AEC
RESEARCH
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DEVELOPMENT
REPORT

**QUARTERLY PROGRESS REPORT
METALLURGY RESEARCH SECTION
OCTOBER, NOVEMBER, DECEMBER, 1965**

THE STAFF OF METALLURGY RESEARCH SECTION

JANUARY 17, 1966

66-063-H

BNWL-207
48-

DATE	FILE NO.	REMARKS
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BNWL-207
UC-25, Metals,
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QUARTERLY PROGRESS REPORT
METALLURGY RESEARCH SECTION
OCTOBER, NOVEMBER, DECEMBER, 1965

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January 17, 1966

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Printed in USA. Price \$3.00. Available from the
Clearinghouse for Federal Scientific and Technical Information
National Bureau of Standards
U. S. Department of Commerce
Springfield, Virginia

Previous reports in this series:

HW-76228	October, November, December, 1962
HW-77052	January, February, March, 1963
HW-77954	April, May, June, 1963
HW-78962	July, August, September, 1963
HW-79766	October, November, December, 1963
HW-81269	January, February, March, 1964
HW-82651	April, May, June, 1964
HW-84281	July, August, September, 1964
HW-84573	October, November, December, 1964
BNWL-79	January, February, March, 1965
BNWL-120	April, May, June, 1965
BNWL-166	July, August, September, 1965

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SUMMARY

PHYSICAL METALLURGY UNIT

PLUTONIUM PHYSICAL METALLURGY

High precision resistivity measurements have shown that beta phase contains significant amounts of retained alpha at relatively high temperatures. Distinct differences in beta formed from alpha and beta formed from gamma have been revealed by the resistometric studies.

During $\beta \rightarrow \gamma$ transformation, resistance fluctuates and assumes values both above and below the values for either pure beta or gamma.

Slip lines developed on polished, highly textured alpha specimens deformed by compression are being related crystallographically to the texture.

For comparable deformation by compression, considerably different loads are required depending on whether the load is applied parallel or perpendicular to the 010 texture direction.

Four papers have been prepared in a form suitable for publication: "Steady State Creep of Plutonium, " "Characteristics of the $\beta \rightarrow \alpha$ and $\alpha \rightarrow \beta$ Transformations in Plutonium, " "Phase Transformation Damage in Plutonium, " and "Comments on Kinetics of the $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ Transformations of Plutonium in the Vicinity of Equilibrium. " A summary of each paper is given.

RADIATION EFFECTS ON METALS

Dark field electron microscopy has been applied to neutron irradiated nickel. Both vacancy and interstitial clusters have been identified; the majority of the clusters are vacancy in nature.

Electron microscopy of neutron irradiated Cu + 8% Al, a low stacking fault energy alloy, has shown the expected defect clusters. Deformation of the irradiated alloy results in a structure similar to the unirradiated condition and in this respect differs from the channeling of dislocations in irradiated nickel and molybdenum.

The absence of small angle scattering from irradiated nickel has led to the conclusion that the cluster defects must be two-dimensional in nature. The only measurable small angle scattering obtained on irradiated material thus far has been from molybdenum irradiated to 1×10^{20} nvt ($E > 1$ MeV). Experimental techniques particularly in eliminating Bragg scattering effects in small angle scattering have been defined.

DAMAGE MECHANISMS

A purification procedure has been applied to iron and molybdenum to reduce the effect of interstitial impurities on thermally activated flow processes. Marked reductions in yield strengths were obtained by purifying samples of Ferrovac E and Battelle zone refined iron in hydrogen at 850 °C, but little change was obtained in molybdenum treated at 1300 °C.

SWELLING OF IRRADIATED FISSIONABLE MATERIALS

Two capsules in which temperature and pressure were controlled and two capsules in which pressure was low, 30 psi, and temperature only was controlled reached goal exposures and have been discharged. The specimens in these capsules represent a variety of dilute alloys with different compositions, heat treatments, and enrichments. Irradiation conditions include 700 °C beta phase irradiations.

Two capsules, one temperature-pressure controlled and the other temperature controlled, have been charged into a reactor to provide additional data on the effects of temperature, pressure, and high burnup (0.75 at. %) on the behavior of fuel.

Postirradiation examination of specimens recovered from three capsules each with pressure controlled at 1000 psi and with temperature controlled at 450, 575, and 625 °C, respectively has been completed. The results show that pressure can markedly reduce swelling in certain instances.

Evidence is presented that carbon in uranium, rather than Fe-Si, is a constituent responsible for reducing swelling in uranium.

Fission rate increases due to increases in the U^{235} content of specimens by a factor as high as 4 do not appear to alter the shape of the swelling-temperature curve of uranium for burnups to ~0.4 at. %.

Metallography on specimens irradiated at 525 °C and then at 200 °C shows that the planes on which tears develop during the 525 °C irradiation are also the planes on which deformation occurs during irradiation at 200 °C.

The numerical evaluation of metallographic data from replicas has been reprogrammed and adapted for UNIVAC-1107 use.

REACTOR METALS RESEARCH UNIT

ALLOY SELECTION

Several nickel base and refractory metal alloys are being irradiated to determine the effects of irradiation upon their mechanical properties. These specimens have been irradiated over a range of temperatures and exposures and are being tested at temperatures applicable to various reactor applications.

During the past quarter several refractory metal alloys were tested at temperatures to 1090 °C. Specimens of W-25 Re rod material were irradiated at 2.4×10^{20} , 3.4×10^{20} , and 5.6×10^{20} nvt ($E > 1$ MeV) in the ETR at 50 °C. Full recovery of properties at this test temperature was not found as indicated by the increase in both yield strength and ultimate tensile strength of the material as compared to the control specimen. The ductility of the specimens was also decreased by the irradiation as indicated by the lower percent reduction in area and total elongation. Neither the control specimen nor the specimens irradiated to 3.4×10^{20} nvt showed any effects of strain hardening, exhibiting low uniform elongation values. The higher exposure specimen (5.6×10^{20} nvt) exhibited significant strain hardening and thus a higher uniform elongation. A significant decrease in reduction in area was observed for this higher exposure specimen.

The results of tensile tests performed on other refractory metal alloys at 1090 °C show that the properties of Cb-752, Cb-1 Zr, and Mo tested after irradiation have essentially completely recovered when compared to the unirradiated control specimens. Strength and ductility of

the pre- and postirradiated specimens are approximately the same. The irradiated specimen of TZM, however, shows a slight (11%) increase in yield strength and a decrease in both total elongation and reduction in area.

IRRADIATION FACILITIES OPERATION

Facilities Operation

With the conclusion of ETR Cycles 73 through 76, over 200 irradiated tensile, stress rupture, and fracture specimens were discharged from the ETR G-7 Hot Water Loop and other core positions. Materials irradiated at 290 and 50 °C include stainless steels, Zircaloy-2, and nickel-base alloys. Over 85 control specimens were discharged from the out-of-reactor loop during this same period of time. Many of these specimens have been tested and the data are currently being processed.

Data Processing

The REM master file currently contains approximately 4000 tensile test records on 40 or more alloys which have been examined on the Irradiation Effects to Reactor Materials Program. Summary reports of the processed data for specific alloys are being generated by the retrieval portion of the REM program. These trial reports will eventually be linked with analytical, statistical, or plotting subroutines to further reduce the time required for engineering analysis. The REM program is being converted to FORTRAN IV for processing on the UNIVAC 1107 computer.

IRRADIATION DAMAGE TO STAINLESS STEELS

Tensile tests have been conducted on AISI 304, 316-L, and 348 stainless steels irradiated in the Engineering Test Reactor (ETR). Tests were conducted at test temperatures between room temperature and 800 °C. Additional irradiations at 60, 290, 600, and 750 °C are in progress on a variety of stainless steels. The purpose of this study is to characterize the mechanical behavior of these materials with respect to irradiation and reactor environment.

In pursuance of the objectives of the program, additional irradiations will be conducted in a predominantly fast flux environment, such as is typical of the EBR-II. Specimens have been characterized and encapsulated and sent to the reactor. Tests have been conducted to 800 °C on the unirradiated material. Additional irradiation assemblies have been constructed which contain identical specimens, with respect to material, geometry, and fabrication history, as were used in irradiation studies in both thermal and mixed spectrum reactors. This will provide a means of comparing the damage that occurs in neutron spectrums which are markedly different.

The results of tests to date on the austenitic stainless steels indicate two areas of low ductility which are of primary concern. These areas are identified as the intermediate temperature region between 200 and 400 °C and the high temperature region at above 600 °C. The regions of absolute ductility minimums vary with fabrication history, chemical composition, metallurgical structure, test temperature, and irradiation temperature, to name but a few parameters. Sufficient tests have not been performed to completely characterize the effects of all these variables. The mode of failure in the intermediate temperature region is primarily transgranular and probably involves an aging process not normally associated with austenitic stainless steels in this temperature range. Further studies of this phenomenon are in progress using transmission electron microscopy as a tool. The high temperature failure is predominantly intergranular in nature and can also be influenced by anything which changes the relative strength of the matrix with respect to the grain boundary, such as carbide or second phase precipitation.

Various thermal and mechanical treatments during the fabrication of reactor components can influence the metallurgical stability of these alloys during reactor service. Therefore, a number of material conditions are being examined to determine under what conditions the component is least likely to develop an unstable condition which could result in a catastrophic failure.

IRRADIATION DAMAGE TO ZIRCALOY-2

Surveillance of NPR Tubing

A paper entitled "The Effects of Irradiation and Environment on the Mechanical Properties and Hydrogen Pickup of Zircaloy-2" was presented at the Electrochemical Society Meeting at Buffalo, New York, in October, 1965. The paper described the results obtained to date from a study of NPR tube material irradiated at 60 and 290 °C. Tensile tests were performed at room temperature and at 300 °C on specimens irradiated to 2.33×10^{21} nvt (> 1 MeV). The greatest property changes occur in the material irradiated at 290 °C and tested at room temperature, but the lowest ductility observed occurs at the 300 °C test temperature. Corrosion rates were found to correlate with either time-at-temperature or neutron exposure, and were an order of magnitude greater in-reactor when compared with the equivalent out-of-reactor exposures. A flux rate dependence was noted in a few critical tests. The amount of hydride pickup was proportional to the corrosion rate. The hydride distribution was influenced by the amount and distribution of second phase material present in each tube examined. This paper has been scheduled for publication in the Journal of the Electrochemical Society sometime between January and March of 1966.

A topical report is being prepared which will contain additional results obtained from this study. These results are also being compared with those obtained on a more comprehensive study of Zircaloy-2 rolled sheet. By means of this comparison and from separate observations on the NPR tube material, the following conclusions were drawn:

- Strong crystallographic textures are developed by different working histories. Variations in the textures examined do not cause important differences in the mechanical properties of the longitudinal specimens examined with irradiation at either 60 or 290 °C.
- A greater change in mechanical properties occurs at room temperature than at 300 °C for the materials irradiated at 290 °C. The effect of test temperature is reduced with increasing neutron exposure.

- No significant changes in mechanical properties were caused by out-of-reactor hot water exposures at 290 °C for greater than 5700 hr.
- Differences in the resulting metallurgical structure appear to influence the corrosion rate and the distribution of hydrides. Hydrides are preferentially precipitated along stringers and second-phase particles in each tube examined. These materials also contain massive hydride platelets within the grains as well as along flow lines and second-phase stringers.
- Hydride content less than 250 ppm is not believed to affect the mechanical properties of the tube materials tested.
- Flux rate appears to affect the corrosion rate even for the lowest integrated exposures obtained. The corrosion rate appears to increase with increasing flux rate for fluxes between 2.0×10^{13} and 1.1×10^{14} nv (> 1 MeV) or 5.0×10^{13} and 2.8×10^{14} nv (thermal).

