Included in the characterization will be chemistry, metallography and mechanical properties.

The chemical compositions of the starting powders as reported by Montecalini are given in Table 7.7. The chemical analysis for billets sent to AI from lot 1g and 3g are shown in Table 7.8. Tensile test data on tests ran on billets from lot 1g and 3g at Montecalini are presented in Tables 7.9 and 7.10 for room temperature and 480 °C (900 °F) tests respectively.

TABLE 7.7. Chemical Composition of Starting Powders

Lot	Powders		Al_2O_3 , %	Fe, %	Si, %	Zn, %	C, %
	Batch	Drum					
1-1g	N114	6	10.6	0.046	0.046	0.0053	0.223
3g	N128	26	6.40	0.054	0.04	0.012	0.12

TABLE 7.8. Chemical Analysis of Specimens Sent to AI

Lot	Al ₂ O ₃ , %	Extracted Gas, cm ³ /100 g	N ₂ , ppm	Fe, %	Si, %	Cu, %	Zn, %	Ti, %	C, %
1g	10.70	1.5	340	0.06	0.04	n.d.	0.005	n.d.	0.12
3g	6.45	1.2	200	0.06	0.04	0.001	0.012	0.001	0.10

TABLE 7.9. Mechanical Properties at Room Temperature

Lot	Billet Number	Al ₂ O ₃ Content	UTS psi	YS psi	UE (A ₄) %	Mechanical Properties
3g	603 (rear)	7%	33,140	21,905	20.0	Longitudinal
1g	510 (front)	10%	41,820	30,580	6.4	Transverse

TABLE 7.10. Mechanical Properties at 480 °C

Lot	Billet Number	Al ₂ O ₃ Content	UTS psi	YS psi	UE(A ₄) %	Mechanical Properties
1g	510 (front)	10%	9,100	8,250	3.2	Transverse
3g	603 (rear)	7%	8,820	8,250	3.2	Longitudinal

The chemical and mechanical data from A.I. for the 2 in. billets will be included in a later report when both SAP 895 and SAP 930 data are available.

IN-REACTOR MEASUREMENTS OF MECHANICAL PROPERTIES

E. R. Gilbert

The in-reactor measurements program is intended to determine the effects of irradiation on the mechanical properties of reactor structural materials, to establish property data suitable for design purposes, and to consider mechanisms controlling deformation using irradiation as a tool in identifying mechanisms through its effects on macroscopic deformation. The program currently involves conducting in-reactor creep measurements on

annealed 304 SS, Hastelloy X, heat-treated zirconium-2.5 wt% niobium, and Zircaloy-2. Capsule development is being pursued in order that program capabilities may be extended.

304 Stainless Steel

In-reactor creep tests and corresponding control tests are being continued. The results have indicated little effect of irradiation on minimum creep rate but have revealed large effects on rupture life and total elongation. The reduction of rupture life due to irradiation appears to be more severe above 700 °C than below 700 °C.

Hastelloy X

The first of a series of in-reactor creep tests to be conducted on Hastelloy

X-280 was tested to rupture at 1000 °C. The total elongation was greater than 11 percent as measured by the in-reactor extensometer system, and the rupture life was less than that predicted from unirradiated data for this alloy.

Zr-2.5 wt% Nb

In-reactor and unirradiated control creep tests are being conducted on heat-treated Zr-2.5 wt% Nb in the temperature range of 300 to 400 °C. The heat treatment consists of a 15 min anneal into the alpha and beta region at 870 °C followed by a quench and a 24 hr aging treatment at 500 °C. In order to study the effect of irradiation under stress on ductility, specimens pre-crept in the reactor at 350 and 400 °C were tested in a universal tensile machine. The unirradiated control specimens and the pre-crept specimens had essentially the same total elongation indicating no appreciable loss of ductility.

DAMAGE MECHANISMS

F. A. Smidt, Jr.

The objective of this program is to determine how irradiation produced defects modify the mechanical properties of metals by interacting with moving dislocations.

Radiation Damage in Alpha Iron

Among the more prominent features of radiation damage in metals is the change in mechanical properties. The understanding of these changes is both an important economic problem and an important scientific problem.

This study was directed toward an investigation of the basic dislo-

cation-defect interactions which give rise to the changes in mechanical properties. At the time of initiation of the study, evidence of the presence of defects in irradiated material was available from direct observations by transmission electron microscopy⁽¹¹⁾, Figure 7.12. It was not apparent from this evidence however, just how the defects were modifying the mechanical properties or indeed whether those visible were actually the source of the observed mechanical property changes since iron contains a very low density of visible defects, Figure 7.13.

The techniques of thermally activated flow⁽¹²⁾ showed promise of correlating the observed microscopic defects with the dislocation motion. Studies of irradiated Cu^(13, 14) have shown that marked changes occur in the temperature dependence and strain rate dependence of the flow stress when defects are introduced into the metal. Although there is general agreement as to the role of the defects in modifying the properties there is as yet no consensus as to the specific mechanism involved in the interaction.

The first results on a bcc metal⁽¹⁵⁾ showed no such pronounced changes as those occurring in fcc metals, with only minor changes in activation volume noted around room temperature and negligible changes at lower temperatures.

Materials and Test Procedures

The specimens tested in these experiments were prepared from two lots of iron whose composition is listed in Table 7.11. Ferrovac E is a vacuum melted electrolytic iron and the zone-refined iron is an iron prepared by a

Neg 2207B

75,000X

FIGURE 7.12. Electron Transmission Micrograph of Molybdenum Irradiated to a Fluence of 1×10^{19} ($E > 1$ MeV) and Subsequently Deformed. (Dark areas are high density of clustered defects, light areas correspond to slip systems in molybdenum.)

Neg 4596B

150,000X

FIGURE 7.13. Electron Transmission Micrograph of Iron Irradiated to a Fluence of 9×10^{19} ($E > \text{MeV}$) at 60°C . (Johnson-Matthey high purity iron, C content unknown but believed to be low. Small black dots are defect clusters.)

TABLE 7.11. *Compositions of Materials Studies (Impurity concentrations in ppm)*

	Ferrovac E, Fe	BMI Zone- Refined Fe
C	50	3.3
N	1	< 1
O	200	2.6
Si	200	10
Ni	20	10
Al	--	15

floating zone induction heating operation by Battelle-Columbus. The tensile specimens were machined from 1/8 in. rod with a reduced section of 1 in. and a gage diam of 0.090 in., electropolished, recrystallized at 750 °C for 1 hr, and furnace cooled.

Two types of tests were used to investigate the thermally activated component of the flow stress, a strain-rate change test and a temperature change test. In the strain-rate change tests, the stress increment accompanying a ten-fold increase in strain rate was measured and used in turn to calculate an activation volume. The base strain-rate was $3.33 \times 10^{-5} \text{ sec}^{-1}$ at each temperature tests were performed. Samples tested at cryogenic temperatures were prestrained at room temperature to inhibit twinning at lower temperatures and to start the tests with the same dislocation density and substructure arrangement.

The temperature change tests were used to determine the temperature at which the effective stress became zero (T_c) and the temperature dependence of the flow stress $(\Delta\tau/\Delta T)_\epsilon$. The latter quantity

is used in determining experimental activation enthalpies. In these tests the temperature is decreased in steps of about 10 °C and the increase in flow stress accompanying this change is measured. A cryostat using a spray of liquid nitrogen as coolant was used in these tests. The techniques and apparatus are described in detail elsewhere.⁽¹⁶⁾

Results - Thermally Activated Flow

A change in the mechanism controlling thermally activated flow can be detected by measuring the activation volume at a fixed temperature, $V^* = kT \left[(\partial \ln \dot{\gamma} / \partial \ln \dot{\gamma}_0) / \partial \ln \tau^* \right]_T$. A change in V^* would be indicative of a change in mechanism.

The results of such experiments at 295 °K on unirradiated Ferrovac E, samples irradiated to a fluence of $1.4 \times 10^{18} \text{ n/cm}^2$ and $8.3 \times 10^{19} \text{ n/cm}^2$ ($E > 1 \text{ MeV}$), and a sample irradiated to 8.3×10^{19} and given a postirradiation anneal at 350 °C for 2 hrs are shown in Figure 7.14 as a function of true strain. It should be noted that the values at low strains for the irradiated samples are significantly lower than those for the control sample and that complete recovery results from the anneal at 350 °C. The reproducibility of these measurements of activation volumes is about $\pm 1.0 \times 10^{-22}$ at $30.0 \times 10^{-22} \text{ cm}^3$ and $\pm 0.5 \times 10^{-22}$ at $15.0 \times 10^{-22} \text{ cm}^3$. Various quenching and aging treatments have been performed on the furnace cooled material to ascertain the influence of carbon in solution or in the form of precipitates on the activation volume. A water quench from 800 °C displaced the curve for the control

FIGURE 7.14. Activation Volume Measurements at 295 °K as a Function of Strain for Ferrovac E Fe for the Following Condition (Control sample, after irradiation to a neutron fluence of 1.4×10^{18} ($E > 1 \text{ MeV}$), after irradiation to 8.3×10^{19} , and after irradiation to 8.3×10^{19} and a postirradiation anneal at 350 °C for 2 hrs.)

sample upward by $1.4 \times 10^{-22} \text{ cm}^3$ and an aging treatment of 24 hrs at 300 °C reduced it by $7.2 \times 10^{-22} \text{ cm}^3$, while a 2 hr anneal at 350 °C had no effect on the activation volume. The changes in activation volume produced by irradiation are thus greater than those produced by a redistribution of carbon in the samples and are considered significant although as will be shown later they are not large enough to indicate

a change in the rate controlling mechanism. Measurements at 200 °K show even less change in the activation volume.

Another feature of these results which should be noted is the increase in activation volume toward the values for the control as the sample is deformed. In molybdenum the deformation has been shown to be highly localized (Figure 7.12) with the first dislocations moving through

the lattice clearing a defect free "channel" which gradually widens as the deformation proceeds. If the initial decrease in activation volume is due to the defects introduced by the irradiation, then their removal by interaction with moving dislocations should produce an increase in activation volume, toward the control, as deformation proceeds.

The same trends are seen in activation volume measurements on Battelle zone-refined iron

(Figure 7.15). The change in activation volume of the control sample with strain is believed to be due to a change in the density of mobile dislocations during the deformation. Similar trends are seen in other materials which do not display a drop-in-load yield point such as high purity Mo.⁽¹⁴⁾ Quenching the BMI iron from 800 °C displaced the curve upward by $0.8 \times 10^{-22} \text{ cm}^3$ and aging for 24 hr at 300 °C did not result in any change from

FIGURE 7.15. Activation Volume Measurements at 295 °K as a Function of Strain for BMI Zone-Refined Fe for the Following Condition (Control sample, after irradiation to a neutron fluence of 1.4×10^{18} ($E > 1 \text{ MeV}$), after irradiation to 8.3×10^{19} , and after irradiation to 8.3×10^{19} and a postirradiation anneal at 350 °C for 2 hr).

the control sample. Irradiation in this case also reduced the activation volume slightly; a post-irradiation anneal at 350 °C for 2 hr resulted in recovery. In this case however the 350 °C anneal and strains of 7-10% gave V^* values above the control. It is not evident why recovery should occur.

Another indication of a change in mechanism can be gained from temperature change tests. These tests are used to determine the temperature dependence of the effective stress and accurately determine T_C , the temperature at which thermally activated flow becomes so rapid that it no longer controls the deformation. In Figure 7.16, it is seen that in

FIGURE 7.16. $(\Delta\tau/\Delta T)_\epsilon$ Data from Temperature Change Tests of Ferrovac E Fe Control Samples and Samples Irradiated to a Fluence of 1.4×10^{18} n/cm² ($E > 1$ MeV).

Ferrovac E irradiation decreases the slope slightly and increases T_C about 15°. Because the 8.3×10^{19} fluence samples failed to work harden at temperatures below 0 °C and no useful data was obtained from them.

The temperature change data for BMI iron is shown in Figure 7.17 for the control sample and for the 8.3×10^{19} fluence samples. Previous tests of BMI iron have shown that the deviation of the $\Delta\tau/\Delta T$ versus T plot from a linearity, the solid line in Figure 7.16, at about 225 °K is due to a decrease in τ_i during the temperature change test. The decrease in τ_i is attributed to a re-arrangement of the substructure

FIGURE 7.17. $(\Delta\tau/\Delta T)_\epsilon$ Data from Temperature Change Tests on BMI Zone-Refined Fe Control Samples and Samples Irradiated to a Fluence of 8.3×10^{19} n/cm² ($E > 1$ MeV).

under increasing stresses at low temperatures.⁽¹⁶⁾ It should be noted that irradiation to a higher fluence level not only increases T_c about 5 °K and decreases the slope but it also prevents this substructure re-arrangement. Tests of 1.4×10^{18} n/cm² samples gave the same temperature dependence and T_c but did not inhibit the substructure re-arrangement. The increases in T_c found in these tests are consistent with the decreases observed in activation volume measurements (V^* is inversely proportional to $\tau^*^{1/2}$).

In a previous paper⁽¹⁶⁾ it was shown that thermally activated deformation in iron could be accurately described by the empirical relation $H/H_0 = T/T_c = (1 - \sqrt{\tau^*/\tau_p})$, where H_0 is the activation enthalpy at T_c , and τ_p is the effective stress at 0 °K. This latter quantity can be evaluated from the temperature dependence of the flow stress and is found to be 57 Kg/mm² in the irradiated samples as compared with 63 Kb/mm² in the control samples. An estimate of H_0 in the irradiated samples was made assuming the slope, dH/dT , was the same as for the control samples and with T_c equal to the observed value in the irradiated samples. H_0 for Ferrovac E increased from 0.93 eV to 0.97 eV and for BMI from 1.00 eV to 1.01 eV. A plot of V^* versus τ^* representative of unirradiated Ferrovac E and BMI iron is shown in Figure 7.18; it can be seen that the observed changes in V^* in the irradiated samples actually represent very small changes in τ^* for the thermally activated process. Thus

FIGURE 7.18. Activation Volume-Effective Stress Relationship for Ferrovac E and BMI Zone-Refined Iron as Deduced from Empirical Equations for Thermally Activated Flow.

it is concluded that the changes in these parameters of thermally activated flow are all quite small and represent only a minor modification in the mechanism of dislocation motion. Other investigations of bcc metals vanadium⁽¹⁸⁾, iron⁽¹⁹⁾, and niobium,⁽²⁰⁾ confirm the conclusion that these changes are of a minor nature.

Results - Athermal Stress

The athermal component of the flow stress is a measure of the internal stresses in a metal arising from stress fields with a longer range than those which can be overcome by thermal fluctuations. Among the factors contributing to τ_i are precipitate particles, dislocation networks produced by cold work, and solute atoms. In these experiments

the lower yield stress at 295 °K was used as an index of τ_i . If absolute values of the yield stress were to be quoted for these experiments a τ^* of about 0.2 to 0.5 Kg/mm² should be subtracted from the lower yield stress to give τ_i . As has been shown above irradiation produced a negligible change in the thermally activated flow curves so the increase in lower yield stress is used here as a measure of the increase in τ_i with exposure. The strengthening produced in Ferrovac E and Battelle zone-refined iron at fluences of 1.4×10^{18} and 8.3×10^{19} are shown in Figure 7.19.

The most prominent feature of these results is the much greater hardening at equivalent neutron fluences in the Ferrovac E iron and therefore a greater rate of strengthening with fluence. Because this material has the higher carbon content, it would appear that carbon is playing a role in the strengthening. The yield stress ($\tau = 6/2$) at a fluence of 8.3×10^{19} is double the yield stress in the control samples while for BMI iron it is about 1.5 times the control sample. Grain size does not influence the accumulation of damage at high fluences although at lower fluences large grained material hardens more

FIGURE 7.19. Increase in Lower Yield Stress as a Function of Square Root of Fluence for Ferrovac E and BMI Zone-Refined Irons.

than small grained material.^(21,22) In the experiments reported here the Ferrovac E had a smaller grain size ($\sim 25 \mu$) than the BMI ($\sim 50 \mu$) so this factor is not influencing the trends observed.

Studies of micro-hardness recovery in iron⁽²³⁾ show that the damage anneals over the range 300-500 °C. An investigation of the micro-structural changes accompanying these changes in hardness⁽²⁴⁾ showed that small spot defects 25-50 Å in diam grew and formed prismatic loops at about 350 °C and these loops were stable to at least 500 °C. These loops have been identified as being interstitial in nature.⁽²³⁾

The results of a study of recovery in the samples irradiated in these experiments are summarized in Table 7.12. The first column shows the percentage recovery after a 2 hr anneal at 350 °C in the lower yield stress and the second column shows the percentage recovery in the $\Delta\tau$ used for activation volume measurements. Examining first the recovery in lower yield stress it is noted that both materials showed greater recovery at the lower

fluence and that the BMI iron showed greater recovery at both fluence values.

It is difficult to compare the rate sensitive stress for the two materials because the BMI iron did not return to the value for the control sample after annealing. It should be noted however that both the Ferrovac E and BMI showed greater recovery in τ^* at the higher fluence which is just the reverse of the behavior of τ_i .

Discussion

A satisfactory explanation of the influence of radiation damage on the mechanical properties of iron must consider (a) the role of carbon, (b) a strengthening mechanism taking into account the defects visible by electron microscopy, and (c) the observed changes in the thermally activated flow stress.

The mobilities of interstitial atoms, vacancies, and carbon atoms were considered and their relative importance during irradiation and annealing is summarized in Table 7.13. The jump frequencies for interstitials and vacancies were estimated from the equation $\Gamma = z \nu \exp$

TABLE 7.12. Recovery of Irradiation Produced Changes by a 2 hr Anneal at 350 °C

<u>Material</u>	<u>$\Delta\tau$ (LYS)</u>	<u>$\Delta\tau$ ($\dot{\epsilon}$ Change)</u>
Ferrovac E - 1.4×10^{18} nvt	92%	80%
Zone-Refined - 1.4×10^{18} nvt	100%	130%
Ferrovac E - 8.3×10^{19} nvt	18%	100%
Zone-Refined - 8.3×10^{19} nvt	47%	175%

TABLE 7.13. Defect Migration in Iron

Defect	Irradiation		Defect Spacing ($\text{\AA}$)	2 hr Anneal 350 °C	
	$\Gamma_{60} \text{ } ^\circ\text{C}$ (sec^{-1})	$\bar{X}(\text{\AA})$		$\Gamma_{350} \text{ } ^\circ\text{C}$ (sec^{-1})	$\bar{X}(\text{\AA})$
Interstitial	7.2×10^8	4900	1000 $\text{\AA}$	1.7×10^{12}	2.8×10^8
Vacancy	7.5×10^3	16	1000 $\text{\AA}$	2.7×10^8	3.4×10^6
Carbon Atom	10		40-80	1.7×10^7	8.9×10^3

Assume: $E_{m,i} = 0.33 \text{ eV}$, $E_{m,v} = 0.68 \text{ eV}$, $E_{m,c} = 0.87 \text{ eV}$.

$\phi = 3 \times 10^{13} \text{ cm}^{-2} \text{ sec}^{-1}$, $c = 5\text{-}50 \text{ ppm}$

$(-E_m/kT)$, where z is the coordination number, ν is the atomic vibration frequency ($\sim 10^{13}$), and E_m is the migration energy. The values of 0.33 eV and 0.68 eV for migration energies were taken from the work of R. A. Johnson.⁽²⁵⁾ The results for carbon were obtained from $\Gamma = 6D/b^2$ where D was given by $D = 0.020 \exp(-0.87/kT)$ ⁽²⁶⁾ and b is the nearest neighbor distance.

An estimate of the annihilation distances during irradiation was made by using the results of Wechsler's calculations⁽²⁷⁾ for displacement production in iron (assumed thermal flux of $3 \times 10^{13} \text{ n/cm}^2/\text{sec}$) and fusing the calculated jump frequencies. An equilibrium concentration during irradiation of about 10^{-8} is obtained for vacancies and interstitials. This obviously is an oversimplification which neglects trapping or losses to sinks other than annihilation but should be adequate for the intended plausibility arguments.

Since the interstitial has the highest jump rate it will control the

mean lifetime of both vacancies and interstitials. If the concentration of vacancies is c and the interstitial jump rate is Γ_i , then the mean lifetime of either defect will be about $1/2(c \Gamma_i)^{-1}$. The random walk migration distance is approximately $\bar{X} = \sqrt{6 D t}$. Substituting $D \approx 1/6 \Gamma b^2$ and the mean lifetime into the above relationship gives $\bar{X} \approx 0.2 b c^{-1/2}$ for the annihilation distance for interstitials and $\bar{x}_v \approx 0.2 b c^{-1/2} (\Gamma_v/\Gamma_i)$ for vacancies.

The annihilation distances of 4900 $\text{\AA}$ and 16 $\text{\AA}$ for the interstitial and vacancy should be compared with the 40-80 $\text{\AA}$ separation of carbon atoms (for 5 and 50 ppm C, all in solution.) It is obvious that during irradiation at 60 °C the interstitial is much more likely to reach a carbon atom than a vacancy. The binding energy of a C atom to a split-interstitial is $\sim 0.5 \text{ eV}$ and to a vacancy 0.4 eV⁽²⁸⁾, so the interstitial should be the species trapped. Carbon motion can be ignored since equilibrium in the

annihilation process is reached in a few seconds.

The last two columns of Table 7.13 show the jump frequencies and migration distances for a 2 hr anneal at 350 °C. It is readily apparent that neither free interstitials or free vacancies would be present in the sample at these temperatures. Accordingly any recovery taking place at this temperature must be due to the breakup of more complex defects. Some clustered defects undoubtedly form by the spike overlap process observed by Beeler in computer experiments⁽²⁹⁾ but if this were the only process for complex cluster formation it would result in equal hardening in both materials. This is not the case.

On the basis of the kinetics of defect migration and the observation of interstitial loops it is concluded that interstitial clusters are nucleated at C atoms and grow during the irradiation. This differs from the scheme set forth by Damask and co-workers⁽³⁰⁾ in their study of radiation damage in high carbon iron. They proposed that the major reaction was the trapping of C atoms by vacancies. At the time of their work the existence of interstitial loops stable to 500 °C was unknown and the presence of these defects was not considered.

The identification of the defects or defect complexes causing hardening is essential to the formulation of a hardening mechanism. At this time the identification has not been satisfactorily completed. Among the pertinent observations are the

facts that hardening is observed at low fluences before defects become visible in the electron microscope ($d < 25 \text{ \AA}$) the lack of recovery below 300 °C, and the presence of prismatic loops at 500 °C after recovery of the hardness is essentially complete.

Defects smaller than 25 Å could include point defects, clusters, and loops. Extensive quenching experiments on the fcc metals have shown that individual vacancies do not contribute to the hardening.⁽³¹⁾ Recent experiments by Ono⁽³²⁾ show that free interstitials can contribute to the hardening. As shown previously their high mobility in iron at the irradiation temperature and the absence of recovery below 300 °C should rule them out as a source of hardening. The recovery in hardness prior to the disappearance of large loops also rules these species out as major sources of hardening. Thus clusters or small loops, most likely of interstitials, are the most likely source of hardening.

Kimura and Maddin^(31, 33) have reviewed possible mechanisms for hardening from loops in quenched fcc metals. Kroupa and Hirsch⁽³⁴⁾, Friedel⁽³⁵⁾, and Fleischer⁽³⁶⁾ have proposed mechanisms which could account for hardening by loops. In the case of clustered defects one would expect a mechanism similar to precipitation hardening⁽³⁷⁾ would be applicable. Recent computer experiments by Foreman and Makin⁽³⁸⁾ have treated random distributions of point obstacles of various strengths.

The hardening observed in the present experiments appears to be due to either small clusters or unresolvable loops and is consistent with the hardening which would be produced by these defects.

One problem is that all the above mechanisms also predict a temperature dependent component to the hardening and this has been observed in radiation damage experiments on Cu.^(13,14) The rate controlling mechanism in the unirradiated iron is generally accepted as the Peierls mechanism at temperatures up to about 200 °K.⁽³⁹⁾ From 200-300 °K another mechanism may be operative in iron but it has not been conclusively identified. If another mechanism is operative in this region it has many properties similar to the Peierls mechanism. In fact the whole range of thermally activated flow can be accurately described empirically with the same activation energy and Peierls stress parameters.⁽¹⁶⁾ Where two mechanisms are competitive the one with the strongest short range stress field is controlling. Arsenault⁽¹⁸⁾ has considered the possibility of observing the Fleischer hardening mechanism in metals where the Peierls mechanism is operative and concluded that it would be observed only in the neighborhood of T_c or above. In these experiments it was shown that T_c shifted only slightly and this shift was not dependent on fluence so it must be concluded that the Fleischer mechanism treated in this manner is not applicable.

A modification of the basic rate controlling process could result in

small changes in parameters such as were produced in these experiments by radiation damage and also those produced by the quenching and aging treatments. Guyot and Dorn⁽³⁹⁾ have considered two such modifications which might occur in the Peierls mechanism, a change in the Peierls stress and a reduction of the free length of dislocation segment. As shown previously there appears to be a slight reduction in Peierls stress as determined by the empirical method but the data is limited and close to the range of experimental error. A change in the length of free dislocation segment in which a double kink could be nucleated does not appear to become important until the pinning points are closer than $20-30 b$ ⁽³⁹⁾ This would result in a decrease in activation volume as observed but the uncertainty in defect concentration in the submicroscopic range makes it difficult to evaluate this possibility.

Arsenault⁽¹⁸⁾ has suggested that the changes observed in activation volume with strain may be due to the highly localized deformation in these materials. Schwink and Neuhauser⁽⁴⁰⁾ have studied this phenomena in irradiated Cu and concluded that such localized deformation leads to drastic discrepancies between the true strain rate and that calculated from cross-head velocities. This analysis seems to ignore the fact that slip is always an inhomogeneous process and the fundamental quantities are mobile dislocation density and dislocation velocity ($\dot{\gamma} = \rho b \bar{v}$). It should make

no difference in strain rate whether the deformation is highly localized or uniform so long as the density of moving dislocations remains constant. This cannot be measured experimentally but is generally considered to remain constant after the initial multiplication at the yield point,⁽⁴¹⁾ especially in cases where there is a drop-in-load yield point.

It is difficult to distinguish between the case where the change in activation volume with strain is due to removal of defects from the slip plane by interaction and the case where the change is due to an increase in the density of dislocations as the deformation becomes less localized with strain. In the second case, one would expect the decreases in activation volume to correspond closely to the degree of localization or the coarseness of slip traces. Following this reasoning then, an increase in fluence, a decrease in deformation temperature, or the difference in hardening in the two materials should all produce a change in the activation volume as a function of strain, but none is observed. This concept is also incapable of explaining the increase in activation volume observed in Mo after irradiation⁽¹⁷⁾ where the localized nature of the deformation is well documented⁽⁴²⁾ and because of the high density of defects is probably more pronounced than in iron.

The defect interaction hypothesis is not an entirely satisfying one either since the mechanism is unknown.

It does offer the advantage that only a single size of defect might influence the activation volume and this need not change with conditions which would otherwise alter the localized deformation. The annealing experiments suggest this is a small defect since the changes in activation volume anneal out before the hardness fully recovers.

From the results of these experiments and other evidence cited the following hypothesis is offered as a model for radiation damage in iron: Hardening is produced by interstitial clusters nucleated at carbon atoms, hence the greater hardening in Ferrovac E. Additional clusters are formed by spike overlap and will be of equal concentration in both samples. Because both types of clusters grow during irradiation, the hardness increases with fluence. There will be a spectrum of sizes produced and the changes in activation volume are attributed to interaction with the smaller clusters. During annealing the smallest clusters dissociate first, thus the greater recovery in τ^* which is sensitive to the small clusters, and the greater recovery in τ_1 at the lower fluences. Interstitials from the breakup of small clusters migrate to sinks or larger clusters which grow during annealing. After reaching a critical size they collapse into prismatic loops which do not contribute appreciably to the hardening. Clusters are sheared by moving dislocations and destroyed, thus leaving "channels" free of visible defects and softer than the

surrounding lattice. This leads to localized deformation which is similar in many respects to the easy glide stage of deformation in single crystals.

Summary

This investigation of the influence of neutron radiation damage on two purities of alpha iron has shown that:

1. The major effect is an increase in internal stress which is attributed to small defect clusters.
2. Carbon impurity atoms serve as traps for interstitials and nucleate the majority of the clusters.
3. Defects in irradiated iron produce a small change in activation volume that recovers upon annealing at 350 °C. This is a modification of the basic rate controlling process rather than a new rate process.
4. Activation volumes recover with strain, reflecting the interaction between defects and dislocations and the localized nature of the deformation.

ELECTRICAL RESISTIVITY STUDIES

E. R. Bradley

Before a complete understanding of the interaction between irradiation produced defects and moving dislocations can be obtained, a knowledge of the form and distribution of the defects is necessary. Electrical resistivity is a physical property of materials which is affected by point defects. An insight into the form and distribution of defects may be obtained by following the resistivity recovery

during annealing. Isochronal and isothermal recovery curves can be used to determine the temperature ranges for the thermally activated recovery processes and also the kinetics of these processes. With this information, along with mechanical properties, microscopy, and length change-lattice parameter measurements, a better understanding of the defect state and the interactions of dislocations with irradiation induced defects will be obtained.

A system for measuring electrical resistivity by the 4-point potentiometric method has been set up and is presently being checked out and evaluated, (Figure 7.20). A Guildline Instruments Ltd. potentiometer (Type 9180) is employed with a Keithley milli-microvoltmeter (Model 149) as a null-detector. The potentiometer is equipped with four ranges to measure potentials from 1×10^{-8} to 2.1010 volts. Thermal compensators are used in both the sample and null-detector circuits to oppose the effect of thermal emf's in the system and allow the more sensitive ranges of the null detector to be used. Measurements with current flow in forward and reverse directions are taken and the average of the two measurements is used to eliminate the effect of any thermal emf's remaining in the system. Shielded wiring with a common floating ground is used throughout the system. The components are housed in a metal cabinet to reduce thermal fluctuations and to shield the components from stray magnetic fields.

Two six-volt wet cell batteries supply current for the potentiometer and sample circuits. These are heavy

FIGURE 7.20. Photograph of Electrical Resistivity Measuring System.

duty automobile batteries which are enclosed in insulated compartments to minimize temperature fluctuations and improve the stability of the current supply. A fixed current of from 20 to 100 milliamperes, depending on sample geometry, is used in the sample circuit. This current is monitored by measuring the potential drop across a 0.01 ohm standard resistor.

The current has been found to vary less than 0.01% during the course of a normal measurement. The reproducibility of the system is about $\pm 0.1\%$ of measured value. Possible causes for these variations are presently being examined and hopefully will be reduced or eliminated in the near future.

HIGH PRESSURE STUDIES

G. L. Kulcinski

The purpose of this phase of the program is to study the effects of ultra high pressures (1,000 to 60,000 atm) on the production, retention and subsequent microscopic configuration of the damage produced in irradiated solids. In addition, the high pressure synthesis of new phases and the high pressure alteration of mechanical properties will be investigated as possible methods of providing more radiation damage resistant materials for nuclear reactors.

Calibration of In-Reactor Diamond High Pressure Cell

The design of this cell was covered in a previous report⁽⁴³⁾ and will not be repeated here. Due to reasons

explained in that report it was necessary to increase the thickness of the sample for satisfactory X-ray analysis at high pressures. This was accomplished by placing the sample in a metallic molybdenum washer. The immediate question then arose as to the relationship between the load applied and the pressure experienced by the sample.

General Considerations

In the simplest case for Bridgman anvils without washers, one could estimate the pressure on a sample by dividing the force applied by the area on which it is acting. This assumes that the pressure is uniformly distributed over the sample. However, it has been shown in the past⁽⁴⁴⁻⁴⁹⁾ that this method of estimating the pressure does not take into consideration the pressure gradients in the sample due to friction forces. As a result, the maximum pressure in the sample may be as much as two times the average pressure as determined by the force/area (F/A) ratio. Specifically, it has been shown that the pressure varies from the center of the sample to a higher^(47,50,51) or lower^(44,45,49,52,53) value near the edge depending on whether deformable (metallic) or nondeformable (diamond) anvils are used respectively.

The introduction of metallic washer around the sample tends to reduce the pressure gradients. It has been shown by Myers et al.⁽⁴⁷⁾ that for sample diameter to thickness ratios of 15 or more, the pressure gradients are reduced to

less than 10%. Jackson⁽⁵³⁾ has treated this problem theoretically and predicts; 1) the pressure gradient will be reduced, and 2) the actual pressure experienced by the sample will depend on the ratio of its yield strength to that of the washer material. While the mathematical analysis of this situation is very difficult, it appears that if the ratio of yield strength is greater than one, the pressure on the sample will be greater than the average applied pressure (as determined by Force/Area). On the other hand if the sample has a lower yield strength than the washer, a most likely situation when metal washers are used, the pressure on the sample will be less than the F/A ratio.

An experimental example of the strong sample-weak washer combination is given by McWhan.⁽⁵⁴⁾ He has calibrated his apparatus by X-ray analysis of a sample surrounded by boron epoxy discs. In this case the average pressure on the sample is 1.5-2 times that determined by the F/A ratio.

There are no known calibration data on the reverse situation although several groups are known to be using high yield strength metals as washers when studying low yield strength compounds and liquids under pressure.⁽⁵⁵⁻⁵⁷⁾ Since most of the work with the cell described in this paper will deal with the latter case, it was necessary to provide such data.

Theory

Let us initially consider the case of a plastic material B surrounded by an elastic material A. (Figure 7.21.) Later we will allow A to become plastic and examine how this affects the pressure to the sample. The axial stress on the sample (B) within the region $0 < r < c$ is given as⁽⁵³⁾

$$\sigma_z(B) = [\sigma_{z(r=c)}(B)] \exp \left(2 \frac{f(c-r)}{h} \right) \quad \dots(1)$$

where $\sigma_{z(r=c)}(B)$ is the axial stress on an increment of sample at $r=c$,
 f is the coefficient of friction between the sample and the anvil,
 h is the thickness of the washer.

Since the radial stress, σ_r , must be continuous between region A and B and from the yield criterion at $r=c$ one finds:

$$\begin{aligned} \sigma_{r=c}(A) &= \sigma_{r=c}(B) \\ &= [\sigma_{z(r=c)}(B) - \sigma_0(B)] \quad (2) \end{aligned}$$

where σ_0 = yield stress of sample.

By substituting the boundary condition of Equation (2) into the general equations for the radial and tangential stresses in the elastic region, $c < r < a$, one can solve for $\sigma_{z(r=c)}(B)$ in terms of the elastic

A - Washer Material

B - Sample

FIGURE 7.21. Geometrical Model for Theoretical Calculation of Pressure Imposed on a Sample-Washer Combination Between Bridgman Anvils

stresses in (A). Such a substitution yields⁽⁵³⁾

$$\begin{aligned} \sigma_r(A) = & \frac{2f}{3h} \sigma_z(A) \left[-r + \frac{c^3 - a^3}{c^2 - a^2} \right. \\ & + \frac{a^2 c^2}{c^2 - a^2} \frac{(a - c)}{r^2} \left. \right] \\ & + [\sigma_{z(r=c)}(B) - \sigma_0(B)] \\ & \times \left[\frac{c^2}{c^2 - a^2} - \frac{a^2 c^2}{(c^2 - a^2)r^2} \right] \quad (3) \end{aligned}$$

and

$$\begin{aligned} \sigma_\theta(A) = & \frac{2f}{3h} \sigma_z(A) \left[r + \frac{c^3 - a^3}{c^2 - a^2} - \frac{a^2 c^2}{c^2 - a^2} \right. \\ & \times \frac{(a - c)}{r^2} \left. \right] + [\sigma_{z(r=c)}(B) - \sigma_0(B)] \\ & \times \left[\frac{c^2}{c^2 - a^2} + \frac{a^2 c^2}{(c^2 - a^2)r^2} \right] \quad (4) \end{aligned}$$

Using the octahedral stress theory which states:

$$\begin{aligned} \sigma_0^2 = & \sigma_1^2 + \sigma_2^2 + \sigma_3^2 - \sigma_1 \sigma_2 \\ & - \sigma_2 \sigma_3 - \sigma_3 \sigma_1 \quad (5) \end{aligned}$$

where $\sigma_1 = \sigma_z$

$\sigma_2 = \sigma_r$

$\sigma_3 = \sigma_\theta$

σ_0 = Yield in tension or compression, and inserting the following

values of σ_z , σ_r , and σ_θ at $r=a$ (where yielding first takes the place in A)

$$\sigma_r(A) = \sigma_1 = 0 \quad (6)$$

$$\begin{aligned} \sigma_\theta(A) = \sigma_2 = & \frac{2f}{3h} \sigma_0(A) \left[a + \frac{c^3 - a^3}{c^2 - a^2} \right. \\ & - \frac{c^2(a - c)}{c^2 - a^2} \left. \right] + [\sigma_{z(r=c)}(B) \\ & - \sigma_0(B)] \times \left[\frac{2c^2}{c^2 - a^2} \right] \quad (7) \end{aligned}$$

$$\sigma_z = \sigma_3 \quad (8)$$

one finds that

$$\frac{\sigma_{z(B)} \text{ave}}{\sigma_T} = \left[\frac{1}{VU} (1 - t^2) + t^2 \right]^{-1} \quad (9)$$

where $\sigma_{z(B)} \text{ave}$ is the average axial stress in B

σ_T is the theoretical stress on the washer and sample = $\frac{\text{Load}}{\pi a^2}$

$$t = \frac{c}{a}$$

V is the factor which relates $\sigma_{z(B)} \text{ave}$ to $\sigma_{z(r=c)}(B)$ and equals

$$1/2 \left(\frac{h}{fc} \right) \times \left[\exp\left(\frac{2fc}{h}\right) - 1 \right]$$

U is the factor relating the $\sigma_{z(r=c)}(B)$ to the yield stress of region A and equals

$$\begin{aligned} \frac{1}{K} + & \left[\left((1 - 2X[]_1) \pm \left\{ (1 + 2X[]_1)^2 \right. \right. \right. \\ & \left. \left. \left. + (4X[]_1) (1 - X[]_1) \right\}^{1/2} \right) / 2A \right] \end{aligned}$$

$$\text{where } X = \frac{2t^2}{3h}$$

$$[]_1 = a \left[1 + \frac{2t^3 - t^2 - 1}{t^2 - 1} \right]$$

$$A = \frac{2t^2}{t^2 - 1}$$

For typical values of $f/h = 10$, $\sigma_Z(A) = \sigma_0$, $k = 8$ and $c/a = 0.5$ one finds that $\sigma_{Z \text{ ave}}(B)/\sigma_T \approx 0.50$.