Transition Joints Between Zircaloy-2 and Inconel 600

A topical report⁽¹⁾ is being published describing the effects of irradiation and environment on Zircaloy-2 coupled with Inconel 600. Transition joints between these two materials were fabricated by coextrusion and by an explosive welding technique. Specimens from each type of joint were irradiated in the ETR G-7 Hot Water Loop at 290 °C. The specimens were subsequently tested in tension at room temperature and at 300 °C. In both types of joints the Zircaloy-2 was found to be the limiting material as far as the mechanical properties were concerned. All but one of the test specimens failed in the Zircaloy-2 portion of the sample.

The hydrogen pickup was different in the two types of joints examined. Originally the hydrogen content in the Zircaloy-2 starting material was about the same for both types of joint. After exposures

1. J. E. Irvin and T. T. Claudson. The Effects of Irradiation and Environment on the Mechanical Properties of Inconel-Zircaloy Transition Joints, BNWL-190. September 29, 1965.

in the ETR G-7 Loop at 290 °C for more than 2200 hr, however, one joint showed a hydrogen content twice as high as the other. A hydrogen gradient also existed in these specimens along the transition joint itself which suggests either an easy diffusion path along the Zircaloy-Inconel interface or a galvanic reaction of sufficient potential to accelerate hydrogen sorption.

The difference in hydrogen content probably contributed to the marked difference observed in mechanical properties of the two types of joints. The microstructure resulting from the different fabrication histories is believed to have significant effects on both the hydrogen pickup and mechanical properties of these joints.

Additional studies in this area are not planned at present and were not provided for in the scope of the original program. However, since a number of transition joints between various materials have been proposed for reactor service, it seems that it will only be a matter of time before such components will actually be placed into service.

IRRADIATION DAMAGE TO NICKEL-BASE ALLOYS

The nickel-base alloys hold promise for high-temperature nuclear reactor application. However, they do suffer embrittlement when irradiated at high temperatures. An effort to modify their microstructure by preirradiation treatment to reduce the effect is continuing.

Previous work on Hastelloy X-280, a solid solution strengthened nickel-base alloy, suggested the use of preirradiation thermal/mechanical structural conditioning treatments as a means of reducing the extent of reactor induced embrittlement. The improvement in ductility would result from controlled second phase precipitation.

On our last reporting, tensile tests of irradiated Hastelloy X-280 showed evidence of ductility improvement after preirradiation structural conditioning. During the last quarter, metallography of tensile specimens that had been tested at 1350 °F showed evidence that strain, irradiation, and combinations of strain and irradiation induce an increase in

precipitate volume in both matrix and grain boundary areas. This induced precipitate may be similar to that found by other investigators to occur after very long thermal exposures, in which case the effect of the strain and/or irradiation is to accelerate the precipitation process. Correlations are being made between observed microstructural changes in Hastelloy X-280 and its mechanical properties.

The effectiveness of preirradiation structure stabilization at temperature and the influence of changing structure on irradiated Hastelloy X-280 strength and creep resistance is being investigated by use of the creep-rupture test. Preliminary creep-rupture data from four of a series of ten irradiated Hastelloy X-280 samples with varying preconditioning treatments have been obtained. The data indicate differences in creep-rupture life as a result of the variation in the structure preconditioning treatments.

Realizing the potential of transmission electron microscopy as a useful tool in these structure modification studies, thin foil sample preparation is under way on Hastelloy X-280 tensile sample sections.

Preirradiation structural modifications on precipitation-hardenable Inconel X-750 are being examined as a companion study with the solution hardenable alloys in the nickel-base program. Irradiated tensile results obtained on preirradiation treated material indicate all specimens were extremely brittle. In addition, the data indicate that both strength and ductility decreased with the degree of over-aging. The excellent agreement found in the data between specimens of the same treatment indicates that the test equipment is functioning effectively and that quality control of specimens during preparation is paying dividends.

FRACTURE STUDIES

The Effect of Irradiation on the Fracture Toughness of Annealed Zircaloy-2

Zircaloy-2 DCB specimens irradiated at 280 °C in the G-7 Hot Water Loop of the ETR were tested to determine their fracture toughness. Specimens were machined from annealed Zircaloy-2 plate and autoclaved

at 100 psi and 525 °C for 24 hr to simulate the condition of actual reactor structural materials. The plane strain fracture toughness (expressed by the stress field intensity, K_{IC}) was determined as a function of temperature and the level of neutron irradiation.

It was found that the fracture toughness (K_{IC}) of Zircaloy-2 was substantially reduced when exposed to irradiation to a level of 5×10^{20} nvt. Brittle behavior was seen to occur at much higher temperatures, indicating an upward shift of the NDT temperature upon irradiation. Other investigators have not found significant changes in the fracture properties of Zircaloy-2, but their samples were irradiated at lower exposures and/or lower temperatures.

The shift in fracture toughness for cracking along the rolling direction was almost identical to the shift for cracking at 90° to the rolling direction. It also appeared that anisotropy in fracture toughness was reduced as the level of irradiation increased. This effect will be further analyzed when complete data on unirradiated Zircaloy-2 are obtained. Specimens irradiated to higher exposures will be available for testing within the next month.

Using an analysis of the effect of crack size and geometry on K_{IC} which was reported in recent literature, it was possible to relate K_{IC} values obtained from the DCB specimen to critical crack depths in tensile plates of Zircaloy-2 as a function of temperature and neutron exposure. It was thus determined that the critical flaw size in a tensile plate increases as the level of irradiation and temperature increases. A more detailed analysis of our data in light of these calculations is intended.

Slow Crack Propagation in High Strength Tool Steel

Investigation of stable crack propagation in D2 tool steel at loads less than that required for dynamic or unstable cracking, has continued since the last report period. Slow cracking in air progressed in discrete jumps, and showed a temperature and stress dependence of the delay time and magnitude of each crack jump. The effect of the environment

was determined by performing identical tests in a vacuum of 3×10^{-20} Torr. The rate of crack propagation in vacuum was greater than an order of magnitude less than that in air for the same value of the stress field intensity coefficient, K_I . Argon gas admitted to the system increased the rate of crack propagation to a value slightly less than that in air. Due to the increased frequency of cracking when the argon was admitted, it was thought that water vapor may have been present in the argon. This possibility will be studied.

For comparable values of the stress field intensity coefficient, K_I (maintained just below K_{IC}), the delay time in vacuum varied from 4 min at 20 °C to 30 sec at 300 °C.

A slight dependence of the delay time on the time at vacuum was observed and will be investigated in further work. It is presently thought that several possible mechanisms are acting to control crack propagation rates, and that the effects being measured are possibly due to the superposition of two or more of these factors.

Fracture Toughness of Graphite DCB Specimens

Preliminary investigations have been carried out to determine the adaptability of the DCB specimen to fracture testing in graphite. Excellent fracture behavior was seen for specimens oriented along the extrusion direction of the graphite rod.

Expressions for K_{IC} derived from the mechanics of the DCB specimen for metals are equally valid for other materials. The fracture toughness values obtained for SGBF and SX-5 types of graphite were approximately $K_{IC} = 1.5 \text{ ksi}\sqrt{\text{in.}}$ and $K_{IC} = 1.2 \sqrt{\text{in.}}$, respectively, as compared to approximately $27.5 \text{ ksi}\sqrt{\text{in.}}$ for 7075-T6 aluminum.

This preliminary work has demonstrated the effectiveness of the DCB specimen in testing brittle engineering materials other than metals.

ENVIRONMENTAL EFFECTS

In-Reactor Corrosion of Zirconium Alloys

Four zirconium alloys, Zircaloy-2, low nickel Zircaloy-2, Zircaloy-4, and Zr-3 Nb-1 Sn, were exposed in the G-7 loop of the Engineering Test Reactor (ETR) for 36 days at 530 °F in pH-10 lithium hydroxide at ~1 ppm oxygen. Coupons were exposed at fast flux levels of 1.9×10^{13} nv and 1.6×10^{14} nv. Samples also were placed in the loop at out-of-flux positions ~1 sec and ~1 min from the flux.

Weight gains on the in-flux samples were up to 10 times the weight gains on corresponding samples at out-of-flux positions.

Weight gains were consistently higher at the higher flux positions.

The Zr-3 Nb-1 Sn alloy showed a low susceptibility to flux-induced oxidation; one of two Zircaloy-2 alloys in the test showed a high susceptibility at the higher flux level. There was essentially no difference in the radiation-induced oxidation of NPR Zircaloy-2, low-nickel Zircaloy-2 and Zircaloy-4.

Heavily (86%) cold worked specimens behaved similarly to annealed specimens of the same alloy.

There was no systematic effect of irradiated coolant on the corrosion behavior of coupons at out-of-flux positions.

ATR GAS LOOP SUPPORT

Corrosion Studies

Nichrome has been found to oxidize according to a cubic rate expression at 1020 and 1120 °C over a pressure range of 0.14 to 85 Torr oxygen. At higher temperatures, oxide loss by evaporation is suspected to affect oxidation kinetics.

Dynamic Materials Test Apparatus

The evaporation rates of Haynes 25 and Hastelloy X have been determined in ultrapure helium gas at 300 psi and 2050 °F as a function of linear

gas velocity. At 500 ft/sec the maximum evaporation rate is about half that found in vacuo. Decreasing the gas velocity decreases the evaporation rate.

PRP MATERIALS DEVELOPMENT

Corrosion of PRTR Zircaloy-2 Process Tube

Investigation of oxide thickness on sections of a discharged PRTR Zircaloy-2 process tube is in progress. Oxide thicknesses for the sections exposed to the highest neutron flux are a factor of 5 higher than the oxide thicknesses measured for sections with virtually no neutron exposure. Large differences in oxide thickness have also been found between the inside and outside surfaces of the process tube.

MATERIALS ENGINEERING UNIT

PRTR PRESSURE TUBES

Properties of Irradiated PRTR Pressure Tubes

Study and testing completed the last quarter year regarding the ability of the PRTR Zircaloy-2 pressure tubes to sustain the PRTR reactor system loads with ever increasing neutron exposure consisted of tensile testing of ring specimens after annealing at 550 °F for 3000 and 4000 hr and of analysis of the data of the entire annealing experiment. The data from the 1000, 2000, 3000, and 4000 hr treatments indicated strength reduction by recovery from the irradiation damage by annealing during the first 1000 hr and then an increase in strength during the remaining 3000 hr. The strength increase indicates an aging process within the Zircaloy-2 alloy.

PRTR Zircaloy-2 pressure tube number 6095 failed during performance of an experiment with the PRTR fuel element rupture facility. Observation of the microstructure near the rupture showed that the tube had been locally heated to a temperature within the range 1480 to 1770 °F, possibly even higher than 1770 °F. Simulation of the event indicated that the strength of the tube at these temperatures would have been overcome by PRTR system pressure. The rupture conditions exceeded the design of the tube.

USAEC-AECL COOPERATIVE PROGRAM

Zr-Nb Pressure Tubing

Additional brittle fracture data have been obtained for hydrided and nonhydrided Zr-2.5 wt% Nb alloy tubing in the 30 and 60% cold worked condition. The brittle fracture temperature of the tubing in the 60% cold worked condition is lower than for the 30% cold worked condition and is believed to be attributable to differences in hydride impurity.

GAS LOOP DEVELOPMENT

Columbium Sleeve-Leak Test

Laboratory tests on a mockup of the seal between the pressure tube of the ATR Gas Loop and the columbium sleeve liner indicate the maximum clearance between the liner and the sleeve should not exceed 0.020 in.

Model Loop

Disassembly of the model loop has started in preparation of the installation of the new model heater and foil insulated primary piping.

Model Gas Loop Heater Piping Modifications

Final assembly of the model heater is now in progress. The first stage, nichrome portion, of the heater has been assembled. The second stage, molybdenum heater is now being assembled. Piping for the loop is being prefabricated into three subassemblies before installation in the loop.