This says that a sample with a yield strength $1/4$ that of its containing washer will experience $\sim 1/2$ the theoretical pressure applied.

The situation in Equation (9) can be extended to a more realistic case under high pressures, namely, by allowing the washer material A to become plastic. The ratio of actual to theoretical pressure then becomes;

$$\frac{\sigma_{Z \text{ ave}}(B)}{\sigma_T} = \left[\frac{Z}{VU} (1 - t^2) + t^2 \right]^{-1} \quad (10)$$

where Z relates $\sigma_{A \text{ ave}}(A)$ to the yield strength of region A and is a function of a , c , h , and f .

$$Z = \frac{h}{2f} \frac{1}{a - c} \left\{ \exp\left[\frac{2f}{h}(a - c) - 1\right] \right\} \quad (11)$$

Substituting the same values used for the previous example one finds $\sigma_{Z \text{ ave}}(B)/\sigma_T \approx 0.45$, that is, the pressure to the sample will be slightly less than $1/2$ that determined theoretically.

While the above values are rather sensitive to f/h and k and are not to be taken as precise values, both indicate that a significant pressure reduction can occur when a weaker material is placed into a stronger washer and both are compressed to high pressures.

Experimental Procedure

In order to test the validity of Equations (9) and (10), two methods of calibration were used:

1. The change in the lattice spacing of NaCl with applied load, and
2. The shift in the optical absorption edge of TlBr with applied load.

Both methods yield information about the absolute pressure experienced by a sample contained by a washer and the second method reveals the magnitude of pressure gradients that may exist in the sample. Both of these methods yield continuous calibration data and neither suffers from hysteresis effects as do most phase transitions.

The shift in the (200) spacing of NaCl was obtained from X-rays taken of the sample under various loads in the Diamond Cell. The X-ray camera described in Reference⁽⁴³⁾ was used for these studies. These changes were then compared to the equation of state for NaCl as derived by Decker.⁽⁵⁸⁾ The specimen to film distance was calibrated by X-rays taken of NaCl at 1 bar and assuming $d_{(200)} = 2.821 \text{ \AA}$. Exposure time depended on the amount of NaCl used (size of hole in washer) and typical values varied from 4-16 hours with Kodak no-screen film.

Thallium bromide is known to have an optical absorption edge that progresses to the red wave lengths as pressure increases.⁽⁵⁹⁾ Thus by noting the wave length of light at which the normally transparent TlBr becomes opaque the pressure on the sample can be determined. In addition, by noting

the wave length at which absorption begins in any part of the solid and the wave length at which the whole solid is opaque, the amount of pressure gradient experienced by a sample can be estimated.

The optical absorption edge was measured by use of a Zeiss Ultraphot II microscope. A gradation filter was used to vary the wave length of light passing through the sample. The absorption edge was noted visually at 100X magnification. The sample was cycled to maximum pressure several times before calibration data was recorded.

The theoretical pressure (F/A ratio) was calculated from load deflection curves for the disc springs and the area of the smallest face diamond. The diamond face areas varied from 2.00 to $2.46 \pm 0.01 \times 10^{-3} \text{ cm}^2$. The load deflection curves for the compression of the disc springs were determined at various strain rates and it was found that increasing the strain rate from 0.025 to 0.25 cm/min had no effect on the curves.

Figure 7.22a shows the load-deflection curves for three different sets of Ti-Al-V springs and two sets of steel springs as arranged in Figure 7.23. The differences in the slopes of the titanium spring set #1 and that of set #2 and #3 stems from the fact that these washer sets were machined at different times. Since the load at any deflection is proportional to the third power of the washer thickness (0.107 cm in. Figure 7.23) normal machining tolerance can have a noticeable effect on the springs load characteristics. The variation between the titanium washers and steel set #1 is a result

FIGURE 7.22. (a) Load Deflection Curves for Disc Spring Arrangements in Figure 7.23. (b) Theoretical Calibration Curves for Disc Spring Arrangements in Figure 7.23 Combined with Designated Set of Diamonds

of the difference in elastic modulus, 2.07×10^6 bar for steel and 1.14×10^6 bar for Ti-6 Al-4V. It will be noticed that the slope of the load-deflection curve for steel set #2 is almost four times that of steel set #1. The factor of two increase in load is due to stacking two washers in series and the reduction in maximum total deflection is due to having only 4 stacks in parallel as opposed to 7 in steel set #1.

It should be emphasized that the curves in Figure 7.22a are for the spring arrangements and dimensions in Figure 7.23 and one could get larger

a) Stacking Sequence for
Tl-Al-V and Steel Disc
Springs Set #1

b) Stacking Sequence for
Steel Disc Springs
Set #2

c) Dimensions

*FIGURE 7.23. Arrangement of Disc Springs
Inside Diamond Cell*

deflection with the same maximum load or larger load at the same deflection simply by placing the springs in series or parallel, or by altering the dimensions.

Figure 7.22b combines the load-deflection curves in Figure 7.22a with the areas of the anvil diamonds to yield typical theoretical calibration curves for various combinations of springs and diamond sets. Again, these curves are characteristic only of the arrangement in Figure 7.23 and virtually any slope could be obtained by proper design of the disc springs.

The washer material used to surround the samples was 0.018 cm thick molybdenum foil prepared in the manner described earlier.⁽⁴³⁾ Hole sizes

varying from 0.0158-0.0428 cm were drilled into the washer with a high speed micro-drill press.

Results

Table 7.14 shows the results obtained from X-ray analysis and Table 7.15 lists results from TlBr absorption edge studies. In the case of NaCl c/a ratios varied from ~0.35 to ~0.83 and for TlBr from 0.31 to 0.88. Theoretical pressures ranged from 10 to 106 kbars by simple rearranging the disc springs. The accuracy of both methods of calibration is assumed to be ± 1 kbar below 20 kbars and ± 2 kbar above 20 kbar.

There are two general trends revealed by both tables:

TABLE 7.14. Summary of NaCl X-Ray Data Used For Calibration of Diamond X-Ray Cell-21 °C

Load Pounds	c/a	Lattice Parameter, Å ± 0.004	Pressure kbar σZ ave (B)	Theoretical Pressure kbar σT	σZ ave (B) σT
50	0.35	2.789	9	10	0.90
	0.535	2.804	5	10	0.50
	0.682	2.799	6	10	0.60
95	0.530	2.778	12	20	0.60
	0.682	2.789	9	20	0.45
150	0.369	2.742	23	30	0.77
	0.535	2.768	15	30	0.50
	0.775	2.778	12	30	0.40
190	0.403	2.738	25	37	0.68
	0.825	2.772	73	37	0.35
205	0.369	2.736	26	40	0.65
	0.535	2.760	17	40	0.42
	0.775	2.763	16	40	0.40
285	0.403	2.715	33	56	0.59
	0.470	2.755	19	56	0.34
360	0.403	2.711	35	73	0.48
380	0.403	2.714	34	75	0.45
	0.470	2.730	28	75	0.37
410	0.403	2.700	42	80	0.53
550	0.403	2.696	44	111	0.39

TABLE 7.15. Summary of TlBr Optical Absorption Data Used for Calibration of Diamond X-Ray Cell at 21 °C

Load Pounds	c/a	Absorption Edge - Å	Pressure kbar σZ ave (B)	Theoretical Pressure kbar	σZ ave (B) σT
50	0.311	4410	9	10	0.90
	0.490	4360	8	10	0.80
95	0.350	4560	15	18	0.83
	0.490	4460	11	18	0.61
	0.875	4350	7	18	0.39
100	0.490	4490	12	20	0.60
	0.875	4380	8	20	0.40
150	0.490	4510	13	30	0.43
	0.875	4475	11	30	0.37
190	0.350	4870	27	37	0.73
	0.490	4695	20	37	0.54
	0.875	4470	11	37	0.27
205	0.490	4565	15	40	0.37
	0.875	4585	16	40	0.40
285	0.35	5090	35	56	0.62
	0.490	4820	25	56	0.45
360	0.527	4770	23	73	0.31
	0.75	4600	16	73	0.22
380	0.400	5190	39	75	0.52

- There is a significant departure from theoretically predicted pressures at the higher loads, approaching $0.2-0.5 \sigma_T$.
- There is a definite relationship between the size of the hole in the washer and the fraction of theoretical pressure on the sample. Specifically the larger value c/a has, the lower the pressure on the sample.

These two trends are amply illustrated by plotting all of the data on a load versus pressure curve in Figure

7.24. Figure 7.25 shows the same data normalized to the theoretical pressure and again the departure is quite evident.

Photographs of the optical absorption in TlBr with and without surrounding washers are shown in Figure 7.26. It is obvious that the addition of a metallic washer around the sample considerably reduces the pressure gradients. Without washers, pressure gradients of as much as 40-50 kbars are found whereas with washers, the gradients are reduced to less than 10-15 kbars.

FIGURE 7.24. Experimental Calibration Curve for Diamond High Pressure X-ray Cell

FIGURE 7.25. Pressure Reduction Factor for Diamond High Pressure X-ray Cell

Discussion of the Results

The major result of these tests is the demonstration that the pressure on a powdered sample surrounded by a metal washer which is compressed between diamond anvils, is considerably lower than that predicted by the theoretical F/A ratio. This is in direct contrast to the situation encountered when surrounding the sample with a soft washer material⁽⁵⁴⁾ or with no washer at all,^(44,45,49,52,53) (Figure 7.26). The factor of 2 or 3 reduction is far in excess of any experimental error and the fact

that the same results were obtained with two completely independent methods of measurement tends to confirm the phenomena.

Not only is there a reduction in pressure but the amount of reduction depends on the size of the hole in the washer. It was shown, again with both X-ray and optical analysis, that as the hole diameter increases, so does the deviation from the theoretical pressure.

This situation is exactly what is predicted by Equation (10), as is seen in Figure 7.27. In this figure the

FIGURE 7.26. Effect of Washers on the Pressure Gradients Between Bridgman Anvils as Determined by TlBr

ordinate is the experimentally measured average pressure and the abscissa is the pressure $\sigma_{Z \text{ ave}}^{(B)}$ calculated from Equation 10. The values of c/a , σ_T , are used from Tables 7.14 and 7.15, f/h is assumed to be 10, the ratio of the yield strength of Mo to NaCl (or TlBr) is taken as 8 and $a = 0.025 \text{ cm}$, $h = 0.0125 \text{ cm}$. These latter two values have been experimentally determined. Bridgman⁽⁶⁰⁾ finds that the shear

strength of Mo at 50 kbars is ~ 12 kbars and that of NaCl at 20 kbars is 1.5 kbars so that at high pressures $k = 8$ is a reasonable value. Considering the fixed values of 'a' and 'h' the assumption of $f/h = 10$ may be somewhat low because $f \approx 0.05$. However, this f refers to the coefficient of friction between the plastic NaCl or Mo and the diamond. This is a factor of two lower than the reported coefficient of friction

between a smooth diamond surface and metal at 1 atmosphere.⁽⁶¹⁾ Considering the assumptions made in the derivation of Equations (9) and (10) it is thought that the use of this order of magnitude of the friction coefficient is justified.

Figure 7.27 should be viewed only in a qualitative manner. There are too many variables, h , c , f , k , and some simplifying assumptions in the theory of plasticity, to be able to obtain more precise information. For example, it was noticed in some tests that at the higher pressures the c/a ratio increased from its initial value by some 10-20%. Certainly the k ratio must be changed, probably

to lower values at higher pressures and the coefficient of friction will probably increase. Time did not permit a detailed study of all of these parameters.

The apparent qualitative agreement between experimental data and theory has great significance even if exact quantitative predictions cannot be made. It not only confirms the pressure loss that most workers in the field have noticed in the past, but it gives a semi-quantitative way of predicting the magnitude of this loss. For sample-washer combinations with values of $k > 8$, i.e. solidified liquids and very weak solids, theory predicts that the pressure loss will be significantly more than with materials such as NaCl and TlBr. On the other hand, if combinations with values of $k < 8$ are used, i.e. metallic powders, the pressure loss should be less than ~50-80% found in this experiment. Furthermore, theory and experiment predict that the larger the hole in the washer, the more the actual pressure to the sample will deviate from the theoretical pressure. One can also state that the higher the theoretical pressure, the more the sample pressure will deviate from it.

With these general guidelines and given c/a , f/h , and σ_T it is thought that one could predict the sample pressure to within 20% by using Equation (10). While this does not preclude the necessity for reporting theoretical pressures, it can cut the uncertainty by a factor of 10 or more at extremely high pressures (>50 kbars).

FIGURE 7.27. Comparison of the Pressure on the Sample as Measured Experimentally (ordinate) and Calculated from Equation 10 (abscissa)

The reduction of pressure gradients within the sample when it is surrounded by a washer was evident in both X-ray and optical calibration measurements. In the X-ray analysis the reduced gradients resulted in sharper Debye-Scherrer lines. Considering the case of TlBr, the maximum pressure gradients were 10-15% (Figure 7.26). This reduction should make quoted pressure values much more meaningful than those associated with large pressure gradients. The homogeneity of the pressure will also tend to reduce the shearing effects on phase transitions as experienced in a previous study with diamond cells.⁽⁶²⁾ Since our diameter to height ratios are ~ 20 , the results of this experiment agree with those of Myers et al.⁽⁴⁷⁾ who found a 5% gradient for d/h ratios of 15 or more with metallic anvils.

It should be mentioned at this point that the change in the NaCl lattice parameter was entirely continuous up to 44 kbar at 22 °C with no evidence of any phase transitions. Pistorius,⁽⁶³⁾ Lawson,⁽⁶⁴⁾ Vereshchagin⁽⁶⁵⁾ claim to have observed a phase transition at 17 kbars, the latter group by high pressure X-ray analysis. However, Jameson,⁽⁶⁶⁾ Corll,⁽⁶⁷⁾ Johnson,⁽⁶⁸⁾ and Jeffery et al.⁽⁶⁹⁾ have tried unsuccessfully to duplicate their results. Our data supports this latter group of investigators.

Conclusions

Calibration of the Diamond High Pressure Cell by X-ray analysis of NaCl and by using the pressure sensitive optical absorption edge of TlBr has demonstrated that the pressure deviates by a factor of 2 or more from

those predicted by a simple force/area ratio. The proposed ratio fcc $\rightarrow$ bcc phase transition of NaCl at 17 kbars was not observed which is in accordance with the more recent findings of high pressure scientists.

Design of Out-of-Reactor Ultra-High Pressure Equipment

To more fully understand the effect of pressure on the damage induced in neutron irradiated solids, an out-of-reactor ultra-high pressure laboratory was established at BNW. This facility is designed to complement information obtained from in-reactor high pressure equipment and in many cases to investigate the effects of preirradiation pressure-temperature treatments on materials of interest to nuclear metallurgists. The main purpose of this section is to explain the basic design features, calibration and general capabilities of the equipment. Future reports will deal more specifically with calibration and the various programs currently underway.

General Capabilities

The basic equipment was purchased from Physical Metallurgy Corporation which is a division of ManLabs Inc. of Cambridge, Massachusetts. Figure 7.28 is a photograph of the working system and its control equipment. There are three distinct units which will be described in more detail below,

- Press (left)
- Pressure and temperature control equipment (center and right)
- Tooling (inside press)

FIGURE 7.28. Ultra-High Pressure Equipment: Press (left), Control Equipment (center and right), Tooling (inside press)

The maximum pressure and temperatures attainable depend on the type of tooling used and are listed below:

	<u>Piston Cylinder</u>	<u>Belt</u>
Typical Sample Volume	1.52 cm diam x 3.05 cm long	0.68 cm diam x 1.52 cm long
Maximum Pressure	25 kbar	60 kbar
Maximum Temperature	1500 °C+	1500 °C+

The press has been modified to allow infinitely variable rates of platen advance from zero to 0.63 cm/min. Appropriate shielding for both radioactivity and rupture hazards is placed between the operator and press.

The pressure may be controlled to 0.1% although uncertainties in calibration far exceed this value. The samples in the high pressure region are heated with small graphite resistance furnaces. A 10 KVA power supply is used to produce temperatures in excess of 1500 °C on the sample. The rate of temperature increase may be varied with an electronic programmer in conjunction with a null detecting controller. This capability allows differential thermal analysis of the samples under pressure.

It is convenient to describe each set of tooling, Belt and Piston-Cylinder separately as their pressure-temperature-sample size characteristics are somewhat different.

Piston-Cylinder

Figure 7.29 is a schematic of this set of tooling. The upper picture shows the arrangement of the tooling in the die set and press while the lower schematic shows a magnified view of the tooling. The function of the clamping plates is to maintain proper alignment of the components and good electrical contact between the bottom of the specimen cell and the backing block which contains the current lead. The die consists of an inner tungsten carbide cylinder with various steel supporting rings shrunk and press fit around it. The assembly is equipped with a cooling chamber which is necessary at high operating temperatures as the strength of the die materials is considerably reduced above a few hundred degrees centigrade.

The piston is made of tungsten carbide and is beveled at its leading edge to accommodate a triangular cross-section steel ring which prohibits extrusion of the sample. As the load is applied, the ring is forced outward to the wall and extrudes into the gap between the piston and wall. Such an arrangement is sufficient when compressing solid media but obviously not useful in compressing liquid samples in the chamber.

Figure 7.30 is a schematic of a typical specimen cell equipped with a collapsible can arrangement. Figure 7.31 is a photograph of such a

FIGURE 7.29. Schematic of Piston-Cylinder Tooling

FIGURE 7.30. Schematic of Sample Cell Assembly for Piston-Cylinder Unit.

cell both in the assembled and dis-assembled condition. The major components of the cell are pointed out in Figure 7.30. The inside dimensions of the can are: 1.42 cm diam by 2.85 cm long before compression, and 2.34 cm long (same diam) after compression. It should be pointed out that the volume occupied by the can (7.1 cc) could be filled with sample material in cases where the applied pressure need not be truly hydrostatic, such as the production of high pressure polymorphs. The can may be filled with liquids to insure that the pressure to the sample is truly hydrostatic. At low temperatures n-pentane is used while at high temperatures, liquid metals such as Na and NaK are necessary.

The electrical heating circuit is as follows: from the transformer through the current lead to the bottom backing block; from the backing block the current travels through the bottom steel closure to the graphite pad and through the thin graphite furnace. The rest of the circuit is out the top pad through the piston to ground of the press. This design offers a maximum of temperature capability with a minimum application of power. Temperatures of 1500 °C can be obtained with 9 kW of energy input.

Belt System

This system gets its peculiar name from the design of the die which acts like a circular belt to enclose and contain the sample as the pressure is applied. Figure 7.32 is a schematic of the unit in the press and

FIGURE 7.31. Exploded View of Piston-Cylinder Sample Cell Assembly.

FIGURE 7.32. Schematic of Belt Tooling

also contains an enlarged cross-sectional view of the tooling. In contrast to the Piston-Cylinder arrangement, there are two conical pistons acting on the sample. These pistons are thrust into each end of a conically shaped tungsten carbide die by the 500-ton press. The pressure is generated by the advancing pistons as they compress the specimen cell and its surrounding gaskets. Unlike the Piston-Cylinder tooling where an effort is made to prohibit extrusion of the pressure transmitting media, the lavite gasket material is allowed to extrude to its equilibrium thickness in the Belt tooling. This extruded gasket not only retains the sample but also provides some measure of support for the pistons.

The pistons themselves are usually made from tungsten carbide with various amounts of cobalt binder. It has been necessary to use 6% Co binder for the higher pressures (~ 60 kbar) whereas 12% is sufficient below 50 kbars. The latter is somewhat more resilient at lower pressures resulting in a much longer working life. The pistons themselves are supported by shrunk fit steel binding rings so that the stresses in the pistons are always compressive except at the very highest pressures. This is necessary because the tensile strength of WC is much lower than its compressive strength. The face diam of the piston is 1.27 cm.

The die arrangement is similar to the Piston-Cylinder unit in that the WC die is supported by shrunk fit steel binding rings and provisions are made for water cooling. The difference between the Belt and Piston-Cylinder is mainly the double conical shape of the die necessary to allow piston advance in the Belt system.

Figure 7.33 is a schematic of a typical specimen cell for the Belt tooling. Figure 7.34 shows an actual model and a blown-up view. The components are pointed out in Figure 7.29 and typical dimensions inside the can are: 0.56 cm diam by 1.45 cm long before compression, and 1.2 cm long (same diam) after compression. As in the case of the Piston-Cylinder unit, the specimen can volume (0.056 cc) can be used for other purposes when true hydrostaticity is not required.

The electrical heating circuit is (Figure 7.32) from the transformer through the current lead and bottom

FIGURE 7.33. Schematic of Sample Cell Assembly for Belt Tooling.

backing block to the bottom piston. From the bottom piston the current travels through the steel end pad, graphite pad, and through the furnace. The rest of the circuit is out through the top piston to the ground of the press. Typical temperatures of 1500 °C can be obtained by an input of 3 kW of power.

IN-FLUX OXIDATION AND HYDRIDING OF TITANIUM AND NIOBIUM

A. B. Johnson, Jr.

Titanium (Grade II), niobium, and niobium-1 wt% zirconium samples were exposed in the G-7 loop of the Engineering Test Reactor. Three one-inch-square specimens of each metal were

FIGURE 7.34. Exploded View of Belt Sample Cell Assembly.

included in the test. Specimens of Zircaloy-2 were exposed in the same specimen holder.

The test conditions are summarized in Table 7.16. Table 7.17 summarizes the metallurgical conditions of the specimens. Out-of-reactor controls were exposed in an autoclave at Battelle-Northwest operated at 280 °C with pH-10 NH_4OH .

The activated titanium isotope (Ti^{51}) has a short half life (5.8 min) and decays by beta emission to stable V^{51} . Impurities in the titanium (probably principally iron) account for some sustained activity. However, approximately six months after discharge, the specimen activity was ~60 mr/hr at 6 in. and the specimens could be weighed on the same out-of-cell microbalance used for pre-exposure weighings. Since the in-flux weight gains on titanium were small, the microbalance weighings were considered necessary to assess the effect of flux on oxidation. Gold interference colors were observed on in-flux and out-of-flux specimens. No attempt was made to weigh specimens of niobium and its alloy on the out-of-cell microbalance, since the in-flux weight gains were relatively large. The niobium specimens were weighed on an in-cell Mettler analytical balance.

Hydrogen samples were taken from the three in-flux titanium specimens and from one each of the niobium and Nb-1% Zr specimens. Hydrogen analyses were conducted by hot vacuum extraction.

In-flux and out-of-reactor weight gains and hydrogen pickups are summarized in Table 7.18, including

Zircaloy-2 specimens for comparison. The data show:

- Low oxidation rates for titanium in-flux and out-of-reactor. However, in-flux weight gains were 5 to 10 times higher than the out-of-reactor weight gains.
- Appreciable hydrogen absorption by titanium out-of-reactor. In-flux absorption represented 130 to 265% of the hydrogen generated by in-flux oxidation of the titanium.
- Relatively high oxidation rates for niobium and niobium-1% zirconium in-flux and out-of-reactor. Variations among identical coupons may indicate spalling of the oxide.
- No detectable in-flux hydrogen absorption by niobium or its alloy. However, pure niobium absorbed hydrogen in a 200-day out-of-reactor exposure.

Zircaloy-2 weight gains were equal in-flux and out-of-reactor. The Zircaloy in-flux weight gains were higher than those of titanium and lower than the mean in-reactor weight gains of niobium and its alloy. In-flux hydrogen absorption is comparable for Zircaloy-2 and titanium. Out-of-flux, Zircaloy absorbed hydrogen while titanium did not in 37 days.

The low weight gains for titanium in pH-10 NH_4OH at 280 °C out-of-reactor are consistent with out-of-reactor weight gains observed by Mettler and Shannon in pH-10 LiOH at 275 °C.⁽⁷⁰⁾

The high and variable weight gains on niobium are consistent with behavior observed at Battelle-Columbus on niobium in water at 316 °C.⁽⁷¹⁾

TABLE 7.16. G-7 Loop Exposure Conditions - Quadrant 217

Time at Temperature	37 Days
ETR Cycles	78 and 79
Time at Full Power	44 Days
Nominal Loop Pressure in Sample Section	2150 psi
Flux	5.9×10^{13} nv, >1 MeV
Integrated Flux	2.2×10^{20} nvt, >1 MeV
Water Chemistry:	
Coolant	pH-10 NH_4OH
Oxygen, ppm	<0.05
Hydrogen, cc/kg	45*
NH_3 , ppm	9.1*
NO_2 , ppm	0.01*
NO_3 , ppm	<0.05*
^{138}Cs , dis/min ml	4×10^4 *

*Mean Values

TABLE 7.17. Metallurgical and Surface Conditions

<u>Specimen</u>	<u>Fabrication</u>	<u>Surface Treatment</u>
Titanium (Grade II)	Initial Forging 900 °C Annealed 700 °C - 2 hr Stress Relief 480-540 °C 45 min.	Etched 90 parts H_2O 8 parts HNO_3 2 parts HF 10 min.
Niobium	Cold Rolled Stress Relief 900 °C 1 hr	Electropolished 90% H_2SO_4 10% HF 4 min., 1.5 amp/cm ²
Niobium-1% Zr	Cold Rolled Stress Relief 900 °C 1 hr	Same as Niobium

TABLE 7.18. In-Flux and Out-of-Reactor Weight Gains and Hydrogen Pickups at 280 °C in pH-10 NH₄OH

Specimen	37-day Weight Gains		Δ Hydrogen Absorption			
	In-Flux	Out-of-Reactor	In-Flux*		Out-of-Reactor**	
	mg/dm ²	mg/dm ²	ppm	mg/dm ²	ppm	mg/dm ²
Titanium, Grade II	2.1	0.4	31	0.69	0	0
	2.1		30	0.67		
	2.9		28	0.62		
Niobium	11.7	78.	0	0	20	1.1
	51.2					
	60.0					
Niobium-1% Zr	41.5	52.	0	0	0	0
	13.4					
	79.9					
Zircaloy-2	11.1	11.0	27	0.5	42	0.78

* After 37 days in-flux.

**After 200 days in out-of-reactor autoclave.

The three in-flux titanium specimens all show appreciable hydrogen absorption. Movement of radiolytic hydrogen through the relatively thin oxide films appear to have been involved, since the absorbed hydrogen exceeded that generated by corrosion in all cases.

Conclusions regarding the in-flux behavior of titanium and niobium will be reserved until results of a 4-cycle G-7 loop exposure are available.

PRESSURE-VESSEL NEUTRON DOSIMETRY

A. DePino, Jr. and R. E. Dahl

We are investigating the possibility of using fission-track detectors as a fluence-monitoring technique for pressure-vessel surveillance. Glass, mica, and plastic samples have been irradiated in test facilities in the Hanford K-Reactor to determine the

limiting exposure level at which the detectors become useless due to radiation damage. Plastics were found to be unsuitable for use at expected pressure-vessel fluences. Fast-neutron irradiation damage limited the use of the micas investigated to fluences less than $\sim 5 \times 10^{15}$ n/cm², E > 1 MeV, (about 10 yr at the surface of a typical pressure vessel). Above this exposure, optical microscopy methods could not be used successfully.

Mica and glass samples were coated with a thin layer of highly depleted uranium and irradiated. This technique appeared an attractive way to monitor fast neutrons and minimize the tracks formed by thermal-neutron-induced fission of ²³⁵U. This coating technique yielded satisfactory results only at fluences less than $\sim 10^{15}$ n/cm².

($E > 1$ MeV). Therefore, coating fissionable material on mica and glass is not suitable for pressure-vessel applications.

Natural mica is a good candidate for a detector material within its exposure limits. Fission fragments are registered with 100% efficiency in mica, and processing techniques, including etching and data analysis, have been established. However, extension of the fluence range will require a more radiation resistant material. To determine whether the accuracy of the method will meet pressure-vessel requirements, further investigation is required for detector calibration, determination of the reproducibility of the fission tracks, and effects on nonhomogeneous distribution of the uranium in the material.

The results of this work have provided a sound basis for further work. We have discussed the use of fission-track dosimetry with Washington-AEC personnel and will propose further work in a research proposal.

INTERCALIBRATION TEST OF COUNTING LABORATORIES

R. E. Dahl, J. A. Ulseth

The Irradiation Standards and Procedures Committee of the Irradiation Effects on Reactor Structural Materials Program has recommended that another intercalibration test be initiated of counting laboratories utilized by program members. The purpose of this intercalibration test is to insure that all participating counting laboratories are consistent in both their determination of monitor activities and conversion of these activities to fluence.

This test is being conducted in a manner similar to the previous intercalibration test.⁽⁷²⁾ Two monitors of each type (Fe, Ni, Ti and Al-0.1% Co) have been irradiated, counted and distributed to the participating laboratories by Pacific Northwest Laboratory (PNL).

Monitor materials were irradiated in the MTR Rabbit Facility to obtain two levels of activity differing by a factor of about 100. Half of the sets were irradiated for 2 hr and the other half for 196 hr. Each participating laboratory has been asked to report total activity (d/s), specific activity (d/s/mg) corrected to discharge date, and total fluence for the monitors received. All data will be returned to PNL for tabulation and comparison.

The eleven participating laboratories are: Argonne National Laboratory, Atomics International, Battelle Memorial Institute, Columbus, Ohio, Brookhaven National Laboratory, General Atomic, General Electric Company - NMPO - Cincinnati, General Electric Company - APED - San Jose, Idaho Nuclear Inc., Oak Ridge National Laboratory, Pacific Northwest Laboratory - Richland, Washington, and Isochem - Richland, Washington (Isochem radiochem. lab. is utilized by PNL to analyze many dosimeters).

FAST REACTOR SUPPORTING STUDIES

FAST NEUTRON MECHANISMS

R. P. Allen

The objective of this program is to determine the effects of fast neutron irradiation and in-core environmental and service conditions on fundamental

aspects of hydrogen and helium behavior in fast reactor alloys. The probable neutronic-hydrogen retention and distribution characteristics of representative iron- and nickel-base alloys are currently being evaluated as the initial part of a study of synergistic damage interactions involving hydrogen, helium, and the irradiation-induced defect state.

Permeation Barrier Effects

The hydrogen generated in endothermically occluding metallic core components by (n, p) nuclear transmutation reactions will be quite mobile at normal fast reactor operating temperatures and after an initial transient period will effuse into the surrounding coolant at a rate equal to the neutronic-hydrogen production rate. The resulting maximum neutronic-hydrogen concentration (C_m) in a particular component is a function solely of the hydrogen production rate (R) and hydrogen diffusivity (D_m) in the component material, if diffusion through the component is rate controlling for the effusion process. Thus, for an approximately planar component of thickness L with desorption occurring at both surfaces,

$$C_m = \frac{RL^2}{8D_m} \quad (1)$$

Calculated values of C_m for representative temperatures, component dimensions, and hydrogen production rate⁽⁷³⁾ are shown in Figure 7.35 for 18-8 type stainless steel.

If a desorption or effusion mechanism, rather than diffusion, is rate controlling, then the concentrations calculated using Equation (1) are no longer

FIGURE 7.35. *Calculated Maximum Neutronic Hydrogen Concentrations for Ideal Effusion Conditions*

applicable, but represent a lower bound for the retention of the neutronic hydrogen, with the condition of complete hydrogen retention as an absolute upper bound. This can be illustrated by considering the effect of surface permeation-barrier formation on expected concentration values. At equilibrium, the permeation rate through a surface region must equal the corresponding total internal hydrogen production rate; for a planar component with barrier regions of thickness T at both desorption surfaces:

$$C_s = \frac{RL^2}{8D_m} \left[1 + 4 \frac{D_m}{L} \cdot \frac{KT}{D_s} \right] \quad (2)$$

where C_s is the maximum internal neutronic-hydrogen concentration for a surface permeation-barrier controlled effusion process; D_s is the hydrogen diffusivity in the barrier material;

and K is the ratio of the unit pressure hydrogen solubility in the component material to that in the altered region. The magnitude of C_s is thus a function of the hydrogen solubility as well as the hydrogen diffusivity characteristics of the barrier region.

In evaluating C_s it is not necessary to know or separately determine K , T , or D_s . If P_m is the experimentally determined hydrogen permeation rate through a planar component with an ideal effusion surface and P_s is the reduced permeation rate for identical conditions and component dimensions, but an altered effusion surface, then:

$$P_m/P_s = 1 + \frac{D_m}{L} \cdot \frac{KT}{D_s} \quad (3)$$

Combining this with Equation (2) gives, for $P_m/P_s \gg 1$,

$$C_s/C_m = 4 P_m/P_s \quad (4)$$

Relative permeation rate data for alloys, surface conditions, and temperatures of interest are limited; those available are primarily for surface oxide films or layers on selected iron-base alloys, for which permeation rate reductions of up to three orders of magnitude have been observed.^(74,75) Specific permeation studies have, therefore, been initiated to determine the effect of complex surface carbide and nitride layers on relative permeation rates and hydrogen desorption behavior in 18-8 type stainless steels. The permeation facility used incorporates a mass spectrometer to permit the additional detection and identification of desorbing hydrogenous compounds.

The effect of constant but nonideal effusion conditions on the duration of the initial transient period and on the corresponding time-dependent maximum neutronic-hydrogen concentrations is illustrated in Figure 7.36 for an assumed P_m/P_s ratio of 25. The approximate time required to reach the maximum steady-state concentration can be obtained by dividing this concentration by the hydrogen production rate; similarly, for times less than this, the maximum transient concentration is given by the integrated hydrogen production rate and this is equivalent to a condition of complete hydrogen retention.

FIGURE 7.36. Calculated Time-Dependent Maximum Neutronic Hydrogen Concentrations for Representative Effusion Conditions.

EBR-II IRRADIATIONS

J. J. Holmes, R. E. Robbins, B. Mastel,
J. L. Brimhall, R. W. Barker

The objective of this program is to determine the combined effects of environment and fast reactor irradiation on the mechanical properties of candidate fast reactor cladding and structural alloys. The program currently in progress is specifically directed at providing a basis for selection of optimum alloys for FFTF applications and at providing a description of material behavior in fast reactor service.

A detailed irradiation program for the EBR-II has been formulated. This effort involves the use of two full subassemblies in the EBR-II--a single Row 2 "B-7" irradiation pin and various space-available A-19 irradiation pins in the reactor core and blanket.

Program emphasis is on creep and tensile properties of austenitic stainless steels in sodium after fast reactor irradiation. Specimens are to be irradiated in the EBR-II to fluence levels of 1×10^{22} , 3×10^{22} and 1×10^{23} and subsequently tested at temperatures from 700 to 1500 °F (370 to 815 °C) at stresses sufficient to cause rupture in time from 1 to 10^4 hr. In addition to postirradiation creep testing, postirradiation tensile testing is also planned along with studies on flowing sodium effects, aging response, and in-reactor creep.

The major portion of the fast reactor irradiations is to be conducted in the two subassemblies. One of the subassemblies will be irradiated to

1×10^{23} total fluence in a Row 2 position, the other in Row 7 will be used to accumulate dose levels of 1×10^{22} and 3×10^{22} . Each subassembly contains nearly identical sets of specimens encapsulated in gamma heated subcapsules designed to operate at three temperatures; namely, 900, 1200, and 1400 °F (482, 649, and 760 °C). Both units will contain mostly 304 and 316 tensile, biaxial creep, and uniaxial creep specimens; but backup FFTF alloys such as 348 and 321 are also included as well as Hastelloy X-280, Inconel 600, Incoloy 800, Inconel 718, Inconel 625, and Inconel X-750. Both subassemblies have been fabricated and placed in the EBR-II for irradiation. It is anticipated that the Row 7 subassembly will be returned to PNL in October.

Comparison of irradiation effects occurring in sodium with those occurring in helium will be evaluated by conducting a limited number of tests in helium and in reactor sodium at ambient temperatures. A MK-B-7 irradiation pin in Row 2 containing 198 miniature specimens in a helium environment is currently being irradiated to a target fluence of 1×10^{23} . The specimens in this pin are primarily AISI 304 and 316; some 348 and 321 specimens are also included. Twelve MK-A type space-available pins have been charged in the EBR-II core. Subassembly X-019 contains eight of these pins and is scheduled for an exposure of 3.0×10^{22} fast fluence. Subassembly X-020 contains four pins and is scheduled for an exposure of 6.0×10^{22} fast fluence. These pins

contain 124 tensile and creep test specimens of AISI 304 and 316 stainless, evenly divided, of which half are exposed to bulk sodium.

Initial tensile test results on annealed AISI 304 SS irradiated at 1000 °F (540 °C) to about 1.7×10^{22} total flux in the EBR-II have been obtained. Tensile properties of annealed 304 stainless steel irradiated in the EBR-II are presented in Figures 7.37 through 7.40 together with "as-received" control data.

The following general characteristics were observed:

- (a) Fast reactor irradiation produces an increase yield strength at all test temperatures in the range of 572 to 1600 °F (300 to 870 °C). Largest increases in yield strength occur at temperatures below 900 °F (480 °C) where a relatively constant increase of a factor of two is observed. Above 900 °F (480 °C) the increase in yield strength decreases monotonically to about 120 percent of the as-received condition at 1500 °F (815 °C). (Figure 7.37)
- (b) The ultimate strength is not appreciably changed by fast reactor irradiation except at room temperature where a 15 percent increase is found. (Figure 7.38)
- (c) Uniform elongation was decreased by about a factor of two at temperatures below 900 °F (480 °C). Between 900 and 1500 °F (480 and 815 °C) uniform ductility decreases monotonically with increasing temperatures from about 20 percent to 0.6 percent at 1500 °F (815 °C) but increases to

3.2 percent at 1600 °F (870 °C). As-received material exhibits a similar decrease above 900 °F (480 °C) but obtains a minimum of about 12 percent. Total elongation follows the same general trends as uniform elongation; however, minimum ductility occurs at 1300 °F (705 °C). Uniform elongation in as-received material is nearly athermal. These characteristics are shown in Figures 7.39 and 7.40.