PHYSICAL METALLURGY UNIT

PLUTONIUM PHYSICAL METALLURGY - F. E. Bowman, H. E. Kissinger, B. Mastel, and R. D. Nelson

The objective of this program is to conduct basic studies on the properties of high-purity unalloyed and alloyed plutonium. Studies include investigation of phase transformation, phase stabilization, deformation, fracture, texturing, internal stresses, microcracking, grain growth, recovery and recrystallization, and measurement of mechanical and physical properties. The unique structure of several of the plutonium allotropes and their narrow temperature span of stability leads to characteristics and anomalies which, if explained, will contribute to the general area of solid state science.

Transformation of Plutonium

The development of equipment capable of measuring electrical resistivity with a high degree of precision has led to the application of resistivity to the study of $\alpha \rightarrow \beta$, $\beta \rightarrow \gamma$, $\gamma \rightarrow \delta$, and $\delta \rightarrow \alpha$ transformation processes in plutonium. Briefly, the equipment consists of 1 ohm standard resistance, maintained at a constant temperature, in series with the plutonium sample. This latter is a cast rod approximately 0.120 in. in diameter. Electrical connections are made with spring loaded alligator clips which accommodate the dimensional changes resulting from the phase transformations. The EMF drop across both the standard resistance and the unknown are measured simultaneously by two microvoltmeters, the outputs of which are recorded by a two pen strip chart recorder. The precision of the system permits the resistivity to be determined to one thousandth of a micro-ohm centimeter. The accuracy, however, is limited by the dimensional uniformity of the specimen and the accuracy with which these dimensions can be determined. It is the relative resistivity values, however, that appear to be significant in the current investigation.

It has, for example, been found that the alpha phase is retained, to a small but significant extent, at relatively high temperatures. The

presence of this retained phase, in amounts not detectable by X-ray diffraction or volumetric measurements, exerts a very significant influence on subsequent phase transformation kinetics. The resistivity studies have yielded additional information which indicates a basic difference in the beta phase formed from alpha as compared with that derived from gamma. At the present time the question of the possible effects of retained phases has not been resolved to the point where definitive values can be assigned for the respective resistivities of the two types of beta.

It is evident, also, from the results to date, that gamma is readily retained in the temperature range of beta stability. This results in resistivity values which exceed that of either of the two phases individually.

The actual transformation processes, particularly the $\beta \rightarrow \gamma$, if followed at a constant cooling rate with this sensitive resistivity apparatus, yield data which are at this time difficult to interpret. There is a wide and rapid fluctuation in the resistivity, the extreme values being both above and below the values for either beta or gamma. The difference between the maximum and minimum in this fluctuation is several microhm centimeters.

Deformation of Alpha Plutonium

Techniques were improved for developing highly textured alpha material by the transformation of beta under a compressive load. Samples of such material have been sectioned longitudinally with the precision saw. The exposed surfaces after metallographic preparation have provided excellent specimens for slip studies. These studies are still under way. Attempts to correlate slip line angles with crystallographic details of the sample texture provide a basis for identifying slip planes.

It has been pointed out previously that it has not, as yet, been possible to establish, unequivocally, the crystallographic details of the texture established by the $\beta \rightarrow \alpha$ transformation under stress. For the purpose of the present discussion, however, it will be assumed that the (010) planes lie perpendicular to the direction of the stress applied on the transforming material.

The application of compressive stress to the polished and etched textured samples has given evidence of deformation both by slip and grain boundary shear as shown in the photomicrographs of Figures 3. 1 through 3. 3. The detailed study of slip lines with respect to their crystallographic significance is as yet incomplete. It is of particular interest, however, to note the larger difference in compressive loads required to produce comparable deformation when applied parallel and perpendicular to the 010 direction. The stress required in the latter situation was approximately twice that in the former. This apparent anisotropy in the strength characteristics will aid materially in interpreting the details of the deformation process.

FIGURE 3. 1

Structure of Textured Alpha Plutonium
as Revealed by Bright Field Etch
(010 direction is essentially vertical.)
250X

FIGURE 3. 2

Surface in Figure 3. 1
After Application of 141, 000 psi
Compressive Stress
Perpendicular to 010 Direction
250X

FIGURE 3. 3

Slip Lines Generated by 68, 000 psi Compressive Stress
Applied Parallel to 010 Direction
500X

Summary of Papers Prepared for Publication

Four papers have been prepared in final form for submission to technical journals. The titles are: "Steady-State Creep of Plutonium, " Institute of Metals; "Characteristics of the $\beta \rightarrow \alpha$ and $\alpha \rightarrow \beta$ Transformations in Plutonium, " Transactions, AIME; "Phase Transformation Damage in Plutonium, " Journal of Nuclear Materials; and "Comments on Kinetics of the $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ Transformations of Plutonium in the Vicinity of Equilibrium, " Journal of Nuclear Materials. A summary of each paper is given here.

Steady-State Creep of Plutonium

Creep of the plutonium allotropes has been investigated with respect to temperature and stress. The creep rates of plutonium allotropes formed by heating a low temperature, stable allotrope decrease in the order of $\epsilon > \delta' > \delta > \beta > \gamma > \alpha$; but the order of β and γ creep rates of the allotropes formed by cooling a high temperature, stable allotrope is reversed, i. e., $\epsilon > \delta' > \delta > \gamma > \beta > \alpha$. The average activation energies for steady-state creep, based on an Arrhenius relationship, are 26, 35, 31, 28, and 25 kcal/g-atom for the α , γ , δ , δ' , and ϵ phases, respectively. These activation energies were determined at stresses of 7500, 600 to 2500, 110 to 600, 110, and 110 psi, respectively. The activation energy for creep of β formed from α was 30 kcal/g-atom at 2500 psi and 17 kcal/g-atom at 7500 psi. At these stresses the activation energy for creep of β formed from γ was 10 to 20% higher than the activation energy for creep of β formed from α .

Characteristics of the $\beta \rightarrow \alpha$ and $\alpha \rightarrow \beta$ Transformations in Plutonium

The characteristics of the $\beta \rightarrow \alpha$ and $\alpha \rightarrow \beta$ transformations in plutonium were studied with particular emphasis on the transformation kinetics and microstructure. Significant observations were:

- The kinetic data show conclusively that the $\beta \rightarrow \alpha$ transformation in high purity plutonium can proceed isothermally with no athermal component.
- Plastic deformation of the stable beta phase retards the subsequent $\beta \rightarrow \alpha$ transformation.
- Plastic deformation of the stable alpha phase accelerates the $\alpha \rightarrow \beta$ transformation; the acceleration is attributed to residual stresses.
- The $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ volume changes occur anisotropically in the textured plutonium.
- An apparent crystallographic relationship exists between the parent and the product phase of the $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ transformations.
- Both applied uniaxial compressive stresses and uniaxial tensile stresses raise the starting temperature for the $\beta \rightarrow \alpha$ transformation.

- A given applied uniaxial tensile stress favors the $\alpha \rightarrow \beta$ transformation more than an equivalent applied uniaxial compressive stress opposes the transformation. These observations of the $\beta \rightarrow \alpha$ and $\alpha \rightarrow \beta$ phase changes in plutonium are consistent with known martensitic transformations.

Phase Transformation Damage in Plutonium

Plutonium may contain a large volume of microcracks which form during the $\beta \rightarrow \alpha$ transformation. The volume of microcracks increases with increasing transformation temperature, metal purity, specimen size, and applied uniaxial tensile stress. Transformation cycling causes additional microcracking, with concomitant swelling in all directions and extensive surface rumpling. For a given $\beta \rightarrow \alpha$ transformation temperature, more damage occurs if the parent beta was formed from alpha rather than gamma. Alpha plutonium containing no microcracks can be produced by quenching the beta phase to -75°C during casting. No physical damage occurs during $\gamma \rightleftharpoons \beta$, $\delta \rightleftharpoons \gamma$, or $\delta \rightleftharpoons \beta$ transformation cycling if the metal initially contains no microcracks.

Comments on Kinetics of the Plutonium $\alpha \rightarrow \beta$ Transformation in the Vicinity of Equilibrium

The results presented by Spriet are discussed and compared to the published results of Nelson. The kinetics data were analyzed by applying the Avrami equation, $x = 1 - \exp(kt^n)$, and a modification of this equation, $\frac{x-1}{1+px} = -\exp(kt^n)$. In these equations x is the volume fraction of the product phase; t is time; k is a temperature dependent constant; n , the time exponent, is a constant; and p is a temperature dependent constant. Spriet reports that his $\alpha \rightarrow \beta$ data indicated a value of $n = 1$, but Nelson reports a value $n \approx 4$ for thin wafers. These values of n are discussed relative to the mechanism of the transformation.

RADIATION EFFECTS ON METALS - J. L. Brimhall, H. E. Kissinger,
B. Mastel, and F. A. Smidt

This program is directed toward establishing the combined effect of impurities and neutron irradiation on the properties and structure of specific metals, and deducing from thermally-activated recovery processes how the damage state can be altered. Present studies involve single and polycrystalline specimens of molybdenum, nickel, rhenium, and copper plus 8% aluminum alloy.

Transmission Electron Microscopy

Radiation damage in nickel, a fcc metal, is being studied in a manner analogous to that of molybdenum, a bcc metal. Examination of nickel samples, 99.997% pure, irradiated to 2.5×10^{18} is essentially complete. A previous Quarterly Progress Report⁽¹⁾ has described electron microscope observations on the irradiated material. Emphasis this quarter has been directed toward dark field observations. Figure 3.4 shows bright and dark field electron micrographs of the same area. The dark field micrograph shows that some of the clusters have reverse images in which the bright streak makes an acute angle with the direction of the positive dark field $\bar{g}$ indicating that these clusters are of the vacancy type. Also present are clusters that have bright streaks in the opposite direction; these clusters are therefore interstitial in nature. The ratio of the vacancy to interstitial clusters is about 3:2. The predominant number of clusters have $\frac{a}{3} \langle 111 \rangle$ Burgers vector. Clusters having $\frac{a}{2} \langle 110 \rangle$ Burgers vectors have also been identified. After annealing the samples for 6 hr at 450 °C, the cluster density was reduced by an order of magnitude, to $2 \times 10^{15}/\text{cm}^3$. No significant change in the ratio of the number of vacancy clusters to interstitial clusters had occurred. Annealing the specimens at 500 °C for 6 hr resulted in a further decrease of the cluster density by several orders of magnitude with no appreciable change in size.

The foils that were examined in the microscope were also analyzed by small angle X-ray scattering techniques. No small angle scattering

1. Quarterly Progress Report, Metallurgy Research Operation, July, August, September, 1965, edited by J. J. Cadwell, BNWL-166.
p. 3.10. September 15, 1965.

(a)

(b)

FIGURE 3.4. DEFECT CLUSTERS IN NICKEL IRRADIATED WITH NEUTRONS TO AN EXPOSURE OF 2.5×10^{18} nvt ($E > 1$ MeV) AT 40°C . (a) Bright Field (b) Dark Field of Area Shown in (a). Note the reverse images present in (b). 150,000X. Neg. 3573b and 3573c.

was observed from any of the foils. The absence of small angle X-ray scattering indicates that the vacancy clusters exist as dislocation loops and not as three-dimensional voids. The results of the electron microscope and small angle scattering observations are being prepared for publication.

To date, the study of radiation effects on metals has been limited to metals of relatively high stacking fault energy. An alloy composed of Cu-8% Al, known to have a very low stacking fault energy, has been prepared, irradiated, and examined in the electron microscope. After irradiation to an exposure of 6×10^{18} nvt ($E > 1$ MeV), the density of defect clusters was about $3 \times 10^{16}/\text{cm}^3$. This density is somewhat lower than that observed in pure copper irradiated to an equivalent exposure. The largest clusters were approximately 75 Å in diameter, significantly smaller than those observed in pure copper. Dark field analysis showed an equal number of vacancy and interstitial clusters to be present. The microstructure of the irradiated and deformed alloy is shown in Figure 3.5. Dislocation pile-ups and wide stacking faults are evident. No channeling of dislocations was observed. This observation is in contrast with observations made on metals of high stacking fault energy.