Irradiation damage to metals has been described in the literature in terms of two distinct behavior modes ⁽⁷⁶⁾ operating in well-defined temperature ranges. Displacement damage is thought to cause increases in strength properties and losses in ductility at temperatures below one-half the absolute melting temperature ($T_m/2$). Above $T_m/2$ displacement damage recovers so rapidly that appreciable damage concentrations are not expected to build up during irradiation so strength and ductility are not affected. At temperatures greater than $T_m/2$, however, a different form of irradiation damage occurs which involves transmutation effects and drastically reduces ductility by weakening grain boundaries. Barnes ⁽⁷⁷⁾ has suggested that the transmutation-induced grain boundary weakening is due to helium at grain boundaries from (n, α) reactions.

The recently-tested EBR-II specimens were irradiated at 1000 °F (535 °C) which is $0.501 T_m$, yet a significant increase in yield strength was observed at test temperatures as high as 1500 °F (815 °C) which is $0.67 T_m$.

FIGURE 7.37.

Ordinate should read 0, 10, 20, 30 and 40. Yield Strength,
psi $\times 10^{-3}$

7.63

BNWL-435

FIGURE 7.37. Comparison of 0.2% Off-set Yield Strength in Annealed and EBR-II Irradiated AISI 304 SS.

FIGURE 7.38.

Ordinate should read Ultimate Strength, psi $\times 10^{-3}$

7.64

BNWL-435

FIGURE 7.38. Ultimate Strength of AISI 304 in the Annealed Condition and After Irradiation in the EBR-II to 1.7×10^{22} Total Fluence

FIGURE 7.39.

Ordinate should read 0, 10, 20, 30, 40 and 50.

7.65

BNWL-435

FIGURE 7.39. Uniform Elongation of Annealed AISI 304 Before and After Irradiation in the EBR-II.

FIGURE 7.40. Total Elongation of Annealed AISI 304 Before and After Irradiation in the EBR-II to 1.7×10^{22} Total Fluence.

This is in marked contrast to classical behavior and indicates that either high exposure or high dose rate in the EBR-II produces a damage state that is relatively stable at temperatures in excess of $T_m/2$. Recent data on AISI 304 SS irradiated to 6×10^{21} (>1 MeV) in the ETR also show hardening persisting to temperatures well in excess of $T_m/2$ indicating that exposure, rather than exposure rate, produces the temperature-resistant defect state.⁽⁷⁸⁾

Thin film electron microscopy has been employed to clarify the nature of damage state in EBR-II irradiated specimens. Examination of foils in the as-irradiated condition and foils given an anneal at 900 °F (480 °C) revealed the following. The damage consists of two components: (1) dislocation loops 500 to 1000 Å in size containing stacking faults and identified as Frank sessile loops and (2) polyhedral voids or gas-filled cavities about 200 Å in size. (Figures 7.41 and 7.42) The number of point defects comprising the stacking fault loops was calculated and compared with the number of point defects comprising the voids. These two numbers were equal within experimental error. This is consistent with a model in which the interstitial atoms form the loops and the vacancies form the voids. Subsequent annealing at 1400 and 1500 °F (760 and 815 °C) for 1 hr completely removed the Frank sessile loops and greatly reduced the size and number of voids. At 1500 °F (815 °C) the voids were almost entirely absent from the structure.

The absence of any observable defect state at 1400 and 1500 °F (760 and 815 °C) suggests the primary

cause of hardening is not either the large Frank loops or voids but some unresolvable defect. The nature of this defect is not obvious at this time but must be considerably different than that thought to cause hardening at low temperatures. The dose dependence of high-temperature hardening and indicated lack of dose rate effects suggests that some transmuted species such as helium is stabilizing displacement damage.

Electron microscopy studies have been supplemented with optical examination of fractured specimens. The fracture mode below 900 °F (480 °C) is entirely transgranular while intergranular fracture predominates above 1100 °F (600 °C). The intergranular fractures below 1500 °F (815 °C), while giving the general appearance of wedge fractures, do not start at triple points but instead are initiated away from the grain corners and propagate to them giving the appearance of wedge fracture. Below 1500 °F (815 °C) the cracks appear to propagate easily and are typically sharp pointed. At 1500 °F (815 °C) intergranular fracture is by cavitation and shows typical voids along the boundary and rounded crack tips.

It should be pointed out that premature grain boundary failure does not appear to be the cause of low uniform ductility in the EBR-II irradiations. Radiation hardening to the extent that the yield approaches the ultimate strength is sufficient for low uniform ductility (Figure 7.43). This is true regardless of any considerations of grain boundary effects. The nonuniform ductility, however, may be decreased by premature grain boundary

FIGURE 7.41. Annealed AISI 304 SS Irradiated to 1.7×10^{22} Total Neutron Fluence at 1000 °F (535 °C) in the EBR II. [Electron micrograph shows (111) frank loops and polyhedral voids]

150,000X

FIGURE 7.42. Annealed AISI 304 SS Irradiated to 1.7×10^{22} Total Neutron Fluence at 1000 °F (535 °C) in the EBR-II. [Polyhedral activities possibly containing some gas phase are believed to result from excess vacancy precipitation. These cavities are almost entirely removed after annealing for 1 hr at 1500 °C (815 °C)]

150,000X

FIGURE 7.43. Tensile Properties of AISI 304 SS after Irradiation in the EBR-II to 1.7×10^{22} total fluence.

failure. Additional studies are needed to clarify this point.

LIQUID METAL CAPSULE IRRADIATIONS

K. R. Wheeler

This program is designed to provide high-temperature irradiations of candidate LMFBR program structural materials in flowing liquid metal environments. From these capsules will come information concerning neutron damage to structures and moving sodium-metal interactions, important to corrosion and mass transfer studies. In addition, the thermal stability of the various alloys at elevated temperature will be studied.

Liquid metal capsule GEH-22-3, containing 32 AISI 316 SS tensile samples, was discharged during shutdown of ETR Cycle 87. The capsule accumulated a fast fluence ($E > 1$ MeV) of 1.38×10^{21} after 99.9 full power days of operation. One thermocouple located in the central sodium column functioned throughout the entire operating period indicating a sodium temperature of 1000 °F (537 °C). Based upon millivolt readings of the other capsule thermocouples prior to their loss, the peak sodium temperature was approximately 100 °F (38 °C) hotter than the continuous 1000 °F (537 °C) reading described above. The capsule has been returned to BNWL for disassembly and specimen retrieval.

A fourth generation liquid metal capsule GEH-22-4, containing a total of 40 AISI 304, 316, and 348 SS tensile samples, began an irradiation in ETR Cycle 87. A design modification increased the radial heat transfer path displacing the temperature control

range upward to realize a control point at 1400 °F (760 °C). As the curve of Figure 7.44 shows, the desired control point was achieved at a 50 Ar-50 He gas mixture. Other design changes should extend capsule life by removing restraints on thermocouple sheathing and the vacuum tube, these restraints producing severe stressing of components during differential thermal expansion. Figure 7.45 shows the tubular connectors between the outer and inner bulkheads. These connectors support the sodium chamber and provide stress-free exit paths for the thermocouples. The curved tube with tube fitting is the sodium filling port. Figure 7.46 presents an exploded view of the complete capsule including the specimen assembly.

GEH-22-4 has completed 15 full-power days of stable operation with all thermocouples operating normally. The capsule will continue to increase its fluence level in future ETR cycles with discharge dependent upon capsule performance.

EXPERIMENTAL TESTING FACILITIES

R. H. Todd, J. A. Yount

The comprehensive investigation of the effects of irradiation and environment upon reactor structural metals and fuel cladding candidate materials requires a testing program and a facility which will accommodate numerous materials and operating variables. The testing conditions under consideration, which range up to 1400 °F (760 °C) in sodium, present environments in which standard materials have not been fully evaluated. The facility which will fill the need for

FIGURE 7.44. Temperature Versus Gas Composition - Liquid Metal Temperature Controlled Irradiation Capsule.

FIGURE 7.45. GEH 22-4 Sodium Chamber
Suspension and T.C. Feed Throughs.

*FIGURE 7.46. GEH 22-4 Sodium Capsule
Exploded View*

testing irradiated samples in sodium and controlled atmospheres is now being built. The assigned building has been improved to the point where the office spaces and workshop can be occupied. This portion of the work was completed on February 7 of this year. Closer supervision and coordination of the work is now possible with the offices and workspaces in close proximity of one another. The workshop is being equipped with the special and standard tools necessary for work with the test stands to be used in this building. Renovation of the second portion of this building, which will include the ventilation and exhaust system, will be done under a separate project proposal which is now awaiting AEC approval.

Four test stands from the CANEL equipment pool have been placed in the workshop. These units have undergone complete overhaul and cleanup, and the associated instruments and controllers

have been standardized. Except for conversion of the controller-recorders to chromel-alumel thermocouple signal input, these four units are ready to begin working. By placing these units in service at the earliest possible date, the data needed for FFTF design criteria will not be delayed as it would be if it were necessary to wait for the completion of the building improvement project. The balance of the CANEL test stands has been moved in to the 300 Area to Building 306, where they will be cleaned, overhauled, and checked. As this work is completed, the test stands will be moved to Building 321-A.

The prototype cell has been moved into the building and the lead brick put in place. The lead glass window has been delivered and was on hand for timely installation. The cell is now nearly complete. Some work is being held up because of lack of support facilities which are to be

provided by the building improvement project. A radiation leak check has been conducted which indicated weak points around the door and the loading port. The changes indicated have been made. A final radiation leak check will be made after all work has been completed on the cell and before it is accepted for operation. The first use of the cell will be in remote testing of the test stands which are to be used in this cell and in the sodium loop facility. Design on these test stands cannot be considered complete until the complete test stand assembly has performed satisfactorily under remote conditions. Assembly and disassembly must be satisfactorily accomplished with master-slave manipulators. No radioactive materials will be introduced to the remote cell until these equipment tests have been completed. The test units which will operate in the prototype cell will require a vacuum system to attain the desired control of environment. The system is now being designed and will provide a vacuum manifold for the five test stands planned initially with capability for serving additional test stands later. The requirement that the manifold shall serve additional test stands at a later date does not increase the cost of providing adequate vacuum to the original five units. As reported in the last quarterly, the creep test rigs have been redesigned with a consequent reduction in size which makes it possible to install 15 test units where only 5 units of the original model could have been accommodated.

Initial installation will be limited to five units, but these will conform to a design which will allow addition of other test units whenever the additional units should be authorized.

The sodium loop which will provide high-temperature flowing sodium testing environments has been rescheduled for shipment from the manufacturer's plant. Shipping date has been set for April 5; the delay has been caused by late delivery of essential valves to the manufacturer. Design of the special creep test apparatus to be used in the sodium loop is complete. A prototype unit is being made up for use in performance tests which will be conducted first in the prototype cell, then in the nonradioactive test segment of the flowing sodium loop. Final acceptance of the design will hinge upon the satisfactory performance of the prototype unit in these tests. The test unit design for service in sodium features smooth-surfaced parts with shoulder-on-flange connections wherever possible rather than threaded connections. The sample loading system is only one-half the height of the original working model, and the extensometry has been moved outside the environmental chamber. The total result is that the overall height of the test unit is approximately half of the first working model devised; and the total cost, parts and machining costs, is also half of that for the original model. The overall simplifications and reduction in size of these test units make possible a considerable reduction in the size and cost of the shielding which will be built around

the test units for irradiated specimens. Design of the support piping and shielding for this portion of the recirculating sodium loop has progressed along with the design of the test stand. The scoping design package for this portion of the facility is 85% complete. It will be turned over to Laboratory Engineering Unit for integration into the overall building improvement project and actual construction.

A special dispenser for high-purity liquid sodium has been devised for transferring precisely-measured quantities of sodium from storage barrels to enclosed capsules or other containers. The receiving containers must be closed and fitted with valves and Swagelok fittings for vacuum, inert gas, and liquid sodium to prevent contamination of the sodium by the room atmosphere. This dispenser will adapt directly to an inert atmosphere glove box and can provide measured volumes of sodium with an estimated accuracy of ± 1.5 cc. Final assembly of this dispenser is now in progress.

The need for inert atmosphere facilities in which alkali metals can be stored, transferred, sealed in containers and cleaned from tools and containers has been recognized; and funds have been appropriated for two pieces of equipment. One will be a high-purity inert atmosphere glove box in which test capsules can be loaded and sealed with an arc weld without contaminating the high-purity alkali metal. The other will be an explosion-proof glove box with a low-grade inert atmosphere and a steam

nozzle for cleaning equipment of any residual alkali metal. Specifications for these items of equipment are being written.

An investigation into the potential fire hazards of sodium and other alkali metals turned up the uncomfortable fact that there is no adequate fire fighting clothing now available. The materials normally used for protective personnel cover in other fire situations have been shown to be dangerous when exposed to alkali metal fires. An example of this is aluminized asbestos, which flares and burns when hit with burning NaK. A search for suitable materials has turned up two which may be used together to make protective blankets and clothing. The outer layer would consist of "pluton" cloth which is made of fibrous graphite. This would be backed up with an insulating layer of one of the several forms of Fiberfrax, a product of the Carborundum Company. Both of these materials have an extremely high-service temperature (above 2300 °F) and are known to be nonreactive when exposed to burning NaK. The graphite cloth retains some strength after direct contact but has essentially no insulating properties. The Fiberfrax material has excellent insulating properties; but, in low-density form, it cannot withstand direct contact with burning NaK. It is hoped that a suitable composite can be made up from these two basic materials. Technical personnel of the Mechanical Metallurgy Unit are working closely with the Safety Engineers for PNL and Atomics International on the development of this material.

ATR GAS LOOP SUPPORTING STUDIES

MODEL GAS LOOP

P. M. Jackson

The model gas loop is a 2100 °F (1093 °C) recirculating helium loop which is operated to determine the effect of the helium atmosphere on materials and specimen holders, and to see if prolonged use will affect the operating characteristics of the new heater. This loop is a one-tenth size model of the gas loop that is being constructed for the Advanced Test Reactor at Idaho Falls.

The gas loop was operated a total of 3110 hr since installation of the new heater; 2130 hr were accumulated this fiscal year, and 920 hr this quarter. Corrosion test assemblies installed in both the vertical and horizontal test sections have undergone 770 and 1305 hr of exposure respectively. Results of periodic examinations of specimens exposed in both locations are reported elsewhere.

A variable frequency generator of foreign manufacture for the gas-bearing blower in the loop has a history of maintenance outages. Since the last modification, however, it has operated 920 hr without trouble.

Studies to Upgrade the Model Gas Loop

Specimens that are irradiated in the ATR Gas Loop will reach temperatures of 2500 °F or more. A study of methods of upgrading the model gas loop in order to provide out-of-reactor specimen evaluation at this higher temperature was completed. A supplemental resistance heater similar to the primary heater will be placed in

the vertical test section. This unit will consist of several molybdenum tube series connected electrically to an external power source. The corrosion specimens will be placed inside the molybdenum tubes and subjected to only a portion of the total helium gas flow. The incoming helium gas at about 1700 °F will split in about a 20-80% ratio; the greater percentage bypassing the corrosion specimens. The 20% portion of the gas will pass through the heater section around the specimens and exit at about 2500 °F. Attenuation of the hot fraction with the 80% bypassed gas, will yield a bulk outlet temperature of about 1900 °F. This gas is then further cooled by operation of the attenuator further downstream to a temperature compatible with the recuperator piping (about 1800 °F). A scope drawing of this heater-specimen holder is shown in the following Figure 7.47.

TEST ASSEMBLY EVALUATION

L. D. Blackburn

During the past several quarters, a refractory metal test assembly has been undergoing high temperature exposure in the model gas loop. The purpose of this experiment is to evaluate the basic design of the assembly itself, and also to study the effects of long term exposure in the high temperature helium atmosphere on the properties of refractory metals. Figure 7.48 illustrates the test assembly. Tensile specimens are mounted in slots in a series of concentric rings. The rings are attached to a central sleeve forming an integral cylindrical unit, or tier. Tiers

FIGURE 7.47. Supplemental Heater for Test Section

FIGURE 7.47. Supplemental Heater for Test Section

FIGURE 7.48. Prototype ATR Test Assembly

slide onto a central rod to form the completed test assembly. Each tier contains eighteen tensile specimens; the unit shown in Figure 7.48 consists of three tiers, while final ATR Gas Loop assembly will contain twelve tiers.

Table 7.19 summarizes the materials in the assembly and the exposure history in the model gas loop. Under the given exposure conditions, the test assembly performed satisfactorily. There was no significant warpage or distortion of the assembly from the elevated temperature exposure and

thermal cycling, nor was there any indication of diffusion bonding within the assembly; specimens were easily removed from the tiers, and the tiers were readily removed from the central rod. The only problem was binding of the retaining nut on the central rod, which resulted from thread galling during initial assembly operations.

Visual examination at selected intervals during the exposure indicated that specimens reacted with contaminants in the helium environment. Early in the exposure, the surface of

TABLE 7.19. Summary of Test Assembly Exposure in Model Gas Loop

Materials:	Nb, Ta, Mo, W Specimens SCb 291 Alloy (Nb-10Ta-10W) Holder
Temperature (Nominal)	940 °C
Axial ΔT	10 °C
Radial ΔT	35 °C
Time at temperature	775 hr
Number of thermal cycles (25 °C-940 °C-25 °C)	18
Average heating time	5 hr
Average cooling time	5 hr
Normal Helium Purity:	H ₂ O, N ₂ , H ₂ , O ₂ , CH ₄ each ≤ 1 ppm

molybdenum samples developed a gray, cloudy appearance. Later, tantalum samples developed a purple and then a black surface discoloration. Finally, niobium samples also developed a black discoloration, and tungsten samples developed a gray, cloudy appearance.

Electron microprobe analysis of the Nb-10 Ta-10 W holder material (which also exhibited black discoloration) revealed that significant quantities of Mo, Cr, Mn, Fe, and O were present on the surface. It seems most probable that the Mo and at least some of the O contamination resulted from oxidation of the Mo heating elements in the model loop heater. With oxygen contamination in the loop, the heating elements may well oxidize to form MoO_3 , which then volatilizes and is transported in the gas stream to the test assembly. The Cr, Mn, and Fe contamination probably results from evaporation of the Haynes 25 liner in the high temperature (1150 °C) outlet

section of the heater, and these vapors are also carried in the gas stream to the assembly. It may be noted that there was no indication of contamination by Ni or Co, the other major alloying elements in Haynes 25.

Results of room temperature tensile tests on specimens from the test assembly, along with those for as-received specimens, are summarized in Table 7.20. The specimens of Nb, Ta, and Mo were recrystallized in the as-received condition. Niobium samples from the model loop exposure show significant increases in strength, while tantalum exhibits a smaller increase. Although neither material shows large changes in room temperature ductility, it seems quite likely that the ductile-brittle transition temperature increased, but still lies well below room temperature. In contrast to the property changes in Nb and Ta, Mo seems to be unaffected by

TABLE 7.20. Room Temperature Tensile Properties of Refractory Metals After Model Gas Loop Exposure

Specimen	Yield Strength, psi	Tensile Strength, psi	Elongation % in 1 In.	Reduction of Area, %
<u>As received</u>				
Nb G24	16,400	30,500	53	98
Nb G26	14,100	29,900	46	98
Ta G15	41,600	50,600	39	97
Mo G32	75,100	75,800	6.3	1.9
<u>Exposed in Model Gas Loop at 940 °C for 775 Hr</u>				
Nb G18	37,000	47,000	35	95
Nb G22	34,100	46,000	35	95
Ta G4	45,500	58,000	44	90
Mo G34	73,300	80,000	4.9	4.8

model loop exposure. At this time, it is believed that interstitial contamination by oxygen and/or nitrogen plays a major role in the strengthening of Nb and Ta, although surface contamination by metal species may also contribute to the observed effects. Additional experiments and metallographic analysis are in progress to verify this hypothesis.