Two publications concerning radiation effects in molybdenum have appeared during this quarter. "The Combined Effect of Carbon and Neutron Irradiation on Molybdenum" has been published in Acta Metallurgica, and "The Effect of Neutron Irradiation on Slip Lines in Molybdenum" has been published in Trans. Met. Soc., AIME.

Small Angle X-Ray Scattering

Experiments have been directed toward the refinement of techniques, with particular attention given the elimination of Bragg scattering effects. Attempts to utilize a collimated direct beam from the X-ray tube have not given satisfactory results, despite the use of filters and pulse-height discrimination to restrict the effective wave lengths. A silicon crystal monochromator was subsequently used to produce a sharp, highly monochromatic beam; however, the intensity was quite low. An improved monochromator was fabricated using a lithium fluoride crystal cut to give an intensifying

FIGURE 3.5. DEFECT CLUSTERS AND STACKING FAULT RIBBONS IN $\text{Cu} + 8\% \text{Al}$ IRRADIATED TO AN EXPOSURE OF 6×10^{18} nvt ($E > 1 \text{ MeV}$) AT 40°C AND SUBSEQUENTLY DEFORMED 3 TO 5%. 85,000X.
Neg. 3646D

effect, as shown in Figure 3.6. This method of preparing a crystal monochromator has been described by Fankuchen.⁽¹⁾

FIGURE 3.6. PRINCIPLE OF CONCENTRATING X-RAY MONOCHROMATOR, Fankuchen⁽¹⁾

The greater scattering power of the lithium fluoride combined with the intensity increase from the bevel-cut crystal results in a nearly fivefold intensity increase over the earlier silicon monochromator. Although still higher intensities would be advantageous, the present arrangement is being utilized to study the scattering at small angles from molybdenum and nickel foils.

Nickel foils have been studied in the severely cold-worked state, and after irradiation to 2.5×10^{18} and 5×10^{18} nvt ($E > 1$ MeV). No effects definitely identified as small-angle scattering have been observed

1. I. Fankuchen. "A Condensing Monochromator for X-Rays," Nature, vol. 139, p. 193-194. 1937.

in any of these foils. Although irradiation results in a concentration of spot and small loop defects visible in the electron microscope, there are apparently no inhomogeneities in electron density which could cause scattering effects, leading to the conclusion that the defects are planar, collapsed loops. The results of the small-angle scattering and electron microscope studies are being prepared for publication.

Molybdenum, cold-worked and irradiated to lower exposures (1×10^{19} nvt or lower), also shows no small-angle scattering. However, after 1×10^{20} nvt ($E < 1$ MeV) the scattering shown in Figure 3.7 is observed. The scattering appears to be the first, second, third, and fourth orders of an interparticle interference effects.

A preliminary analysis of the scattering in Figure 3.7 has been performed by the method of Hosemann.⁽¹⁾ This method is based upon the assumption that the particles responsible for the interference must be more or less regularly arranged in the matrix, and for nearest neighbors at least, approximate a close-packed lattice. The scattering observed is then successive orders of diffraction from close-packed layers. For the data of Figure 3.7, the fourth-order maximum is at about 9.5 minutes of angle, so the first-order maximum must be near 2.4 minutes. From Bragg's law, the spacing between close-packed layers is then about 2200 Å, which leads to the nearest-neighbor distance of about 2700 Å. From this, the density of defects responsible for this scattering is about $7 \times 10^{13}/\text{cm}^3$.

Earlier work (HW-84573) has shown the density of visible defects in this material to be about $1 \times 10^{16}/\text{cm}^3$. The small-angle scattering observed is unlikely to be a result of the visible defects, but the true source of the scattering is not yet determined. Further experiments and more detailed analyses will be carried out to provide clarification of these results.

1. R. Hosemann, "Röntgeninterferenzen an kolloiden Systemen," Kolloid-Z., vol. 117, pp. 13-41. 1950.

FIGURE 3.7. SMALL-ANGLE X-RAY SCATTERING FROM MOLYBDENUM IRRADIATED TO 1×10^{20} nvt ($E < 1$ MeV)

DAMAGE MECHANISMS - F. A. Smidt and W. S. Bennett

The objective of this program is to determine how the mechanical properties of the irradiated bcc metals, iron and molybdenum, are modified by interaction of moving dislocations with irradiation induced defects. The effects are being studied by several techniques, among them thermally activated flow measurements and electron transmission microscopy. Both these techniques indicate the role of interstitial impurities is important in the nucleation of defect clusters observed in samples bombarded by fast neutrons ($E < 1$ MeV) at ambient reactor temperatures.

One obvious approach to study this problem is to prepare high purity samples free of interstitial impurities. Although this is an obvious approach it is not a simple one, because the influence of trace impurities on the mechanical properties is not really well understood and because of the difficulty in attaining the purities required. Stein, Low, and Seybolt⁽¹⁾ have described a technique employing a ZrH_2 exchange reaction to achieve purities greater than any previously obtained with the conventional wet hydrogen purification method and observed attendant changes in the mechanical properties. These purities are also higher than can be obtained by zone refining iron. A system similar to that described by Stein, et al., but capable of higher temperatures so that the process can be used to purify molybdenum, has been built and is presently under evaluation.

The system is shown in Figure 3.8. It consists of separately controlled furnaces for heating the ZrH_2 (800 °C) and the samples to be purified (up to 1500 °C), a rotary glass pump to circulate the hydrogen, a vacuum system to evacuate the system, and a manometer to measure hydrogen pressure. During a typical run the system is evacuated to 1×10^{-6} Torr, the system is pressurized to 550 mm of hydrogen, the hydrogen is gettered by circulation over hot ZrH_2 , and the specimen furnace is brought up to temperature. The hydrogen is then circulated over the specimens for a period of time calculated to permit diffusion of hydrogen into and

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1. D. F. Stein, J. T. Low, Jr., and A. V. Seybolt. "The Mechanical Properties of Iron Single Crystals Containing Less than 5×10^{-3} ppm Carbon," Acta Met., vol. 11, p. 1253. 1963.

and diffusion of the reduced impurities from the center of the samples. The system is then pumped out, the samples annealed in vacuum to remove the hydrogen, and then the samples are furnace cooled.

FIGURE 3. 8. ZIRCONIUM HYDRIDE-HYDROGEN PURIFICATION SYSTEM

The results to date show marked improvement in the properties of iron but less conclusive results for molybdenum. A purification run of 24 hr at 850 °C for iron samples of two purities removed the drop-in-load yield point and markedly decreased the yield strength for the two irons. One sample was Ferrovac E iron (~50 ppm carbon) which prior to purification had a lower yield strength of 35.8 kg/mm², and after purification had a yield strength of 6.60 kg/mm². The other sample was a Battelle zone-refined iron (~3.3 ppm carbon) which prior to purification has a yield strength of 23.6 kg/mm² and after purification had a yield strength of 5.14 kg/mm². These results compare very favorably with the shear stress value of 3.0 kg/mm² obtained by Stein on single crystals (tensile stress ~6.0 kg/mm²).

The initial experiments on molybdenum have included runs up to 240 hr at 1300 °C with little reduction in the yield stress although the ductility appears to be somewhat improved.

SWELLING OF IRRADIATED FISSIONABLE MATERIALS -

R. D. Leggett, C. R. Hann, B. Mastel, and K. R. Merckx

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 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 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 interrelationships 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

Two controlled temperature-pressure capsules reached their goal exposures and were discharged. The capsules were irradiated in tandem to a burnup of 0.16 at. % at respective control temperatures of 550 °C and 625 °C while at a common pressure of 500 psi. Irradiation in tandem permits more efficient use of reactor space and provides an identical neutron environment for more precise comparison of the effects of temperature and pressure. The capsules were controlled at 375 and 450 °C when the reactor was down to prevent any high pressure sintering which may occur during reactor down times. Each capsule contained two types of high purity uranium (6 and 484 ppm carbon), British "adjusted" uranium, and a U + Fe-Si alloy. Several different heat treatments were used to evaluate the effect of grain size, orientation, and phase distribution.

Two controlled temperature, low pressure (~30 psi) capsules were successfully irradiated and discharged. One of the capsules operated at 700 °C burnup (beta phase) to a burnup of 0.09 at. %; the other operated at 500 °C to a burnup of 0.04 at. %. The 700 °C irradiation, which was controlled at 500 °C while the reactor was down to avoid annealing effects, will provide additional information on the effect of burnup in the beta phase and the effect of minor alloying additions on fuel stability at this temperature. The 500 °C irradiation which contained 1.44% enriched uranium specimens subjected to various heat treatments will provide information on the effect of fission rate on fuel behavior.

A general swelling capsule which is operating successfully at 700 °C (beta phase) towards a goal exposure of 0.2 at. % burnup will provide information on the effect of higher burnup and minor alloy additions on the beta phase behavior of uranium base fuel.

A tandem assembly consisting of a controlled temperature-pressure capsule and a controlled temperature capsule was charged into a reactor and is operating successfully. The controlled pressure-temperature capsule is operating at a pressure of 1000 psi and a temperature of 450 °C. Goal exposure is 0.75 at. % burnup. The second capsule of the tandem pair is

is operating at low pressure (~ 30 psi) and 525°C). Its goal exposure is 0.4 at.% burnup. These capsules, containing enriched and natural uranium specimens, will provide data needed in evaluating the effects of temperature, pressure, and high burnup on the behavior of fuel.

Postirradiation Examination

Effect of Pressure. The postirradiation examination of the specimens recovered from the first series of three controlled temperature-controlled pressure capsules is essentially complete. The capsules were controlled at 1000 psi and at respective temperatures of 450, 575, and 625°C . A second series of three capsules controlled at 500 psi and at the same respective temperatures have completed their irradiation and the first of these have been opened. Four types of uranium are included in these capsules: high purity-low carbon (T-3), high purity-high carbon (PT3-NA), a U + Fe-Si alloy, and a "British" or U + Fe-Al-Si alloy. The exact compositions are given in Table 3.1. Several different metallurgical states are represented for each material.

TABLE 3.1. ANALYSES OF URANIUM IN CONTROLLED
PRESSURE-TEMPERATURE CAPSULES

	<u>High Purity Uranium</u>		<u>Uranium Alloys</u>	
	<u>Low Carbon (T-3)</u>	<u>High Carbon (PT3-NA)</u>	<u>U + Fe-Al-Si "British"</u>	<u>U + Fe-Si</u>
Aluminum	<5	10	645	25
Beryllium	<0.2	<1	<1	<1
Bismuth	<1	<1	--	--
Cobalt	-	<2	--	--
Chromium	10	--	7	8
Copper	10	10	5	--
Iron	64	54	407	140
Manganese	5	2	8	9
Nickel	20	<2	20	26
Silicon	25	34	85	95
Tin	0.5	0.5	2	--
Zirconium	-	--	30	7
Carbon	6	484	500	400
Nitrogen	8	24	23	14

The pertinent metallurgical histories, irradiation parameters and measured volume changes are summarized in Tables 3.2 and 3.3. The specimen number in these tables is coded such that the first letter and number refer to the parent Capsules P2, P3, and P4, respectively; the second letter refers to positions A, B, C, D, or E in the capsule; and the number following the dash (-) refers to either half 1 or half 2 of the specimen pair at a given position. The influence of 1000 psi hydrostatic pressure in inhibiting swelling was quite pronounced in all materials and reduced the swelling that had been previously observed by a factor of 5 to 10. In the case of the "British" composition which swells but very little at low pressures, the swelling was reduced to the theoretical level normally ascribable to solid fission products (Table 3.2).

The data for the U + Fe-Si specimens is also summarized in Table 3.2 and the swelling observed is compared with that observed at low pressure (approximately 30 psi) in Figure 3.9. The shape of the swelling-temperature curve is essentially the same for both low and high pressure but the amount of swelling has been reduced by about a factor of 5 by the 1000 psi pressure. Metallographic examination revealed that the swelling that occurred at 550 °C (Spec. P3E-1) was due to tearing associated with twin band interfaces and was identical to low pressure irradiations but of lesser magnitude. No tearing was positively identified in the specimen irradiated at 415 °C, consistent with the small density change. The specimen irradiated at 585 °C had a few tears located at grain boundaries and twin bands.

The data for the two types of high purity uranium are summarized in Table 3.3 and the swelling is compared in Figure 3.10. Where duplicate data are available, average values have been plotted. The density values for specimens P3D-1 and P4D-2 are probably much too high as metallography revealed more tearing than indicated by the density. There is a pronounced difference in behavior of these two high purity uranium materials. The PT3-NA material, containing 480 ppm carbon, swells less than the T-3 material, containing less than 10 ppm carbon, by about a factor of 3 in the 500 to 600 °C temperature range at 1000 psi. Data are

TABLE 3.2. SWELLING IN U + Fe-Al-Si
AND U + Fe-Si IRRADIATED AT 1000 psi

Specimen Number	Condition	Burnup at. %	Irradiation Temperature, °C		As-Irradiated Density, ρ_f g/cm ³	Swelling, % $\frac{\rho_i - \rho_f}{\rho_f} \times 100$	"R" p' % Swelling/ at. % Burnup	"R"*
			Reactor Up	Reactor Down				
<u>U + Fe-Al-Si**</u>								
P2B-1	A	0.13	430	430	18.85	0.3	2.0	15
P2B-2	B	0.13	430	430	18.80	0.5	4.1	15
P3B-1	A	0.15	565	540	18.72	1	6	14
P3B-2	B	0.15	565	540	18.82	0.4	3	14
P4B-1	C	0.20	590	415	18.83	0	0	7
P4B-2	B	0.20	590	415	18.67	0.9	4.5	7
<u>U + Fe-Si[†]</u>								
P2E-1	D	0.13	415	425	18.83	0.6	4.8	15
P2E-2	B	0.13	415	425	18.80	0.8	6.2	15
P3E-1	D	0.15	550	550	18.13	5	35	120
P3E-2	E	0.15	550	535	18.41	3	20	120
P4E-1	C	0.20	585	415	18.45	2.2	11	45
P4E-2	B	0.20	585	415	18.75	1.1	5	45

* "R" is the swelling typically observed for an equivalent irradiation at low pressure (~30 psi).

** British "adjusted" composition; 407 ppm Fe, 645 ppm Al, 85 ppm Si, 500 ppm C, 23 ppm N

† U + Fe-Si material: 140 ppm Fe, 25 ppm Al, 95 ppm Si, 400 ppm C, 14 ppm N

A As-extruded

B 730 °C - 15 m - O.Q.

C Beta heat treated in bulk prior to specimen machining

D 1000 °C - 24 hr - W.Q.

E 1000 °C - 24 hr - W.Q. + 730 °C - 15 m - O.Q.

TABLE 3.3. SWELLING IN HIGH PURITY URANIUM
IRRADIATED AT 1000 psi

Specimen Number	Condition	Burnup at. %	Irradiation Temperature, °C		As-Irradiated Density, ρ_f g/cm ³	Swelling, % $\frac{\rho_i - \rho_f}{\rho_f} \times 100$	"R" p % Swelling/ at. % Burnup	"R"*
			Reactor Up	Reactor Down				
High Purity-High Carbon**								
P2A-1	A	0.13	375	380	18.85	0.5	3.9	No Data
P2A-2	A	0.13	375	380	18.80	0.8	6.1	
P2C-1	A	0.13	450	450	18.80	0.8	6.1	
P2C-2	A	0.13	450	450	18.63	1.7	13	
P2D-1	B	0.13	430	430	18.70	1.3	10	
P2D-2	B	0.13	430	430	18.50	2.4	19	
P3A-2	A	0.15	540	510	18.07	4.9	33	
					18.16	4.3	29	
P3C-1	A	0.15	575	575	18.42	2.9	19	
					18.15	4.3	29	
P3D-1	B	0.15	570	565	18.81 ^{††}	0.7	4.6	
P4A-2	A	0.20	520	~345	18.31	3.5	17	
P4D-1	B	0.20	620	~450	18.70	1.3	6.5	
P4D-2	B	0.20	620	~450	18.85 ^{††}	0.5	2.5	
High Purity-Low Carbon [†]								
P3A-1	A	0.15	540	510	17.15	11	71	400
					17.33	10	65	400
P3C-2	A	0.15	575	575	16.88	13	84	330
					16.85	13	85	330
P4A-1	A	0.20	520	~345	15.96	19	92	400
P4C-1	A	0.20	625	~450	18.57	2.5	12	60
P4C-2	A	0.20	625	~450	18.71	1.7	8.5	60

* "R" is the swelling typically observed for an equivalent irradiation at low pressure (~30 psi)

** PT3-NA material: 54 ppm Fe, 10 ppm Al, 34 ppm Si, 480 ppm C, 2 ppm N

† T-3 material: 64 ppm Fe, 5 ppm Al, 25 ppm Si, 6 ppm C, 8 ppm N

†† Metallographic examination revealed more swelling than these density values would indicate

A As-extruded
B 730 °C - 15 min - W.Q.

FIGURE 3.9. INFLUENCE OF PRESSURE ON SWELLING IN A U + Fe-Si ALLOY

FIGURE 3.10. SWELLING IN HIGH PURITY URANIUM IRRADIATED AT 1000 psi

not yet available for comparisons at the lower temperatures. A portion of the low pressure swelling-temperature relationship determined for high purity-low carbon uranium is included in Figure 3.10 for comparison purposes. The large effect of pressure is quite obvious. As can be seen in Table 3.3, 1000 psi reduces the amount of swelling in the 500 to 625 °C range by about a factor of 5 for T-3 material. (The high carbon PT3-NA material has not as yet been evaluated at low pressure.) The magnitude of the effect is evidence that pressure is overcoming swelling by interfering with the mechanical processes which give rise to microtearing. Because the swelling-temperature curve still shows a maximum even under conditions of high pressure, the swelling process is far more complicated than a process involving inert gas agglomeration. Data will be available shortly for the series of 500 psi irradiations and data will be forthcoming for 5000 psi irradiations.

The marked influence of carbon is a little surprising and bears additional study. The preirradiation microstructures are compared for the two carbon levels in Figure 3.11. The carbides are quite fine and the grain size is somewhat smaller for the PT3-NA uranium. The improved behavior of the high carbon uranium is possibly associated with the fine carbides which interfere with the mechanical processes which give rise to swelling. This material develops the worked microstructure but does not tear in the 400 to 500 °C range at 1000 psi. In the 500 to 600 °C range little or no aligned tearing is present within the grains but porosity or tearing is present at grain boundaries. In the low carbon uranium, pressure has effectively reduced the the magnitude of the aligned tearing but has not completely eliminated it. The optical microstructures of low carbon specimen P3C-2 and high carbon specimen P3C-1 which were irradiated at the same position in the capsule are shown in Figure 3.12. The microstructures observed in the electron microscope are illustrated in Figures 3.13 and 3.14, respectively. Both materials exhibit a high density of very small ($<0.05 \mu$) particles which are unidentified. No size-distribution measurements have been made. There is some doubt that these particles are real. They may be artifacts introduced by preparation.

Polarized Light

100μ

a) High Carbon, 480 ppm

100μ

Polarized Light

100μ

b) Low Carbon, 6 ppm

100μ

FIGURE 3.11. PREIRRADIATION APPEARANCE OF THE TWO TYPES OF HIGH PURITY URANIUM EMPLOYED IN CONTROLLED PRESSURE CAPSULES. Neg. No. 4L2192B, C; 4652188B, C

a) High Carbon (484 ppm) (P3C-1)

100 μ

b) Low Carbon (6 ppm) (P3C-2)

100 μ

FIGURE 3.12. TWO TYPES OF HIGH PURITY URANIUM IRRADIATED TO 0.15 at. % BURNUP AT 575 °C AND 1000 psi. a) $\Delta V/V = 3\%$; b) $\Delta V/V = 13\%$. Neg. No. D673, D687.

FIGURE 3.13. HIGH CARBON (484 ppm)-HIGH PURITY URANIUM
IRRADIATED AT 575 °C TO 0.15 at.% BURNUP (P3C-1) AT 1000 psi.
 $\Delta V/V = 3\%$. Neg. No. 3149E.

10 μ

FIGURE 3.14. LOW CARBON (6 ppm)-HIGH PURITY URANIUM IRRADIATED AT 575 °C TO 0.15 at.% BURNUP (P3C-2) AT 1000 psi. $\Delta V/V = 13\%$. Neg. No. 3345B.

This marked effect of carbon places the value of the iron and silicon additions in the U + Fe-Si alloy under suspicion. Figure 3.15 compares the swelling observed at 1000 psi for the high purity-high carbon uranium and the U + Fe-Si alloy. It is obvious that a single curve can be drawn through the data points. It is impossible to distinguish one behavior from the other. (The spread on two of the points represents the variation in density observed with repeat measurements on these two samples.) Corresponding data will be obtained at lower pressure. It would appear that carbon is the important additive in the U + Fe-Si alloy insofar as swelling is concerned. Carbon undoubtedly also contributes to the improved swelling resistance exhibited by the "British" uranium but the other additives, iron and aluminum, must also impart some resistance as this alloy is distinctly superior to the others studied on this program. The mechanism of the improvement is not understood.

FIGURE 3.15. SWELLING IN HIGH CARBON-HIGH PURITY URANIUM AND IN U + Fe-Si ALLOY

Capsule P-5 controlled at 450 °C and 500 psi during irradiation to a reported exposure of 0.16 at. % burnup in the specimens was opened in Radiometallurgy. Examination of the specimens is in progress. Extensive surface roughening and sample distortion developed due to irradiation growth. Density measurements were difficult because of this but preliminary estimates indicate that this 500 psi pressure was not effective in reducing the swelling that occurs at low pressure (~30 psi). This supports the previously advanced concept that mechanical processes rather than fission gas agglomeration are responsible for swelling in uranium and its alloys. If fission gases were responsible for swelling, then swelling behavior should be a relatively simple inverse function of pressure. Since increasing the pressure from ~30 to 500 psi apparently has no effect on swelling while increasing the pressure to 1000 psi reduced swelling by a factor of 5, it is obvious that a simple relationship does not exist between pressure and swelling.

Effect of Enrichment. Three low pressure capsules, 31, 30, and 24, containing only high purity enriched uranium specimens were opened and the specimens recovered for radiometallurgical examination. Capsules 31 and 30 were controlled at 375 and 400 °C, respectively, and the 2.88 at. % U^{235} specimens were irradiated to estimated burnups of 0.34 and 0.22 at. %, respectively. Density measurements and macro observations revealed that extensive swelling had occurred in these specimens. Thus, the peak in the low pressure swelling-temperature curve is displaced to lower temperatures than had been inferred previously from very low burnup data. The specimens from Capsule 24 were enriched to 1.44 at. % U^{235} . This capsule was controlled at 625 °C and the burnup in the specimens was estimated to be 0.13%. These specimens were in good condition as anticipated from the operating temperatures. These swelling results confirm previous conclusions that varying the fission rate by a factor of 4 (natural uranium containing 0.72 at. % U^{235} versus enriched uranium containing 2.88 % U^{235}) does not significantly alter the swelling-temperature relationship established for high purity uranium at low pressure.

Dual Irradiation Temperature. Metallograpny has been completed on specimens irradiated at low pressure at 525 °C to 0.037 at.% burnup and at approximately 200 °C for an additional 0.05 at.% burnup. The pertinent irradiation data concerning these specimens were summarized in HW-84573 (Quarterly Report, October-December, 1964) in Table 3.4. High purity-low carbon uranium in several metallurgical states, U + Fe-Si, and "British" alloy were included. Optical and electron micrographs of the high purity specimen in the as-extruded condition are illustrated in Figures 3.16 and 3.17. Rows of aligned tears that formed during irradiation at 525 °C are still present but the rows are no longer straight. They have become curved as the grain in which they formed has undergone plastic deformation during the irradiation at the lower temperature. This indicates a crystallographic relationship between the planes on which tears develop and the low temperature deformation planes. Grain boundary tearing, particularly at triple points, is also present and is believed to have formed at the low temperature. As this temperature is considerably lower than that at which grain boundary tearing is normally encountered, it is felt that this was probably initiated by the aligned, 525 °C tears.