SUPERALLOY AND REFRACTORY METAL CORROSION STUDIES

L. A. Charlot

The weight change data from superalloy and refractory metal samples exposed in the ATR Model Loop and reported last quarter⁽³⁾ suggest that metal contamination of niobium and tantalum could have been partially responsible for their weight gain. Refractory metal samples taken from the 2100 °F test section and examined for possible contamination were first scanned through their cross-section with an electron beam microprobe, and, in the case of the tantalum sample, the reaction surface itself was scanned directly. The analytical results for samples exposed 504 hr in the Model Loop are discussed in the following section.

Molybdenum

Nothing unusual in microstructure was observed. Some iron and chromium presumably from the evaporating superalloy samples, were present as thin film on sample surface. Cobalt and nickel were not detected. Hardness was not determined.

Tungsten

Nothing unusual in microstructure was observed. A trace of iron, and a possible trace of chromium were found on the sample surface. Cobalt and nickel were not detected. Hardness was not determined.

Tantalum

Some small inclusions were noted in the microstructure. A possible trace of chromium was found on surface. Black, sooty surface deposit was not identifiable by either microprobe or X-ray diffraction analysis. The black deposit may bear a similarity to the surface case found on the niobium sample.

Niobium

The microstructure of this sample is shown in Figure 7.49. In addition to the surface case, contamination is evidenced by a large number of inclusions in the base metal. Microprobe analysis failed to reveal any metal contamination of the sample surface. X-ray diffraction investigation of the surface case showed it to be a Nb-N-O ternary compound, possibly of stoichiometry near $\text{Nb-N}_{0.9}\text{-O}_{0.1}$.⁽⁷⁹⁾ This finding implicates atmospheric gases as the major contaminant source, at least in the case of niobium.

Hardness traverses were made through the cross sections of the contaminated niobium and tantalum samples, and as-received samples of the same materials, to gain an idea of the extent to which their mechanical properties had been altered during the 504-hr Model Loop

250X

FIGURE 7.49. Microstructure of Niobium Sample Exposed in Model Loop for 504 hr at 2100 °F (Etchant: 30 Lactic Acid, 10 HNO₃, 10 HF)

exposure. Results of the traverses are shown in Table 7.21.

Note that there is a great deal of contamination-induced hardening in the exposed samples, indicating appreciable contaminant absorption. Diffusion calculations show that both nitrogen and oxygen will diffuse rapidly enough through the sample coupons to effect almost complete homogenization within the time duration of any one run. Because the samples were cooled slowly from the operating temperature, it is not possible to determine contaminant

levels or meaningful contaminant distributions by comparison with the microhardness data of other workers, nor is it possible at present to conclude which contaminant, oxygen or nitrogen, is the principal hardening agent.

Duplicate samples were added to the test holder in place of those analyzed. These samples have been through two cycles for a total of 763 hr at temperature. Table 7.22 summarizes the weight change of all samples to date.

TABLE 7.21. Microhardness Traverses VHN, 1 kg Load

Nb Sample		Ta Sample	
As-Received	Contaminated	As-Received	Contaminated
69	250	83	379
71	242	90	370
77	270	96	379
73	250	94	360
85	256	91	355
76	242		374
	245		365
			351

Future work will entail continued exposure of the corrosion samples to loop conditions. Samples will be added to or taken from the test pri-

marily in an effort to determine the extent of contamination in niobium and tantalum.

TABLE 7.22. Corrosion Samples Exposed to Model Loop Conditions

Material	Sample Number	Average Temperature	Weight Change, mg/cm ²	Time at Temp., hr	Number of Cycles
Hastelloy X	2	2100 °F	-4.85	1267	6
Haynes 25	2	High Gas	-4.56	1267	6
Haynes 25	7	Velocity	-3.68	1055	3
Hastelloy X	6	Section	-3.25	763	2
Haynes 25	6		-3.17	763	2
Molybdenum	4		-0.04	763	2
Niobium	3		1.83	763	2
Tantalum	4		1.12	763	2
Tungsten	4		-0.02	763	2
Niobium, 1 Zr	1		2.39	535	1
Hastelloy X	3	2025 °F	-1.96	1267	6
Hastelloy X	4	Low Gas	-1.81	1267	6
Haynes 25	3	Velocity	-2.26	1267	6
Haynes 25	4	Section	-2.10	1267	6
Molybdenum	3		-0.04	1267	6
Niobium	2		2.12	1267	6
Tantalum	2		1.26	1267	6
Tungsten	3		-0.05	1267	6
Hastelloy X	5		-1.80	1055	3
Haynes 25	5		-2.10	1055	3
Niobium	5		1.95	1055	3
Tantalum	3		1.15	1055	3
Niobium, 1 Zr	2		1.82	535	1
TZM	1		0.01	535	1

* A cycle refers to loop "start up" which consists of loop opening, closing, evacuation, and refilling with high purity helium (<1 vpm impurity) to 300 psi.

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ATR GAS LOOP OPERATION AND MAINTENANCE

G. A. Last

MODEL GAS LOOP STUDIES

The Model Gas Loop has operated a total of 3108 hr since installation of the new heater. Although the gas impurity level is maintained at less than 1 ppm by the by-pass cleanup system, there is evidence from corrosion specimens in the loop of in-leakage of air. Tests are planned to determine the source and amount of this in-leakage.

The refractory metal test assembly has been dismantled following a total exposure of 775 hr at 1700 °F (925 °C) in the Model Gas Loop. The Nb-10 Ta-10 W holder and the Nb and Ta specimens showed considerable black discoloration, while the Mo and W specimens exhibited gray, cloudy discoloration. Electron microprobe analysis revealed significant amounts of Mo, Cr, Mn, Fe, and O contamination on the surfaces of the holder. It seems probable that MoO_3 , Cr, Mn, and Fe vapors are formed in the heater by oxidation of the Mo heating elements and evaporation from the Haynes 25 liner, and these vapor species are then carried through the gas stream to the test assembly.

Room temperature tensile tests demonstrated significant strengthening of Nb, only modest strengthening of Ta, and no strength change of Mo as a result of the model loop exposure. Since no large changes in ductility accompanied the strengthening of Nb

and Ta, the ductile-brittle transition apparently still lies well below room temperature.

Specimens irradiated in the ATR Gas Loop will reach temperatures up to 2500 °F (1370 °C). A study is being made of methods to raise the specimen temperature within the vertical test section of the Model Gas Loop in order to more closely simulate these temperatures. Three methods have been considered: (1) heating the gas with a resistance type heater, (2) induction heating the specimens, and (3) resistively heating tubular sections which would contain the test specimens. The third method has been selected as the one having the greatest potential of success and requires the least amount of development effort. This arrangement would utilize a number of molybdenum tubes that are electrically connected in series. The test specimens would be placed inside these tubular heating elements and completely insulated (electrically) from them. The cluster of tubes would be arranged to flow a portion of the helium over the specimens and by-pass the remainder of the gas through the annular passage between the present test section and the auxiliary heater. The specimen temperatures will be controlled by varying the gas flow or the power to the auxiliary heater. A computer program will be used to determine the specimen temperatures that can be

reached by this method under varying flows and power settings.

ANALYTICAL INSTRUMENTATION FOR THE ATR GAS-COOLED LOOP

The transfer facility for the gas loop is designed to operate with dry air at a dew point of -150°F (-100°C). The instrumentation for measuring the dew point was inspected by PNL and Ebasco personnel to determine acceptability of the units.

Performance of the hygrometers was monitored by supplying them with a gas of known dew point. The gases were generated by use of a tempering coil and cold bath. Liquid nitrogen was used to prepare a gas that contained less than 2.5×10^{-19} mm water vapor. Although this value is considerably lower than the hygrometers will measure, it did provide the zero point gas to determine whether the zero suppression on the hygrometers was adequate to give a base line within the accuracy of our specifications.

After the system had been dried out, the recorder indicated a reading of 0.06 ppm which corresponds to a frost point of -136°F (-93°C) at the local atmospheric pressure. This put the minimum reading within the tolerance of the specifications.

Other monitors in the system are used at the higher range of water vapor and the accuracy in these ranges was checked and found to be adequate. Based on our requirements and specifications, the system was accepted for shipment.

Continual use of the Greenbrier chromatographs on the Model Gas Loop has shown minor weaknesses in the

equipment associated with an instability of the base line. This instability appeared to be mainly from the loss of voltage regulation in the electrometer. The manufacturer has supplied two new electrometers, one for the chromatograph and one for the total impurity monitor. These units have been installed and are in the process of checkout.

Recent studies in the Model Loop have proven that extreme sensitivity in the chromatographs will be required to monitor impurity levels in the ATR Gas Loop. Work will continue on the units to ensure that total impurities can be measured at levels below 1 ppm.

INVESTIGATION OF TYPE 304H STAINLESS STEEL LONGITUDINAL PIPE WELDS

In compliance with a request by the Idaho Operations Office, gas tungsten-arc welds made by Swepeco Tube Corporation were evaluated by W. F. Brown, Battelle-Northwest. These welds were from a section of the pressure containment pipe for the ATR Gas Loop. The Solar Aircraft Company, who is fabricating the piping assembly, purchased the 12 in., schedule 40, type 304H stainless steel piping from Swepeco Tube Corporation.

Swepeco's manufacturing process consists of forming plate stock into a tubular configuration and welding the longitudinal square groove butt joint using their gas tungsten-arc welding process called "Syncroweld." The Syncroweld process utilizes two torches positioned so that welding is performed from the underside of the joint as well as the upper side simultaneously without filler wire addition. This welding

procedure yields a joint configuration comparable to a double-welded butt joint.

Evaluation of the 7 1/2 in. long weld was based on the results of visual examination, X-ray examination, fluorescent penetrant inspection, and metallographic examination. The criterion for evaluation was Section III, Nuclear Vessels, ASME Boiler and Pressure-Vessel Code.

Fluorescent penetrant inspection revealed several surface cracks. Metallographic examination revealed that over 50% of the joint length had incomplete fusion penetration. Although diffusion bonding had occurred in the unfused areas from high temperature and pressure, the bond was of relatively poor quality compared with the fused area. Although X-ray could not detect this condition, the metallographic examination indicated that the process was out of control.

Based on this investigation, it was concluded that the welds submitted for evaluation were not acceptable and did not meet the intent of Section III of the ASME Boiler and Pressure Vessel Code.

SUPERALLOY AND REFRACTORY METAL CORROSION STUDIES

Corrosion coupons exposed in the ATR Model Loop (504 hr total exposure at temperature) continue to follow the weight change trend previously reported. Metallography and microprobe analysis of the samples taken from the high gas velocity section (2100 °F) (1150 °C) is presently being completed. Cursory examination of the microstructure of Hastelloy X-280 and

Haynes 25 which had weight losses of 2.77 and 2.67 mg/cm² respectively, show metal loss from grain boundaries and what appears to be subsurface voids. Niobium, 2.24 mg/cm² total weight gain, shows a continuous surface case approximately 8 μ thick. The base metal also contains what appear to be intermetallic inclusions. After removal from the Model Loop, the tantalum sample, 1.77 mg/cm² weight gain, exhibited a loose, easily wipeable black deposit on the surface. However, metallography failed to show a well defined subsurface layer. The contaminant has yet to be determined for either niobium or tantalum.

Duplicate coupons were added to the test holder in place of those analyzed and the assembly will again be exposed to loop conditions.

Electron microprobe analysis of the tantalum, niobium, molybdenum and tungsten samples taken from the 2100 °F (1150 °C) heater discharge section of the Model Loop after a 504 hr exposure failed to show foreign metal contamination of their respective surfaces. Constituents of the black surface noted on tantalum and the surface case on niobium were not identifiable by microprobe. X-ray diffraction of these two samples did reveal the nature of the contamination on the niobium sample. Strong diffraction lines suggest Nb-N-O, a ternary compound of niobium, nitrogen, and oxygen of stoichiometry Nb-N_{0.9}-O_{0.1}. The contamination on tantalum, although not identified by X-ray diffraction, may be similar to the niobium contamination.

Corrosion coupons in the lower temperature (2025 °F) (1105 °C)

discharge section of the loop have about 732 hr total exposure time at temperature. The coupons replacing those taken from the higher temperature section now have 228 hr exposure. Within experimental tolerances, these coupons follow the weight change behavior established by the first set. The samples are continuing their exposure in the Model Loop.

THERMAL-HYDRAULIC ANALYSIS

A steady-state heat transfer program was set up to calculate temperatures of a niobium hanger rod and test section liner under an assumed "worst case" condition in the ATR helium loop. Temperatures were calculated for a representative horizontal cross section through the test section. Thermal radiation effects were accounted for. Helium temperature was taken as 2000 °F (1095 °C), and a heating rate of 25 W/g was assumed.

At the above conditions, the hanger rod temperature will be 2530 °F (1390 °C), the liner temperature will be 3450 °F (1900 °C), and the tube wall will be at approximately 950 °F (510 °C). Since the liner will not bear any structural load other than its own weight, the temperature, while it is high, should not lead to any gross structural failure. The strength of the niobium hanger rod at 2530 °F (1390 °C) will be investigated, and some means of lowering the rod temperature may have to be devised.

It is planned to run more computer cases to calculate hanger rod and liner temperatures with varying helium

temperatures, materials, and heating rates.

Experimental measurements of the pressure drop across the test assembly in the Model Gas Loop at several temperatures and gas flow rates have been obtained. Pressure drops at temperatures above 500 °F (260 °C) were higher than those obtained in similar experiments conducted two years ago. In both sets of experiments, however, the measured pressure drop multiplied by the helium gas density is a linear function of the square of the mass flow rate. This is the expected relationship for frictional losses in a fluid flow system. Extrapolation of the higher pressure drop data from the recent experiments to ATR operating conditions still leads to the conclusion that the maximum allowable pressure drop for the ATR specimen test assembly will not be exceeded with the current design.

VENDOR DATA REVIEW

About 60% of the vendor data on the ATR Gas Loop has been reviewed and comments submitted to the architect-engineer.

Contract submittals on the most recent ATR Gas Loop orders have been reviewed. Some of the submittals from the various vendors, such as the heat exchangers, require a complete review of the analysis to determine code and material compliance. The superalloys used in the regenerative exchanger are being reviewed thoroughly based on our past experience with these materials in the Model Gas Loop.

METALLIC FUELS

G. A. Last

The inherent high density, mechanical strength, high thermal conductivity, and low fabrication costs associated with metallic fuels combine to make the goal of improving swelling resistance and corrosion resistance of fuel elements worthwhile.

The Metallic Fuels Program is combining the fundamental concepts obtained from various metallic fuel research efforts with the knowledge gained from the actual operating behavior of metallic fuels to develop fuel elements exhibiting superior in-reactor performance. This program includes studies of thorium and uranium base alloys irradiated as prototype fuel elements in pressurized hot water loops as well as studies of clad rods irradiated in temperature-monitored, NaK-filled capsules. Both material parameters and fuel element design parameters are being evaluated.

THORIUM BASE ALLOYS

R. K. Marshall and J. W. Goffard

The use of metallic thorium as a fertile material in the fuel of a nuclear reactor offers the advantages of long life and high specific power operation. The isotropic crystal structure of thorium obviates concern over irradiation "growth" or "growth induced" swelling which are important considerations for anisotropic fuels such as uranium. The high melting point (1750 °C) of thorium is also an advantage in that fission gas swelling would be expected to be minimal below about 800 °C (0.53 of the absolute

melting temperature). Furthermore, thorium possesses excellent thermal conductivity (about twice that of stainless steel). Thus, high specific powers and surface heat fluxes can be achieved without undue regard that the fuel temperatures will become excessive. The present program is engaged in evaluating the suitability of prototype thorium-uranium elements under power reactor operating conditions.

Irradiation Testing

Three thorium-2.5 wt% uranium (03.2% ^{235}U)-1.0 wt% zirconium tubular fuel elements clad in Zircaloy-2 are under irradiation in the P-7 loop in the ETR. Three fuel elements which were being irradiated in the M-3 loop are being stored in the viewing basin at the ETR site. The P-7 loop is normally operated at 260 °C and 1600 psi and has a peak thermal flux of 3.7×10^{13} n/cm²-sec. The pH is maintained at 9 to 10 with LiOH. The M-3 loop is operated at 260 °C and 2,000 psi and has a peak thermal flux of 2.0×10^{13} n/cm²-sec. The pH is maintained at the same value as the P-7 loop but with NH₄OH.

The current status of the six test elements is summarized in Table 9.1. The accumulated exposures are based on loop calorimetric data and vary from 2,500 to 17,700 MWd/ton of fuel alloy with corresponding volume changes varying from -0.5% to 3.1%. The fuel volume increases reported were obtained by weighing the fuel elements in water

TABLE 9.1. Irradiation Data on Th-2.5 wt% U-1 wt% Zr Fuel Elements

GEH-10	Percent Fuel Swelling	Burnup		Surface Temp., °C	Maximum Core Temp., °C	Specific Power W/g	Surface Heat Flux, Btu/hr/ft ²	Thermal Cycles†
		Fissions/cm ³ , MWd/ton	at. %					
65*	3.1	6.0 x 10 ²⁰ (17,700)	2.03	295	480	42	6.1 x 10 ⁵	375
64*	1.7	4.3 x 10 ²⁰ (12,300)	1.41	285	430	33	4.9 x 10 ⁵	314
71*	0.9	3.0 x 10 ²⁰ (8,400)	0.96	295	510	48	7.0 x 10 ⁵	175
72**	0.1	1.5 x 10 ²⁰ (4,300)	0.49	300	490	43	6.2 x 10 ⁵	103
70**	-0.5	1.3 x 10 ²⁰ (3,900)	0.45	295	470	39	5.6 x 10 ⁵	103
84**	0.1	0.9 x 10 ²⁰ (2,500)	0.29	290	440	33	4.8 x 10 ⁵	58

* Temperatures, corrected for oxide buildup. Heat generation conditions during ETR Cycle 87.

** Temperatures, not corrected for oxide buildup. Heat generation conditions during ETR Cycle 84.

† A thermal cycle is defined as a change from 90 to 100% of maximum power to 0 to 10% of reactor power and return to 90 to 100% of reactor power.

during reactor shutdowns. The rate of swelling is roughly 2% per 10,000 MWd/ton which is slightly greater than a value calculated by considering the conversion of ²³²Th atoms to more dense ²³³U atoms and the conversion of ²³⁵U atoms to less dense fission product atoms. Periodic visual examinations of the elements continues to show excellent irradiation stability with no indication of warping, bowing or closure corrosion.

The maximum exposure element, GEH-10-65, has experienced more than 690 effective days of irradiation at maximum fuel temperatures between 350 and 600 °C. The temperature history and cumulative swelling of this element is shown in Figure 9.1, as a function of exposure. The measured swelling for this element is only 3.1% after

2.0 at.% burnup (R=1.5) which is slightly greater than the calculated theoretical minimum value.