Second Phase Agglomeration. A comparison was made between the agglomeration of second phase particles occurring during irradiation and during out-of-reactor annealing at high alpha phase temperatures for the British adjusted uranium studied on this program. Figure 3.18 shows this U + Fe-Al-Si alloy in the as-extruded condition (625 °C extrusion temperature), after vacuum annealing at 600 °C for one month and a after being exposed in-reactor at 600 °C for about three months. Pronounced coalescence of the phase believed to be U_6Fe occurred during both the vacuum anneal and the irradiation. Resolution was not sufficient to evaluate the condition of the finer UAl_2 particles. This observation would appear to be somewhat in contrast to others that have been made: that second phase particles are put into solution and reprecipitated on a finer scale during irradiation. In the case of the samples depicted in Figure 3.18, very similar agglomeration behavior was noted in- and out-of-reactor.

100μ

100μ

FIGURE 3.17. LOW CARBON HIGH PURITY URANIUM (22B-1) IRRADIATED AT 525 °C TO 0.037 at.% BURNUP AND AN ADDITIONAL 0.05 at.% BURNUP AT 200 °C. $\Delta V/V = 9\%$. Neg. No. D2169, D2170.

10μ

FIGURE 3.17. LOW CARBON-HIGH PURITY URANIUM (22B-1) IRRADIATED AT 525 °C TO 0.037 at.% BURNUP AND AN ADDITIONAL 0.05 at.% BURNUP AT 200 °C. Neg. No. 3548D.

FIGURE 3.18. AGGLOMERATION OF SECOND PHASE PARTICLES IN
 U + 640 Al-400 Fe-85 Si-500 C. Neg. No. 0653217.

Quantitative Metallography

As part of the fundamental study of the swelling phenomena, quantitative metallographic techniques are being developed which will be useful for determining which physical mechanisms are active. The statistical foundation was developed for a quantitative technique used in estimating the three-dimensional distribution of pore sizes from measurements made on the two-dimensional replicas prepared from irradiated uranium samples. Specializations of this generalized approach yield methods for estimating the three-dimensional size distribution which is the same as either the Saltykov or Saltykov-Johnson methods. In addition, this generalized approach also estimates the variances of the three-dimensional distribution estimates. A computer program for numerically evaluating data from replicas has been reprogrammed and adapted for UNIVAC-1107 use. Debugging of this program has been completed and check cases have been run using the revised program.

REACTOR METALS RESEARCH UNITALLOY SELECTION - T. T. Claudson

Several nickel base and refractory metal alloys are being irradiated to determine the effects of irradiation upon their mechanical properties. These specimens have been irradiated over a range of temperatures and exposures and are being tested at temperatures applicable to various reactor applications.

During the past quarter several refractory metal alloys were tested at temperatures to 1090 °C. The results of tensile tests performed at 1090 °C on W-25 Re rod material is shown in Figure 4.1. Specimens were irradiated at 2.4×10^{20} , 3.4×10^{20} , and 5.6×10^{20} nvt ($E > 1$ MeV) in the ETR at 50 °C. Full recovery of properties at this test temperature was not found as indicated by the increase in both yield strength and ultimate tensile strength of the material as compared to the control specimen. The ductility of the specimens was also decreased by the irradiation as indicated by the lower percent reduction in area and total elongation. Neither the control specimen nor the specimens irradiated to 3.4×10^{20} nvt showed any effects of strain hardening, exhibiting low uniform elongation values. The higher exposure specimen (5.6×10^{20} nvt) exhibited significant strain hardening and thus a higher uniform elongation. A significant decrease in reduction in area was observed for this higher exposure specimen.

Table 4.1 shows the results of tensile tests performed on refractory metal alloys at 1090 °C. The properties of Cb-752, Cb-1 Zr, and Mo tested after irradiation show essentially complete recovery when compared to the unirradiated control specimens. Strength and ductility of the pre- and postirradiated specimens are approximately the same. The irradiated specimen of TZM, however, shows a slight (11%) increase in yield strength and a decrease in both total elongation and reduction in area.

FIGURE 4.1 EFFECTS OF 50 °C NEUTRON IRRADIATION UPON THE 1090 °C MECHANICAL PROPERTIES OF W-25 Re ALLOY

TABLE 4.1. EFFECTS OF NEUTRON IRRADIATION AT 50 °C UPON THE MECHANICAL PROPERTIES OF REFRACTORY METAL ALLOYS TESTED AT 1090 °C

<u>Alloy</u>	<u>Specimen</u>	<u>nvt (E > 1 MeV)</u>	<u>0.2% Yield Strength, psi</u>	<u>Ultimate Tensile Strength, psi</u>	<u>% Uniform Elong.</u>	<u>% Total Elong.</u>	<u>% Red. Area</u>
W-25 Re	- -	Control	88,240	94,960	1.79	23.30	75.21
W-25 Re	474-1	2.4×10^{20}	108,040	113,620	0.25	14.34	65.62
W-25 Re	484-6	3.4×10^{20}	107,140	114,710	2.63	13.88	65.13
W-25 Re	476-1	5.6×10^{20}	121,500	147,200	12.58	16.28	33.18
Cb-752	8	Control	21,920	24,290	7.02	33.38	86.70
Cb-752	9	Control	17,900	24,030	5.38	30.33	87.63
Cb-752	475-3	9×10^{20}	17,890	23,790	6.87	33.38	87.89
Cb-1 Zr	10	Control	9,450	10,550	1.39	52.34	99.58
Cb-1 Zr	454-1	5.9×10^{20}	9,120	9,910	1.25	49.21	99.56
Mo	- -	Control	24,160	24,370	0.56	33.80	92.44
Mo	481-6	2.98×10^{20}	22,550	22,770	0.42	27.37	91.49
Mo	482-2	3.17×10^{20}	23,830	24,040	0.49	38.64	88.09
TZM	14	Control	51,450	53,320	1.12	11.60	65.98
TZM	481-2	2.4×10^{20}	57,140	60,500	1.16	7.98	47.48

IRRADIATION FACILITIES OPERATION - J. E. Irvin

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 through ETR Cycle 76 are given in Table 4.2 along with the estimated neutron fluxes and exposures ($E > 1$ MeV). There were no capsule discharges from any of the ambient temperature reactor core positions at the conclusion of Cycle 73. The operating histories of the ETR and the G-7 Hot Water Loop are given in Table 4.3. The temperature efficiency for the G-7 Loop was unusually low for ETR Cycles 73 and 76, because of malfunctioning loop equipment. During these particular cycles it was necessary to operate the G-7 Hot Water Loop for extended periods of time at temperatures between 450 and 500 °F. The history and discharge schedule for specimens in the out-of-reactor loop are given in Table 4.4. At the end of ETR Cycle 74 the G-7 Hot Water Loop was modified to provide for low oxygen (< 0.1 ppm) operation. An ammonium-base resin was used as a deoxygenating agent. Sampling of the loop water from several positions within the G-7 loop system, is being performed on a daily, weekly, and cycle basis. The loop modifications and sampling procedures are being performed under the supervision of Chemical Metallurgy personnel. Water chemistry changes in the out-of-reactor loop were made to coincide with these changes in the G-7 loop. Consequently, the water chemistry of both loops is still very similar.

TABLE 4.2. SUMMARY OF EXPERIMENTS DISCHARGED
FROM THE ETR AFTER CYCLES 73 THROUGH 76

<u>Experiment Designation</u>	<u>Number and Type of Specimens</u>	<u>Estimated Flux, nv^(a)</u>	<u>Estimated Exposure, nvt^(a)</u>
<u>Quadrant Discharges</u>			
<u>Cycle 73</u>			
188	6 Nickel-Base Tensiles	7.30×10^{13}	1.63×10^{20}
189	6 Hastelloy X-280 Tensiles & S. R. ^(b)	2.71×10^{13}	1.05×10^{20}
194	18 AISI 316-L Tensiles	4.96×10^{13}	1.11×10^{20}
<u>Cycle 74</u>			
191	2 Zircaloy-2 DCB ^(c)	5.5×10^{13}	4.00×10^{20}
197	12 Zr-Alloys Corrosion	1.87×10^{13}	7.80×10^{19}
198	12 Zr-Alloys Corrosion	1.57×10^{14}	6.55×10^{20}
200	6 AISI 348 Tensiles	2.39×10^{13}	4.64×10^{19}
<u>Cycle 75</u>			
192	2 Zircaloy-2 DCB	6.8×10^{13}	6.00×10^{20}
202	6 Inconel 600 Stress Rupture	3.7×10^{13}	6.70×10^{19}
203	6 Nickel-Base Stress Rupture	4.5×10^{13}	8.20×10^{19}
204	5 Inconel 600 Tensile & S. R.	6.5×10^{13}	1.20×10^{20}
<u>Cycle 76</u>			
196	18 AISI 316-L Tensiles	8.0×10^{13}	6.0×10^{20}
201	6 AISI 304 Tensiles	6.0×10^{13}	3.3×10^{20}
205	18 Zr-Alloys Corrosion	1.1×10^{14}	4.0×10^{20}
206	18 Zr-Alloys Corrosion	2.5×10^{13}	9.0×10^{19}
213	6 Hastelloy X-280 Tensile	8.0×10^{13}	1.5×10^{20}
<u>Capsule Discharges</u>			
<u>Cycle 74</u>			
325	11 Zircaloy-2 Tensiles	1.6×10^{14}	1.04×10^{22}
<u>Cycle 75</u>			
468	8 AISI 348 & 350 Tensiles	1.8×10^{14}	5.62×10^{21}
<u>Cycle 76</u>			
466	8 AISI 348 Tensiles	1.7×10^{14}	5.63×10^{21}
467	8 AISI 410 & 350 Tensiles	1.8×10^{14}	5.42×10^{21}
667	8 Zircaloy-2 Tensiles	1.3×10^{14}	1.10×10^{21}
668	8 Zircaloy-2 Tensiles	1.3×10^{14}	1.10×10^{21}
669	8 Zircaloy-2 Tensiles	1.2×10^{14}	1.02×10^{21}

(a) Neutrons with energies greater than 1 MeV

(b) Stress rupture specimens

(c) Double cantilever beam specimens

Total specimens discharged, Cycles 73 through 76 = 206

Total specimens discharged, ETR G-7 Loop, Cycles 73 through 76 = 147

Total specimens discharged, ETR G-7 Loop, to date = 2563

TABLE 4.3. OPERATING HISTORY OF ETR
AND G-7 HOT WATER LOOP FACILITY

<u>Operating History</u>	<u>ETR Cycle Number</u>				
<u>1. Reactor History</u>	<u>72</u>	<u>73</u>	<u>74</u>	<u>75</u>	<u>76</u>
Startup ^(a)	5-28-65	6-29-65	8-9-65	9-25-65	11-13-65
End of Cycle	6-20-65	8-1-65	9-12-65	10-24-65	12-5-65
Megawatt Days	3348	4516	3920	3566	1847
Effective Days at 175 MW	19.1	25.8	22.4	20.3	10.6
Number of Scrams ^(b)	8	13	6	6	6
Number of Shutdowns	1	3	3	3	3
<u>2. G-7 Hot Water Loop History</u>					
Maximum Temperature	530 °F	530 °F	540 °F	540 °F	530 °F
Effective Days Above 200 °F	19.8	27.5	22.9	21.5	13.9
Effective Days at Oper. Temp.	16.8	17.6	18.4	17.7	9.3
Operating Efficiency ^(c)	104.0%	106.0%	102.0%	106.0%	131.0%
Temperature Efficiency ^(d)	85.0%	62.5%	80.5%	82.4%	67.1%

(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 with respect to effective days of reactor operation at 175 MW.