The bulk outlet temperature of the P-7 loop water was reduced 50 °C (90 °F) beginning with Cycle 85 to an operating temperature of 204 °C (400 °F) in order to reduce the temperature of the cladding. Examination of a fuel element which had been returned to BNW after attaining an exposure of 11,850 MWd/ton revealed a 1.3 mil thick oxide on the surface of the clad which probably increased the clad surface temperature to 350 °C due to the insulating nature of the oxide. This increased clad temperature could result in an increased clad corrosion rate which would limit the goal exposure of the fuel. To avoid accelerated corrosion, the loop

FIGURE 9.1. Swelling Behavior of Th-U-Zr Fuel Element GEH-10-65 LiOH Demineralizer

temperature was decreased to reduce the clad surface temperature to 300 °C which is in keeping with the original objectives of the test. The temperature data for fuel elements GEH-10-64, 65, 71 listed in Table 9.1 were corrected for oxide buildup by estimating a 50 °C temperature rise across the oxide film. No attempt has been made to correct data which were obtained before Cycle 85.

Postirradiation Examination

The results of the postirradiation studies conducted with the Th-U-Zr element (GEH-10-66) removed after reaching an exposure of 11,850 MWd/ton (1.4 at.% BU) are being summarized in a report "Irradiation Behavior of Th-U-Zr Metallic Fuel Elements," being written by J. W. Goffard and R. K. Marshall. This report will summarize the behavior to date of these

elements still under irradiation, Table 9.1.

HIGH EXPOSURE URANIUM IRRADIATION TEST

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R. E. Leggett, R. K. Marshall,
J. W. Weber

Irradiation studies have shown that uranium swelling can be reduced significantly by external pressure and by appropriate alloying additions to uranium to produce increased solid solution and second phase inter-metallic precipitates. It has also been observed that under irradiation uranium takes on plastic characteristics.

A fuel element irradiation test has been designed which capitalizes on these known characteristics. The fuel specimens, incorporating a void in the center of the uranium, are co-extrusion clad with Zircaloy-2. The combined effect of the uranium plasticity and the restraints from the cladding and the pressurized loop will direct the uranium swelling inward where it will be accommodated by the central hole.

The fuel specimens are 0.45 in OD by 6.25 in. long including end caps. Two thicknesses of Zircaloy-2 cladding, 0.025 and 0.050 in., and three uranium void volumes, nominally, 5, 10, and 20% are combined in this test. Two uranium alloys, U + 150 ppm Fe-100 ppm Si and U + 350 ppm Fe-800 Al, are utilized in the study in order to establish the influence of alloying additions on the performance of this type fuel element.

Fabrication

Fabrication of the Zircaloy-2 fuel elements through coextrusion, drilling of the central hole, and brazing and welding of the end caps has been described in previous quarterly reports.^(1,2) Preirradiation characterization of the elements consists of dimensional measurements of length, diameter and warp and determination of bulk fuel element density by dry and submerged weight. Volume of the central hole is determined prior to brazing in the end caps by measuring the weight of CCl_4 required to fill the hole. Additional fuel elements are being fabricated to replace some of those now under irradiation in the ETR but scheduled for early removal and examination.

Irradiation Testing

The test was designed for irradiation in the ETR M-3 water loop. This facility operates with a water temperature of 260 °C at 2,000 psi. The pH is controlled at 9 to 10 by NH_4OH . The 6.25 in. long rods are supported in an assembly consisting of four clusters of 6 rods in hexagonal arrays.

Two additional cycles of irradiation were successfully completed during this report period. A total of twenty-seven fuel elements have been irradiated in the test, eleven elements for three cycles, nine elements for two cycles, and seven elements for one cycle. The exposures vary from a maximum 3344 MWd/ton to

a minimum of 281 MWd/ton. The maximum fuel core temperatures range from 365 °C to 540 °C. After each irradiation cycle the fuel elements are removed from the basket and assembly holder for examination and weight measurements in water in the ETR basin.

Details of the irradiation conditions and results of the interim weight measurements are given for each element in Table 9.2. Fuel element volume changes were calculated from submerged weight measurements. The average fuel irradiation temperatures have not varied appreciably during the three irradiation cycles, ETR 85, 86, and 87. The exposure and volume changes for each cycle are shown along with the accumulated exposure and accumulated volume changes.

All fuel elements show an accumulated volume decrease, ranging from 0.1% to a maximum of 1.8%. If all the volume decrease was from diameter change, this maximum of 1.8% represents a decrease in diameter of approximately 0.004 in. The volume decrease on most elements now ranges from 0.5 to 1.0%.

The volume decrease as a function of exposure is shown by the curves in Figures 9.2 through 9.7. Each figure represents a single set of nominal void volume and cladding thickness. Each curve represents the volume change with progressive exposure on a single fuel element. The changes are small and the data reveals some inconsistencies but there are several trends that are developing. There appears to be an exposure range at which the volume decrease stops

and begins to reverse that is dependent on the cladding thickness and initial central void volume in the fuel. For elements with 0.050 in. thick Zircaloy-2 the volume decrease has stopped at exposures as low as 1,000 MWd/ton where the initial internal void volume is 20%. Where the initial internal void volume is 10% the decrease in fuel element volume does not appear to stop until the exposure is about 2,000 MWd/ton. The elements with 5% void volume have not reached high enough exposures yet to show much of a trend. For elements with 0.025 in. thick Zircaloy-2 the range of exposures is not as great as for the heavier clad elements because of their lower flux positions in the reactor. However, with the thinner cladding all elements having 20% initial void volume except for one of alloy type 1 have exceeded 1,600 MWd/ton with no apparent halting of the volume decrease. The thinner clad elements with 10% void volumes show no indication that at the present exposures the volume decrease has stopped.

With a 0.025 in. cladding the initial rates of volume decrease appear to be less for the U + Fe-Al (alloy 1) than for the U + Fe-Si (alloy 2) at all three initial void volumes. With 0.050 in. cladding there is no significant difference in the initial rate of volume decrease between elements of alloy 1 and alloy 2.

The rate of volume decrease for elements with the 0.025 and 0.050 in. thick cladding are essentially the same, despite the fact that the maximum fuel core and fuel surface

TABLE 9.2. Irradiation Data on Hollow Core Metallic Uranium Fuel Elements

GEH-10	Preirradiation	Zr-2 Cladding Thickness (in.)	Alloy*	Average Irradiation				Cycle 85		Cycle 86		Cycle 87		Total Accumulated	
	Uranium			Temperatures for Cycles 85, 86, 87	Exposure	Fuel Element Volume Change %	Exposure	Fuel Element Volume Change %	Exposure	Fuel Element Volume Change %	Exposure	Fuel Element Volume Change %	Exposure	Fuel Element Volume Change %	
	Void														
	Volume														
%		Max. Core °C	Fuel Surface °C	MWd/ton		MWd/ton		MWd/ton		MWd/ton		MWd/ton			
103	21.5	0.025	1	425	370	690	-0.3	970	-0.3	---	(1)	---	1660	-0.6	
102	20.5	0.025	1	430	370	690	-0.3	970	-0.3	506	-0.2	---	2166	-0.8	
101	18.2	0.025	1	400	345	510	-0.1	725	-0.4	376	0	---	1611	-0.5	
104	15.5	0.025	1	405	345	510	-0.1	725	-0.3	376	-0.3	---	1611	-0.7	
105	7.7	0.025	1	370	320	340	0	485	-0.1	---	(1)	---	825	-0.1	
109	28.4	0.050	1	510	460	1050	-0.5	1455	+0.1	744	+0.1	---	3249	-0.3	
151	26.0	0.050	1	525	470	---	(1)	---	(1)	---	-0.6	---	804	-0.6	
108	25.2	0.050	1	485	440	---	(1)	---	---	-0.6	---	(1)	---	1515	-0.6
110	16.5	0.050	1	485	430	---	(1)	---	---	-0.5	633	-0.1	---	1873	-0.6
107	11.8	0.050	1	525	460	860	-0.4	1205	-0.3	632	+0.1	---	2697	-0.6	
111	8.7	0.050	1	465	405	---	(1)	---	---	-0.4	502	-0.1	---	1482	-0.5
112	7.3	0.050	1	455	405	---	(1)	---	---	-0.1	---	(1)	---	980	-0.1
120	21.2	0.025	2	475	400	850	-0.5	1190	-0.5	611	0	---	2651	-1.0	
121	21.1	0.025	2	470	400	850	-0.5	1190	-0.5	---	(1)	---	2040	-1.0	
146	12.8	0.025	2	410	355	---	(1)	---	---	-0.4	414	-0.6	---	1219	-1.0
122	11.4	0.025	2	365	320	340	-0.3	485	-0.3	252	-0.2	---	1077	-0.8	
150	10.6	0.025	2	383	331	---	(1)	---	(1)	---	-0.5	---	281	-0.5	
119	10.4	0.025	2	440	365	555	-0.4	785	-0.3	414	-0.1	---	1754	-0.8	
124	5.0	0.025	2	395	330	365	-0.3	525	-0.2	274	-0.2	---	1164	-0.7	
123	4.7	0.025	2	395	330	365	-0.3	525	-0.2	---	(1)	---	890	-0.5	
152	22.9	0.050	2	534	475	---	(1)	---	(1)	---	-1.8	---	828	-1.8	
114	22.6	0.050	2	540	480	1080	-0.7	1500	+0.1	764	0	---	3344	-0.6	
115	18.9	0.050	2	505	455	---	(1)	---	---	-1.3	---	(1)	---	1560	-1.3
113	16.4	0.050	2	525	460	905	0.4	1265	-0.2	649	0	---	2819	-0.6	
116	14.7	0.050	2	520	455	---	(1)	---	---	-0.6	666	-0.1	---	1976	-0.7
117	6.0	0.050	2	485	425	---	(1)	---	---	-0.4	---	(1)	---	1040	-0.4
118	5.9	0.050	2	490	425	---	(1)	---	---	-0.7	532	-0.1	---	1572	-0.8

* Alloy Compositions:

1. U + 350 ppm Fe + 800 ppm Al

2. U + 150 ppm Fe + 100 ppm Si

(1) Not irradiated this cycle.

FIGURE 9.2. Volume Change for
Zircaloy-2 Clad Uranium Fuel Elements
with Hollow Cores

FIGURE 9.3. Volume Change for
Zircaloy-2 Clad Uranium Fuel Elements
with Hollow Cores

FIGURE 9.4. Volume Change for
Zircaloy-2 Clad Uranium Fuel Elements
with Hollow Cores

FIGURE 9.5. Volume Change for
Zircaloy-2 Clad Uranium Fuel Elements
with Hollow Cores

FIGURE 9.6. Volume Change for
Zircaloy-2 Clad Uranium Fuel Elements
with Hollow Cores

temperatures may run 75 to 100 °C hotter on the thicker clad elements.

Neutron radiographs were obtained on eight elements discharged from the assembly after Cycle 86. These were elements 103, 105, 108, 112, 115, 117, 121, and 123. The neutron radiography was performed by Battelle Memorial Institute, using the Battelle Research Reactor at Columbus, Ohio. Figure 9.8 through 9.11 show positive prints of the neutron radiographs along with their comparable preirradiation gamma ray radiographs. The rods were chosen for comparison of the pre and interim irradiation conditions of the central void hole in elements from each alloy

at the 5% and 20% nominal void volumes and with 0.025 and 0.050 in. Zircaloy-2 cladding.

There is no measurable change in the central hole diameters. Several contour features discernible in the preirradiation radiographs can still be readily identified in the interim neutron radiographs. There may be a slight amount of surface roughening, but no general collapse of the uranium into the hole.

The circular dark areas on the neutron radiographs were caused by drops of water on the elements during the radiographing. The horizontal streaks near the top of 103, 105, 108 and 112

FIGURE 9.7. Volume Change for
Zircaloy-2 Clad Uranium Fuel Elements
with Hollow Cores

are from the radiography holders. Resolution of the radiographs limits the accuracy of the diameter measurements to about ± 0.010 in. Actual diameter decreases in the center hole for the maximum possible external diameter decrease on any of the elements radiographed would be less than the accuracy of measurement. These eight elements were returned to the ETR and are now being irradiated again. Additional neutron radiographic examination is planned as these and other fuel elements reach higher exposures.

During the visual examination in the reactor basin of those elements irradiated during Cycle 87, elements 116 and 152 each showed evidence of accelerated corrosion on a weld and end cap. This was evidenced by a light gray area covering about 100° of the weld circumference and extending over part of the end cap. The accelerated corrosion is believed caused by excess Zr-Be braze in the weld and some braze left on the end cap after the final machining and cleaning. Element 152 also showed the most severe

GEH 10
 Preirradiation Void
 Alloy
 Exposure
 Maximum Fuel Temperature
 Surface Fuel Temperature
 Fuel Element Volume Change

105
 7.7%
 U+350 ppm Fe + 800 ppm Al
 825 MWD/T
 365 °C
 320 °C
 -0.1%

123
 4.7%
 U+150 ppm Fe + 100 ppm Si
 890 MWD/T
 385 °C
 330 °C
 -0.5%

* Postirradiation Neutron
 Radiographs Taken
 at 0° and 90°

** Preirradiation
 Radiographs Taken
 at 0° and 90°

*FIGURE 9.8. Radiographs of Hollow
 Core Uranium Fuel Elements Clad with
 0.025 in. Zircaloy-2*

GEH 10
 Preirradiation Void
 Alloy
 Exposure
 Maximum Fuel Temperature
 Surface Fuel Temperature
 Fuel Element Volume Change

103
 21.5%
 U+350 ppm Fe + 800 ppm Al
 1660 MWD/T
 415 °C
 360 °C
 -0.6%

121
 21.1%
 U+150 ppm Fe + 100 ppm Si
 2040 MWD/T
 455 °C
 390 °C
 -1.0%

* Postirradiation Neutron
 Radiographs Taken
 at 0° and 90°
 ** Preirradiation Radiographs
 Taken at 0° and 90°

Neg 671079-4

FIGURE 9.9. Radiographs of Hollow
 Core Uranium Fuel Elements Clad with
 0.025 in. Zircaloy-2

GEH 10
 Preirradiation Void
 Alloy
 Exposure
 Maximum Fuel Temperature
 Surface Fuel Temperature
 Fuel Element Volume Change

112
 7.3%
 U+350 ppm Fe + ppm Al
 980 MWd/T
 455 °C
 405 °C
 -0.1%

117
 6.0%
 U + 150 ppm Fe + 100 ppm Si
 1040 MWd/T
 485 °C
 425 °C
 -0.3%

* Postirradiation Neutron
 Radiographs Taken at
 0 and 90°
 ** Preirradiation Radio-
 graphs Taken at
 0 and 90°

Neg 671079-1

FIGURE 9.10. Radiographs of Hollow
 Core Uranium Fuel Elements Clad with
 0.050 in. Zircaloy-2

GEH 10
 Preirradiation Void
 Alloy
 Exposure
 Maximum Fuel Temperature
 Surface Fuel Temperature
 Volume Change

108
 25.2%
 U + 350 ppm Fe + 800 ppm Al
 1515 MWd/T
 485 °C
 440 °C
 -0.6%

115
 18.9%
 U + 150 ppm Fe + 100 ppm Si
 1530 MWd/T
 505 °C
 455 °C
 -1.3%

* Postirradiation Neutron
 Radiograph Taken at
 0 and 90°
 ** Preirradiation Radio-
 graphs Taken at
 0 and 90°

Neg 671079-2

FIGURE 9.11. Radiographs of Hollow
 Core Uranium Fuel Elements Clad with
 0.050 in. Zircaloy-2

warp observed on any element in this test to date. The warp has not been accurately measured but it is known to be less than 0.1 in. Elements 116 and 152 were removed from the test for further examination. Warp observed on other elements during the earlier irradiation cycles does not appear to be increasing.

Continued interim weight measurements, neutron radiography, and visual examinations will provide the needed information to evaluate the irradiation performance of this fuel element

design. As more data becomes available for higher exposures on the fuel elements with 10 and 5% nominal void volumes and for the 0.025 in. Zircaloy-2 clad elements, better analysis can be made as to the effects of the many variables on the irradiation performance of the fuel elements.

At the present levels of exposures there does not appear any problems to prevent these fuel elements from achieving their intended high goal exposures of 10,000 to 20,000 MWd/ton.

NONDESTRUCTIVE TESTING RESEARCH

J. C. Spanner

ELECTROMAGNETIC TESTING RESEARCH

A comparison of the relative effectiveness of several test coil excitation methods for eddy current nondestructive tests is being made. The main objectives of the study are to clarify the relationships between different excitation methods and to determine whether an excitation method can be found which will result in simplification of analyzing circuits. This simplification of circuits is needed to reduce circuit complexity as the multiparameter eddy current test is expanded to separate a greater number of parameters.

The study will cover several phases including: (1) a review of the theory relating the different methods of test coil excitation, detection, and output signal analysis; (2) a check of the theory by comparing results of applying the different excitation methods to simulated and real eddy current tests; and (3) an investigation of signal-to-noise problems relating to the various excitation methods and signal analysis techniques.

Resistance-capacitance (R-C) networks have been selected to serve as simulators of eddy current test specimens and test coil assemblies in this study to replace inductance-resistance networks which were used in some previous studies. The R-C networks have one main superior quality for comparative studies which is due to capacitors having, in general, higher quality (lower losses) than inductors.

Thus measured performance is based upon the simplest theoretical considerations.

R-L Eddy Current Test Model

The simplest eddy current test in theory, but one which is never exactly realized, is that which involves the propagation of plane electromagnetic waves in a conducting semi-infinite space. In this simple case, a wave function (U) may be shown to vary with depth χ in the semi-infinite half space as:

$$U = U_0 e^{-\gamma \chi} \quad (1)$$

where: e = base of natural logarithms

$\gamma = a + jb$ = propagation constant

χ = distance

α = attenuation constant

β = phase shift or wavelength constant

It can be shown that the propagation constant for the case being considered is:

$$\gamma = \sqrt{\frac{\omega \mu \sigma}{2}} + j \sqrt{\frac{\omega \mu \sigma}{2}} = \frac{1}{\delta} + j \frac{1}{\delta} \quad (2)$$

where;

$j = \sqrt{-1}$

$\omega = 2 \pi f$

ν = permeability of free space
(for nonmagnetic metals)

σ = electrical conductivity of the metal

δ = skin depth (depth at which the wave function is reduced by a factor of e).

Equation (2) may be written in another form using the equality

$$\frac{1+j}{\sqrt{2}} = \sqrt{j} \quad ; \quad \gamma = \sqrt{j\omega\mu\sigma} \quad (3)$$

The propagation constant given in operational form is:

$$\gamma(s) = \sqrt{s\mu\sigma} \quad (4)$$

where: s = the generalized frequency

The units of the permeability of free space are inductance per unit length (for example, henrys per meter), and placing the conductivity equal to the reciprocal of the resistance R per unit length Equation (3) is rewritten:

$$\gamma = \sqrt{\frac{j\omega L}{R}} \quad (5)$$

A transmission line equivalent to the metal for this plane wave case can be now obtained by comparing the elements of Equation (5) with those of Equation (6) which gives the relation-

ships between series impedance (Z) per unit length, shunt admittance per unit length, and the propagation constant (γ) of a transmission line having distributed parameters:

$$\gamma = \sqrt{ZY} \quad (6)$$

A reasonable assumption is to relate $j\omega L$ of Equation (5) with the Z of Equation (6) and $\frac{1}{R}$ of Equation (5) with the admittance (Y) of Equation (6). This gives a transmission line equivalent to the metal, for the case of plane wave propagation, having a series inductance equal to L henrys per meter, and a shunt resistance equal to R ohms per meter as shown in Figure 10.1. The circuits shown here are used to represent either a transmission line having distributed constants, or a network having lumped constants. In the lumped constant representation, it is understood that the transmission line equations do not apply except in the limit as the number of network sections per unit distance increases without limit. For the lumped network, network theory applies and electrical behavior can be described to any desired accuracy.