(d) Effective days of loop operation between 500 and 550 °F with respect to days of operation above 200 °F

TABLE 4.4. HISTORY AND DISCHARGE SCHEDULE
FOR THE OUT-OF-REACTOR LOOP

<u>Loop History</u>	<u>Cycle Number</u>			
	<u>72</u>	<u>73</u>	<u>74</u>	<u>75</u>
<u>1. Time at Temperature, hr</u>				
200 °C (392 °F)	25.3	42.9	37.7	53.2
218 °C (424 °F)	5.1	25.6	13.9	4.6
246 °C (475 °F)	42.3	161.6	55.8	32.6
282 °C (540 °F)	<u>405.0</u>	<u>422.1</u>	<u>441.2</u>	<u>424.9</u>
Total Time, hr	477.7	652.2	548.6	515.3
<u>2. Specimen Discharge (Material, Specimen Type, and Number)</u>				
Nickel-Base Tensiles	--	--	18	--
Inconel X-750 Tensiles & Stress Rupture	6	4	--	5
Inconel 600 Tensiles & Stress Rupture	--	--	--	12
Hastelloy X-280 Tensiles & Stress Rupture	--	8	--	--
Zircaloy-2 Tensiles	<u>--</u>	<u>--</u>	<u>24</u>	<u>--</u>
Total number discharged	6	12	42	17

Total specimen discharged to date = 1281

Data Processing

The REM master file currently contains approximately 4000 tensile test records on 40 or more alloys which have been examined on the Irradiation Effects to Reactor Materials Program. Summary reports of the processed data for specific alloys are being generated by the retrieval portion of the REM program. These trial reports will eventually be linked with analytical, statistical, or plotting subroutines to further reduce the time required for engineering analysis. The REM program is being converted to FORTRAN IV for processing on the UNIVAC 1107 computer.

IRRADIATION DAMAGE TO STAINLESS STEELS - J. E. Irvin,

J. L. Brimhall, and B. Mastel

The purpose of this phase of the program is to determine the combined effects of irradiation and environment on stainless steels. Changes in mechanical properties will be determined for several irradiation and testing temperatures to establish the limiting conditions these alloys may receive in reactor service. Particular emphasis will be placed on establishing the service conditions under which these alloys are metallurgically unstable and to determine the mechanisms by which irradiation-induced property changes contribute to this instability.

Austenitic Stainless Steels

Tensile and creep specimens were fabricated from 5/8 in. diam rods of AISI 304 SS program material in the annealed condition. The detailed fabrication history of this material is given elsewhere⁽¹⁾ but the certified chemical analysis and mechanical property tests are given in Tables 4.5 through 4.7 for comparison with data obtained to date on this material. The difference in mechanical properties between the plate and rod material is caused by the cold straightening of the rod material after annealing in a coil. To obtain fully annealed material the specimens were fabricated from rods which had been given an anneal at 1850 ± 25 °F for 30 min and water quenched.

TABLE 4.5. CERTIFIED CHEMICAL ANALYSIS OF AISI 304 STAINLESS STEEL.
HEAT No: 55697

Item	C	Mn	P	S	Si	Cr	Ni	Cu	Mo	Pb	Ca	Sn	Ti	N
Ladle	0.051	0.83	0.020	0.012	0.47	18.30	9.50	0.13	0.090	<0.001	0.11	0.01	<0.01	0.032
Check	0.050	0.88	0.019	0.010	0.50	18.21	9.57	0.21	0.18	<0.001	0.11	0.004	<0.01	0.034
Check	0.050	0.88	0.018	0.010	0.49	18.29	9.53	0.21	0.18	<0.001	0.11	0.006	<0.01	0.024
Check	0.060	0.86	0.019	0.010	0.49	18.26	9.43	0.21	0.18	<0.001	0.11	0.008	<0.01	0.032

Total rare earths <0.001

1. T. T. Claudson. Fabrication History of Alloys Used in the Irradiation Effects on Reactor Structural Materials Program, BNWL-CC-236. October, 1965.

TABLE 4.6. CERTIFIED MECHANICAL PROPERTIES
FOR AISI 304 STAINLESS STEEL PLATE. HEAT No.
55697

<u>Item</u>	<u>Yield Strength, psi</u>	<u>Tensile Strength, psi</u>	<u>Percent Elongation</u>	<u>Hardness, BNH</u>	<u>R. A.</u>	<u>G. S. ASTM</u>
1/2 in. plate	39,700	77,100	65	126	60.8	4.5
1/2 in. plate	39,500	77,000	65	126	60.5	4.5
1 in. plate	41,200	81,800	65	153	72.2	4.5
1 in. plate	41,200	81,700	65	153	72.0	4.5
2 1/2 in. plate	40,600	81,300	70	137	71.5	4.5
2 1/2 in. plate	40,400	80,700	70	137	71.5	4.5

Oxalic Acid Test Satisfactory
 Bend Test Satisfactory

TABLE 4.7. CERTIFIED MECHANICAL PROPERTIES
FOR AISI 304 STAINLESS STEEL RODS. HEAT No.
55697

<u>Item</u>	<u>Yield Strength, psi</u>	<u>Tensile Strength, psi</u>	<u>Percent Elongation</u>	<u>R. A., %</u>
Bar 82	50,500	81,500	61	75
Bar 80	53,000	86,000	61	77

A series of tests are being conducted on these round tensile and creep specimens at temperatures between room temperature and 800 °C. A portion of the results of these tests is given in Table 4.8. As has been noted previously⁽¹⁾ a plateau or minimum exists in the strength and ductility of this material in the test temperature range between 200 and 400 °C. It is in this intermediate temperature range that the absolute minimum ductilities have been observed for both AISI 304 and 348 SS irradiated and tested up to 700 °C. At test temperatures above 600 to 700 °C a difference in deformation

1. Quarterly Progress Report, Metallurgy Research Operation, April, May, June, 1965, edited by J. J. Cadwell, BNWL-120.

TABLE 4.8. TENSILE PROPERTIES OF ANNEALED AISI 304 STAINLESS STEEL (WORKING DIRECTION: R.D.)

Test Temp., °C	Strength, 10 ³ psi		% Strain		Reduction of Area, %	Plastic Work, ft-lb
	0.2%	UTS	Uniform	Necking		
R. T.	28.4	87.0	85.2	7.8	80.1	139.6
R. T.	27.0	86.1	93.6	8.6	79.1	154.4
200	21.9	59.7	44.4	6.9	76.1	56.0
200	20.6	60.2	44.9	7.0	73.1	53.1
300	17.0	61.9	47.1	4.6	69.2	52.6
300	17.3	61.9	46.4	5.3	70.2	53.2
350	17.8	63.1	45.9	5.1	63.7	52.7
350	18.1	63.7	45.9	5.2	68.2	53.1
400	18.8	68.2	46.2	4.9	64.5	56.2
400	18.4	67.8	46.3	4.9	64.5	56.4
450	17.2	65.6	45.4	4.5	64.7	53.3
450	18.0	65.8	45.2	4.7	69.6	53.8
500	16.2	60.0	46.0	4.3	67.0	49.2
500	14.4	54.5	47.4	5.1	68.2	47.0
550	15.0	54.5	46.1	6.9	56.2	48.5
550	15.9	54.7	45.5	5.2	66.6	49.3
600	14.9	46.0	37.3	9.3	43.8	37.9

mode also results in a ductility minimum. Therefore, both the intermediate and high temperature deformation modes are of considerable interest depending upon the intended application.

These changes in mechanical properties have been observed and described in detail by a number of investigators. The basic mechanisms underlying the irradiation effects to the engineering properties, however, are not well understood. Transmission microscopy is being utilized to investigate the irradiation induced changes produced in these materials and better understand the basic mechanism operating.

AISI 304 and 348 SS have been characterized in the as-fabricated condition. Microstructures have been obtained from transmission studies on both annealed and 25% cold-worked material. Specimens suitable for transmission studies were prepared by sectioning and electrolytically thinning bulk samples. The typical microstructure of the AISI 304 SS is shown in Figure 4.2. A high dislocation density, 3×10^9 dislocations/cm², was observed in the annealed material shown in Figure 4.2(a). The dislocations are associated with grain boundaries and second phase particles tentatively identified as carbides of the $M_{23}C_6$ type ranging in size from 150 Å to 2 μ in diameter. Figure 4.2(a) also shows dislocations originating from one of the carbides, probably due to the difference in thermal expansion between the particle and the matrix.

The microstructure of the 25% cold-worked material is extremely complex as shown in Figure 4.2(b). The predominant features are the bundles of stacking faults incorporated among dislocation tangles. The structure observed is typical of highly deformed materials having low stacking fault energies.

The AISI 348 SS microstructure was also characterized and was found to be quite similar to that of the AISI 304 SS. The major difference was the greater number of carbides precipitated found in the AISI 348 SS because of the tantalum and niobium which are carbide formers. A greater variety of precipitate sizes was observed in the AISI 348 than in the AISI 304 SS. Characterization of the microstructures of both AISI 304 and 348 SS in the unirradiated condition is essentially complete now, and studies are progressing on specimens in the irradiated condition.

Irradiations are currently being conducted in predominantly thermal, mixed spectrum, and fast flux reactors on AISI 304, 348, and 316 SS. Irradiation and test temperatures to 800 °C are being conducted to determine the effects of environments such as sodium, helium, and pressurized water on these materials.

Flat tensile specimens of AISI 316-L SS were tested in the as-machined condition at temperatures between room temperature and 800 °C. Both

(a)

(b)

FIGURE 4.2. MICROSTRUCTURE OF 304 STAINLESS STEEL. (a) ANNEALED AT 1800 °F AND AIR COOLED. (b) 25% COLD WORK. Neg. No. 3648F, 3651C. 73,000X.

annealed and 25% cold-worked specimens from the transverse direction with respect to rolling were tested at cross-head speeds of 0.05 and 0.005 in./min. Another series of tests was conducted at room temperature on 25% cold-worked AISI 316-L SS after 1 hr isochronal anneals at temperatures up to 900 °C. These tests were run at 0.005 in./min. The results of both series of tests are shown graphically in Figures 4.3 through 4.5. It can be seen from Figure 4.3 that both the strength and ductility are affected by test temperatures as low as 400 °C. Both the yield and ultimate strength are reduced drastically at test temperatures between 300 and 400 °C for both the annealed and 25% cold-worked material. A plateau with a slight hump which may be indicative of an aging process is shown in the elongation curves for both annealed and cold-worked material. The values obtained from reduction of area measurement were generally consistent with these trends, but show a tendency for scatter at the higher test temperatures. There was no difference in the values obtained for comparable specimen conditions at either of the cross-head speeds used.

The recovery of cold work damage to this material is essentially complete only at annealing temperatures near 1000 °C as shown in Figures 4.4 and 4.5. Annealing temperatures below this result in a partial recovery, the amount being proportional to the annealing temperature. At intermediate annealing temperatures near 300 or 400 °C, a strengthening accompanied by a loss in ductility is observed. It is probable that the combined treatment of cold work prior to anneal, annealing at 300 to 400 °C, and straining at room temperature is more than sufficient to precipitate second phase particles in this material. Electron microscopy will be utilized in determining the nature and effects of this phenomenon.

AISI 316-L SS specimens in both the annealed and 25% cold-worked condition were irradiated in the ETR G-7 Hot Water Loop at 290 °C to an exposure of 1.11×10^{20} nvt (>1 MeV). After discharge tensile tests were conducted at test temperatures to 750 °C on these irradiated specimens. The results of these tests are illustrated graphically in Figures 4.6 through 4.12. After irradiation the strength of the irradiated material declines gradually with increasing test temperature and does not undergo

FIGURE 4.3. EFFECT OF TEST TEMPERATURE ON THE TENSILE PROPERTIES OF AISI 316-L SS. (ALL TRANSVERSE SPECIMENS)

FIGURE 4. 4. THE EFFECTS OF ANNEALING TEMPERATURE ON THE ROOM TEMPERATURE STRENGTH OF AISI 316-L STAINLESS STEEL (All specimens 25% cold worked in the transverse direction.)