FIGURE 10.1 R-L Network Model of an Eddy Current Test.

However, in this discussion, the transmission equations are used, realizing that they are only approximate for the lumped case.

An equivalent transformer section has been placed at the input end of the transmission line (or lumped network) to represent the eddy current test coil inductance (L_1) and its mutual inductance (L_M) electromagnetic coupling with the metal.

A convenient way to use this model is to drive it with a fixed a.c. input current and observe variations in input voltage as a function of line length (metal thickness) or $\frac{1}{R}$ (metal conductivity). The complex voltage observed then represents the input impedance since I_{in} is constant and

$$E_{in} = I_{in} Z_{in} \quad (7)$$

R-C Eddy Current Test Model

The dual of the circuit of Figure 10.1 can be formed to give the resistance capacitance circuit shown in

Figure 10.2. This dual is formed by replacing: (1) series inductors with shunt capacitors, (2) shunt inductor with a series capacitor, and (3) shunt resistors with series conductances.

The role of currents and voltages, and admittance and impedance, are also interchanged, then if the circuit in Figure 10.2 is driven with a constant voltage, the resulting input current flowing will vary as the voltage did at the input of the network in Figure 10.1. Thus,

$$I_{in} = E_{in} Y_{in} \quad (8)$$

These relationships have been confirmed by deriving Equations (9) and (10) for the input impedance Z_{in} of the network in Figure 10.1 and the input admittance Y_{in} for the network in Figure 10.2 respectively.

$$Z_{in}(s) = \frac{s^2(L_1 L_2 - L_M^2) + s L_1 \sqrt{s L R}}{s L_2 + \sqrt{s L R}} \quad (9)$$

$$Z_{in}(s) = \frac{s^2(C_1 C_2 - C_M^2) + s C_1 \sqrt{s C G}}{s C_2 + \sqrt{s C G}} \quad (10)$$

FIGURE 10.2. R-C Network Model of an Eddy Current Test

Eddy Current Coil Design Studies

An investigation is being conducted on the theoretical and practical aspects of eddy current probe design so that general guidelines can be developed for future probe construction. A literature search and review is underway to collect pertinent information from related fields such as conventional eddy current NDT theory, transmission line theory, and network analysis.

Each testing situation is characterized by a number of parameters such as; operating frequency, probe configuration, type of operation (absolute or differential), and the specific physical characteristics of the probe. The first three test conditions above are generally dictated by the test specimen and the properties to be measured or detected. Most of the design criteria for determining these test conditions, over a limited frequency range, appear in the literature. Most treatments of eddy current theory in the literature attempt, however, to rationalize out the effects of the physical characteristics of the probe coil by dividing the impedance of a coil near a metal by the impedance of the probe coil in air. This is an approximation, although useful at low frequencies, that becomes increasingly inaccurate as the operating frequency approaches the resonant frequency of the coil. As the test sample becomes thinner, the eddy current frequencies are higher and the use of probes at or above their natural resonant frequencies becomes more common. It is important, therefore, to determine carefully how the complex impedance of the

probe varies at frequencies near or above resonance.

The decisions made in specifying the test conditions outlined above also determine the operational characteristics of the test system such as sensitivity, stability, and area of search. The problem which must be solved, therefore, is to determine the relationship between the test condition and the operational characteristics so that the test conditions can be controlled to yield the desired operational characteristics such as increased sensitivity and stability.

An equivalent circuit is being developed which can be used to simulate the eddy current coils for mathematical analysis. Concurrently, detailed definitions of sensitivity, stability, and area of search are being developed. In this regard, there is a strong indication that the maximum sensitivity may be obtained at or near the resonant frequency of the sensing coil which makes it even more important to extend the study of probe impedance patterns to frequencies at, and well above, resonance.

The impedance of several probe coil configurations was measured as a function of frequency from 1 kHz to 200 kHz. One probe is constructed so that a single sensing coil can be used in three ways. It can be placed up against flat metal plates, inserted into 1/2 in. diam holes, and have 1/4 in. diam rods or tubes passed through it. Figure 10.3 shows how the impedance of this probe varied as a function of the conductivity of the metal specimen at three different frequencies.

FIGURE 10.3 Complex Impedance of Probe Under Various Conditions.

Note that the general shape of the conductivity locus is retained (as the frequency is changed) in agreement with conventional eddy current theory. Note also that the conductivity loci are similar even though the materials were inside, outside, and adjacent to the probe. This indicates that a single equivalent circuit may be useable to represent an eddy current probe regardless of its intended use. The major exception to this observation is the effect of magnetic materials (mild steel in Figure 10.3) which appears to vary with configuration.

The coil used to obtain the data shown in Figure 10.3 had a resonant frequency well above 200 kHz (the upper limit of present equipment) so that additional shunt capacitance was necessary to study the variation of coil impedance at various conditions in the vicinity of resonance. Figure 10.4 shows how the coil impedance varied as a function of specimen conductivity at several conditions below, near, and above resonance. In this figure the origin is located in the center of the left margin with inductive reactance being plotted vertically upward, capacitive reactance vertically downward, and resistance to the right. The complex coil impedance at any constant frequency, is represented by a resistance and a reactance added in quadrature and therefore can be plotted as a single point on this type of chart.

This experiment was conducted at a frequency of 200 kHz by inserting 1/4 in. diam metal rods through the center of the coil. The solid curves labeled with low values of capacitance represent loci of specimen conductivity at

frequencies below resonance. The curve labeled "0 pf" represents conditions similar to those represented by the curve in the upper right hand corner of Figure 10.3. As the shunt capacity (or operating frequency) was increased, the values on the conductivity loci progressed up and to the right along the nearly circular dashed curves until they dropped to a value of low reactance and high resistance which denotes resonance. Above resonance, the probe became capacitive and began to lose its sensitivity to conductivity.

A number of interesting observations can be made from these data. For example, the sensitivity appears to be maximum at or near resonance and the probe appears just as sensitive above resonance as below it. There appears to be a frequency near resonance where the conductivity locus can be made straight. The general shape of the conductivity loci at frequencies significantly above resonance appears to be similar to those below resonance except that the position of the materials has been reversed on the curve.

These data are being studied to assist in the development of an equivalent circuit for the probe; however, the possibility of other applications has already become evident, such as the use of a single coil operated at a single frequency to obtain multiparameter discrimination capability by varying the value of a tuning capacitor placed across the coil.

Infrared and Thermal Research

A thermal wave transducer system is being developed for measuring the thermal properties of materials. One of the advantages of this method is that

FIGURE 10.4 Complex Probe Coil Impedance as a Function of Tuning.

no special shaping of the samples, other than providing one reasonably flat surface, is required. Such a flat surface can easily be produced by pressing the samples against a flat grinder. The thermal transducer method is not only applicable to thermal property measurements per se, but also has general application in nondestructive testing; e.g., measurements on fuel materials made external to the cladding.

Attempts to apply the miniature thermal wave transducer (pictured in the previous quarterly report) in making accurate thermal conductivity measurements on high conductivity samples showed that further improvement in reliability and sensitivity was required. The size of the transducer was increased to 3 x 3', and the thermocouple previously used to sense the transducer surface temperature was replaced with the smallest commercial thermistor available which improved the signal-to-noise ratio.

Substituting a fixed water-cooled resistor for a power rheostat in the power control system improved the signal-to-noise ratio by a factor of approximately five. The short-term noise equivalent temperature (temperature change required to produce a signal change just equal to the noise) of the new transducer and electronic system is 0.0003 °C, including temperature variations due to noise in the power drive regulating system. Input thermal impedance of the transducer can now be measured with a short term accuracy of approximately $\pm 0.01^\circ$ in phase angle and $\pm 0.1\%$ in amplitude. This short term accuracy is sufficient, even for thermal property measurements on copper.

However, long term tests over an eight week period showed errors as large as 1° in phase angle and 12% in amplitude. An investigation to determine and correct the cause of long term drift is underway. Measurements on the electronic system indicate that its long term accuracy is holding steady which indicates problems in the construction of the transducer. A new method of transducer construction using a solid backing material on the exciter foil is now being investigated.

Work is underway on a remote method for measuring surface thermal impedance values which does not require the use of a transducer. While the method described above involves a steady-state measurement, the new remote method utilizes a transient technique.

As mentioned in a previous quarterly report, the steady-state impedance can be obtained from the transient response as

$$Z(j\omega) = \left\{ \begin{aligned} & \left[\int_0^\infty f(t) \cos \omega t \, dt \right. \\ & \left. - j \int_0^\infty f(t) \sin \omega t \, dt \right] \\ & \div \left[\int_0^\infty y(t) \cos \omega t \, dt \right. \\ & \left. - j \int_0^\infty y(t) \sin \omega t \, dt \right] \end{aligned} \right\} \quad (11)$$

where $f(t)$ is the temperature response and $y(t)$ is the heat input to the sample surface.

One means of generating a heat flux into a sample is by means of a light source such as a high intensity xenon flash lamp powered by a large capacitor bank. The material absorbs energy from the short duration light flash, resulting in the sample surface temperature being raised a measurable amount.

The initial effort involved with this new technique was to design a suitable flash lamp system. Since such a system employs high voltages, safety is of prime importance. In addition to the required capacitor bank and high voltage power supply, an inductor capable of passing large surge currents at high voltage levels is needed. The system designed for use in the laboratory employs an E.G. & G., FX-60 xenon flash lamp. A capacitor bank with a total capacity of 500 microfarads is charged to 4000 volts and then discharged into the flash lamp through an 850 microhenry inductor. The test sample is positioned such that the resulting intense light burst from the flash lamp falls upon its surface.

For purposes of safety, the flash lamp, inductor, and sample are enclosed in a sealed box which is electrically grounded. Thus in the event of a short circuit, the high voltage would be harmlessly returned to ground. Due to the large physical size of the capacitor bank and the high voltage power supply, each is contained in a separate enclosure. Personnel safety is insured by means of safety interlocks in the enclosures.

The temperature transient resulting at the sample surface is measured by means of a Barnes R8T1 infrared radiometer. This device generates an output voltage which is proportional to the temperature it is monitoring.

In order to provide a useful test system, it is desirable to evaluate equation (11) automatically. Knowing the functions $f(t)$ and $y(t)$, it should be possible to accomplish this electronically. The radiometer output

provides the function $f(t)$ directly. The function $Y(t)$, representing the heat flux into the sample, is determined by the type of excitation used to heat the sample surface. An electronic system, capable of performing this function, is currently being designed.

Detection of Irradiation-Induced Shift in Nil-Ductility-Transition Temperature

An ultrasonic method has given promising results in detecting the presence of fast neutron induced embrittlement of steels used in reactor pressure vessels. Further investigation using the method is aimed at determining the cause of various observed testing anomalies and at defining the extent of test correlation to nil-ductility-transition temperature shift.

An improved test-specimen and transducer manipulator has been fabricated (Figure 10.5). This manipulator, as has its predecessors, will permit precision adjustment of angular and linear spacing of transducers with respect to a test specimen. Measurement precision has been enhanced by addition of a thermostatically controlled immersible cooler and a filtered, recirculating water supply; water and test specimen temperatures and their effect on sound velocity and Rayleigh wave critical angle will be held constant. Chart recordings of test response throughout the length of a specimen will be permissible through use of a speed-reduced motor driven horizontal translatory slide. The motor driven specimen translator will allow simple comparison of irradiated specimens against control samples for each chosen test frequency.

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FIGURE 10.5 Test Specimen and Transducer Manipulator.

A comprehensive testing program was defined. Three different steels, ASTM-A302B, ASTM-A542 Class II, and AISI-304 will be irradiated at six or more exposure levels. Samples of each steel at each exposure level will be irradiated at a temperature considerably below 450 °F and other samples at a temperature considerably above 450 °F. Each test specimen will be individually encapsulated as shown in Figure 10.6. The specimen within the capsule is surrounded by a helium atmosphere to pre-

vent surface corrosion during irradiation. Individual, rather than group, encapsulation is employed to obtain more uniform heating amongst the various specimens. Specimens for low flux, low temperature exposures have been fabricated and are scheduled for loading in the ETR in late April. Two capsule assemblies were fabricated and are shown together with the capsule outer holders in Figure 10.7. Three exposure levels, about 2.4×10^{18} , 4.0×10^{18} , and 6.4×10^{18} n/cm², at

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FIGURE 10.6 Specimen Encapsulation

Neg 0670997-5

FIGURE 10.7 Specimen Capsule Assemblies

greater than 1 MeV, will be included in this group with five specimens at each exposure level. Besides the A542 and 304 specimens, two A302B and one temperature monitor specimen are included at each exposure level. Half of the A302B specimens are cut from the plate

surface and the other half from the middle of the same plate.

An electronic system suitable for use in conducting ultrasonic test measurements was fabricated and is expected to be operational by May.

FAST REACTOR DOSIMETRY AND DAMAGE ANALYSIS

R. E. Nightingale

HIGH-TEMPERATURE FLUENCE MONITORS

E. A. Snad Jr and J. A. Ulseth

Monitors to measure neutron fluence are a necessary part of any carefully planned materials irradiation experiment. Current trends toward higher testing temperatures place limitations on the monitor materials that can be used. Materials experiments are planned that will have sample temperatures of 2500 °F (1370 °C). The fluence monitors in such a system could, as a result of gamma heating and poor heat transfer, reach temperatures of 3000 °F (1650 °C) or higher. As shown in Figure 11.1, the metal monitors are virtually eliminated and only some type of oxide or ceramic composites will be useful.

Ceramic monitors using an Al_2O_3 matrix have been studied but the variation in metal content from pellet-to-pellet has required individual precalibration of each pellet. In addition, evidence that the metal migrates through the matrix and is lost has virtually eliminated this type of system from extensive use.

A high-temperature monitor will eventually be needed by experimenters; and based on the criteria that it must remain stable at 3000 °F (1650 °C) and have a consistent pellet-to-pellet metal content that will not require precalibration of each pellet, a monitor is being developed consisting of a solid solution of a metallic

oxide in magnesium-oxide. Monitors composed of a magnesium-oxide carrier doped with 1 wt% of either iron, nickel or cobalt oxides have been fabricated using the following process:

- Mix MgO carrier with doping compound.
- Ball-mill mixture for 16 hr in alcohol.
- Dry powder and mix 10% binder (20% carbowax in H_2O) with powder.
- Presinter at 1100 °C for 3 hr to remove binder.
- High fire monitor pellets at 1500 °C for 4 hr.

Thirty small pellets of each type approximately 0.150 in. diameter and 0.150 in. long were produced. Fifteen of each type were taken at random and irradiated to determine the pellet-to-pellet variation in metal content. Comparison of the cobalt monitors at 95% confidence level shows that the Al_2O_3 matrix pellets vary in metal content $\pm 12\%$, whereas the MgO matrix pellets vary only $\pm 0.7\%$. The improved pellet-to-pellet cobalt consistency eliminates the need for neutron-activation calibration of each individual monitor as would be required with the Al_2O_3 pellets. The high-temperature stability of the cobalt pellets is now being tested.

The nickel and iron pellets had a pellet-to-pellet variation of greater than 1% and were considered unacceptable. Work is in progress to produce

Neg 671100-1

FIGURE 11.1. Comparison of Melting Points for Flux Monitor Materials

nickel and iron pellets with a variation in metal content of less than 1%.

FAST-REACTOR DOSIMETRY

J. L. Jackson

The objective of this work is to develop, test, and apply methods for measuring the neutron flux and spectra in fast-breeder reactors. Initial efforts have been in the study of the EBR-II, and include dosimetry experiments and calculations of spectra and monitor response functions. The objectives of these experiments and calculations are to evaluate different monitor materials for fast reactor use, aid in evaluating the monitor cross sections, and obtain information of

existing flux gradients and spectral shifts at different positions in the EBR-II.

The dosimetry studies are of two types, low-power tests at 30-50 kW-hr and multicycle full-power tests. The monitor reactions studied are in the following:

Flux monitors for the low-power test were located radially in Rows 1, 4,

and 6 and axially from the bottom of the core into the axial blanket. Monitors have been returned to Pacific Northwest Laboratory from two low-power tests and are being counted and evaluated. The full-power dosimetry tests are included in both standby pins that are placed in the reactor on a space-available basis, and regular materials subassembly tests. Assistance has been provided to the materials experimenters by supplying the dosimeter materials and advising on the location of monitors to obtain the maximum information on the flux and flux distribution. Radial and axial spectral calculations have been completed for the EBR-II core and blanket. Spectra were calculated using a one-dimensional transport-theory code, DTF-IV. The radial case was calculated in cylindrical geometry and the axial case in slab geometry. The Russian 26-group fast-reactor cross sections were used in the spectral calculations.

The calculated axial spectra have been used as input to the SAND-I (Spectrum Analysis Neutron Detection I) code. The SAND-I code uses a library of activation cross sections and the input spectra to compute a spectrally-averaged activation cross section, the energy range of monitor sensitivity, and the response function ($\sigma\phi$) for each monitor. Monitor responses calculated for both a core spectrum and an axial blanket spectrum are shown in Figures 11.2 and 11.3, respectively. Threshold monitors such as $^{54}\text{Fe}(n,p)$, ^{54}Mn , $^{58}\text{Ni}(n,p)$, ^{58}Co , and $^{27}\text{Al}(n,\alpha)^{24}\text{Na}$ respond similarly whether in the core or the blanket, but are sensitive to less than 10% of the total neutrons.

Monitors such as $^{59}\text{Co}(n,\gamma)^{60}\text{Co}$ and $^{58}\text{Fe}(n,\gamma)^{59}\text{Fe}$, etc., respond to a much greater percentage of neutrons and show a significant change in response to the spectral shift encountered when moving from the core to the axial blanket.

The results to date indicate that characterization of the nuclear environment in test facilities and service locations by dosimetry techniques is particularly important in fast reactors, since, with existing reactor physics methods, it is more difficult to calculate local perturbations or spectra at a particular location in fast reactors than in thermal reactors. Analyses are generally made for smeared zones in a reactor from which neutronic parameters are calculated. Spectra and flux calculated for a zone must be adjusted with experimental dosimetry data for a specific irradiation facility to achieve the accuracy required in materials studies.

Experience has further demonstrated that neutron dosimetry in fast reactors is very complex. The spectra typical of fast reactors shift the response of many of the common resonance and thermal monitors to high energies because there is essentially no flux in the resonance range and only the high-energy tail of the cross-section curves are weighted. The $^{59}\text{Co}(n,\gamma)$ reactions are excellent examples. The possibility definitely exists for monitoring most of the neutrons which damage materials in fast reactors, whereas in a thermal reactor only about 10% of these neutrons can be monitored. The response of monitors is very

Neg 671100-2

FIGURE 11.2. 90% Monitor Response
Range in EBR-II Core

Neg 671100-3

FIGURE 11.3. 90% Monitor Response
Range in EBR-II Axial Blanket

dependent upon neutron spectra, and the spectral shifts encountered in axial and radial traverses of fast reactors cause radical changes in monitor re-

sponse. These data can be interpreted to meet the requirements of fundamental and applied materials studies only if better methods are developed.

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