FIGURE 4.5. THE EFFECT OF ANNEALING TEMPERATURE ON THE DUCTILITY OF AISI 316-L STAINLESS STEEL (All specimens 25% cold worked in the transverse direction.)

FIGURE 4.6. EFFECT OF TEST TEMPERATURE ON THE STRENGTH OF IRRADIATED AISI 316-L SS. (IRRADIATION TEMPERATURE $\sim 280^{\circ}\text{C}$).

FIGURE 4.7. EFFECT OF TEST TEMPERATURE ON THE STRENGTH OF IRRADIATED AISI 316-L SS. (IRRADIATION TEMPERATURE $\sim 280^{\circ}\text{C}$)

FIGURE 4.8. EFFECT OF TEST TEMPERATURE ON THE DUCTILITY OF IRRADIATED AISI 316-L SS. (IRRADIATION TEMPERATURE $\sim 280^{\circ}\text{C}$).

FIGURE 4. 9. EFFECT OF TEST TEMPERATURE ON THE DUCTILITY OF IRRADIATED AISI 316-L SS. (IRRADIATION TEMPERATURE $\sim 280^{\circ}\text{C}$).

FIGURE 4.10. EFFECT OF TEST TEMPERATURE ON THE ENERGY TO CAUSE FAILURE IN IRRADIATED AISI 316-L SS. (TRANSVERSE SPECIMEN, IRRADIATED AT $\sim 280^{\circ}\text{C}$).

FIGURE 4.11. EFFECT OF TEST TEMPERATURE ON THE STRENGTH OF IRRADIATED AISI 316-L SS. (TRANSVERSE SPECIMENS, IRRADIATED AT $\sim 280^{\circ}\text{C}$).

FIGURE 4.12. EFFECT OF TEST TEMPERATURE ON THE DUCTILITY OF IRRADIATED AISI 316-L SS. (TRANSVERSE SPECIMENS, IRRADIATED AT $\sim 280^{\circ}\text{C}$).

the accelerated decrease note in the 300 to 400 °C range noted for the unirradiated material. Figures 4.6 and 4.7 show that this is true for both the yield and ultimate strength. Full recovery of the original strength values for this material seems to occur between 750 and 800 °C.

The ductility increases slightly at test temperatures between room temperature and 400 °C, reaching a maximum in the 300 °C range as shown in Figures 4.8 through 4.10. The annealed material shows the greatest difference between the irradiated and unirradiated elongation values. The cold-worked material shows there is little difference in either total or uniform elongation at about 300 °C between the irradiated and unirradiated condition. Hence, at this particular temperature, the test temperature appears to exert as much influence on the material behavior as does the irradiation damage. The plastic work illustrated in Figure 4.10, which is a measure of the work required to break the specimen, also exhibits this behavior.

Figure 4.11 shows that cold work raises the yield strength at a greater rate than the ultimate strength and that this difference is preserved at all test temperatures after irradiation to 1.1×10^{20} nvt (> 1 MeV). The difference between the strength of the annealed and 25% cold-worked material is reduced gradually, however, with increasing test temperature. The greatest difference in the elongation values for irradiated material in the annealed and cold-worked conditions, however, occurs at test temperatures near 300 °C, as shown in Figure 4.12. The fact that there is an increase in the ductility of the annealed material and not the cold-worked material indicates some annealing of irradiation damage is occurring in this temperature range which is far below that required to anneal out cold work damage.

The change produced by irradiation in both the annealed and cold-worked materials is shown in Figures 4.13 and 4.14. The increase in strength shown in Figure 4.13 indicates that the greatest increase occurs in the ultimate strength of the cold-worked material for all test temperatures. The change in yield strength, however, between the irradiated and

FIGURE 4.13. EFFECT OF TEST TEMPERATURE ON THE CHANGE IN STRENGTH OF AISI 316-L SS DUE TO IRRADIATION AT $\sim 280^{\circ}\text{C}$.

FIGURE 4.14. EFFECT OF TEST TEMPERATURE ON THE CHANGE IN DUCTILITY OF AISI 316-L SS DUE TO IRRADIATION AT $\sim 280^{\circ}\text{C}$.

unirradiated material indicates that below about 325 °C the annealed material shows the greatest increase. Above 325 °C the cold-worked material shows the greatest change due to the combined strengthening of irradiation and precipitation hardening. Because of the low values of ductility in the unirradiated cold-worked material, the decrease due to either irradiation or precipitation hardening is small. Therefore, the decrease in ductility is greatest at all test temperatures for the annealed material as shown in Figure 4.14.

The chemical analysis and mechanical properties supplied for the AISI 316-L SS by the vendor are given in Table 4.9. The material was cold rolled from 1/4 in. plate to a final thickness of 0.100 in. Intermediate anneals at 1100 °C were made after each series of breakdown steps.

TABLE 4.9. CHEMICAL ANALYSIS AND MECHANICAL PROPERTIES
OF AISI 316-L SS

Chemical Analysis, Heat No. 21313-16

Carbon	0.021
Manganese	1.26
Silicon	0.60
Sulfur	0.020
Phosphorus	0.014
Chromium	17.5
Nickel	13.72
Boron	0.0028
Molybdenum	2.78

Mechanical Properties

Condition	Annealed
Hardness	BHN 143
0.2% Yield	47,300
Ultimate	89,200
% Elongation (in 2 in.)	55
% Reduction in Area	57.8

The microstructure was determined for the AISI 316-L SS in both the annealed and cold-worked conditions. Additional studies are in progress on the unirradiated material to determine the effects of test temperature. The microstructure of a 25% cold-worked specimen tested at 800 °C is shown in Figures 4.15 through 4.17.

(a)

100X

(b)

250X

FIGURE 4.15. MICROSTRUCTURE OF AISI 316-L SS TESTED AT 800 °C (a) AT FRACTURE SURFACE, (b) AWAY FROM FRACTURE AREA. Neg. No. 4652237-C, 4652237-E.

(a)

1000X

(b)

1000X

FIGURE 4.16. MICROSTRUCTURE OF AISI 316-L SS AFTER TESTING AT 800 °C (a) AWAY FROM FRACTURE SURFACE, (b) NEAR FRACTURE SURFACE. Neg. No. (a) 4652237-G, (b) 4652237-F.

(a)

4500X

(b)

15,000X

FIGURE 4.17. MICROSTRUCTURE OF AISI 316-L SS TESTED AT 800 °C.
Neg. No. (a) 3658-C, (b) 3659-C.

The mode of failure was entirely intergranular as shown in Figures 4.15 and 4.16. Microcracks are initiated at the triple-points and propagate along the grain boundaries. There is greater evidence of grain boundary tearing nearer the fractured surface. These intergranular failures are due in part to the precipitate which occurs in the grain boundary at these temperatures, as shown in Figure 4.17. The microstructure shown in Figure 4.17 was obtained using conventional electron microscopy techniques for cellulose acetate replicas. A negative replica was prepared from chemically etched surface using HCl and H₂O₂. Figure 4.17(a) shows the second phase which has precipitated within the grain boundary. This second phase has been tentatively identified as sigma phase. Grain boundary movement is occurring as is evident from Figure 4.17(b), which shows a segment of serrated grain boundary containing second phase material. Second phase material has also precipitated along slip lines and regions of highly deformed material. Additional metallography is being obtained on material tested at other temperatures and in several different metallurgical conditions.

IRRADIATION DAMAGE TO ZIRCALOY-2 - J. E. Irvin

The purpose of this phase of the program is to investigate the combined effects of irradiation and environment on the mechanical properties of Zircaloy-2. Special attention will be given to the determination of mechanical property changes produced by irradiation at elevated temperatures. Changes in mechanical properties due to hydride content and morphology, fabrication history, and chemistry will be studied on tube, sheet, and rod materials.

Surveillance of NPR Tubing

A paper entitled "The Effects of Irradiation and Environment on the Mechanical Properties and Hydrogen Pickup of Zircaloy-2" was presented at the Electrochemical Society Meeting at Buffalo, New York, in October, 1965. The paper described the results obtained to date from a study of NPR tube material irradiated at 60 and 290 °C. Tensile tests were performed at room temperature and at 300 °C on specimens irradiated to 2.33×10^{21} nvt (>1 MeV). The greatest property changes occur in the material irradiated at 290 °C and tested at room temperature, but the lowest ductility observed occurs at the 300 °C test temperature. Corrosion rates were found to correlate with either time-at-temperature or neutron exposure, and were an order of magnitude greater in-reactor when compared with the equivalent out-of-reactor exposures. A flux rate dependence was noted in a few critical tests. The amount of hydride pickup was proportional to the corrosion rate. The hydride distribution was influenced by the amount and distribution of second phase material present in each tube examined. This paper has been scheduled for publication in the Journal of the Electrochemical Society some time between January and March of 1966.

A topical report is being prepared which will contain additional results obtained from this study. These results are also being compared with those obtained on a more comprehensive study of Zircaloy-2 rolled sheet. By means of this comparison and from separate observations on the NPR tube material, the following conclusions were drawn:

- Strong crystallographic textures are developed by different working histories. Variations in the textures examined do not cause important differences in the mechanical properties of the longitudinal specimens examined with irradiation at either 60 or 290 °C.
- A greater change in mechanical properties occurs at room temperature than at 300 °C for the materials irradiated at 290 °C. The effect of test temperature is reduced with increasing neutron exposure.
- No significant changes in mechanical properties were caused by out-of-reactor hot water exposures at 290 °C for greater than 5700 hr.
- Differences in the resulting metallurgical structure appear to influence the corrosion rate and the distribution of hydrides. Hydrides are preferentially precipitated along stringers and second phase particles in each tube examined. These materials also contain massive hydride platelets within the grains as well as long flow lines and second phase stringers.
- Hydride content less than 250 ppm is not believed to affect the mechanical properties of the tube materials tested.
- Flux rate appears to affect the corrosion rate even for the lowest integrated exposure obtained. The corrosion rate appears to increase with increasing flux rate for fluxes between 2.0×10^{13} and 1.1×10^{14} nv (> 1 MeV) or 5.0×10^{13} and 2.8×10^{14} nv (thermal).

Transition Joints Between Zircaloy-2 and Inconel 600

A topical report⁽¹⁾ is being published describing the effects of irradiation and environment on Zircaloy-2 coupled with Inconel 600. Transition joints between these two materials were fabricated by coextrusion and by an explosive welding technique. Specimens from each type of joint were irradiated in the ETR G-7 Hot Water Loop at 290 °C. The specimens were subsequently tested in tension at room temperature and at 300 °C. In both

1. J. E. Irvin and T. T. Claudson. The Effects of Irradiation and Environment on the Mechanical Properties of Inconel-Zircaloy Transition Joints, BNWL-190. September 29, 1965.

types of joints the Zircaloy-2 was found to be the limiting material as far as the mechanical properties were concerned. All but one of the test specimens failed in the Zircaloy-2 portion of the sample.

The hydrogen pickup was different in the two types of joints examined. Originally the hydrogen content in the Zircaloy-2 starting material was about the same for both types of joints. After exposures in the ETR G-7 Loop at 290 °C for more than 2200 hr, however, one joint showed a hydrogen content twice as high as the other. A hydrogen gradient also existed in these specimens along the transition joint itself which suggests either an easy diffusion path along the Zircaloy-Inconel interface or a galvanic reaction of sufficient potential to accelerate hydrogen sorption.

The difference in hydrogen content probably contributed to the marked difference observed in mechanical properties of the two types of joints. The microstructure resulting from the different fabrication histories is believed to have significant effects on both the hydrogen pickup and mechanical properties of these joints.

Additional studies in this area are not planned at present and were not provided for in the scope of the original program. However, since a number of transition joints between various materials have been proposed for reactor service, it seems that it will only be a matter of time before such components will actually be placed into service.

IRRADIATION DAMAGE TO NICKEL-BASE ALLOYS - I. S. Levy and

K. R. Wheeler

The combination of oxidation resistance and high temperature strength places the nickel-base alloys among the more promising materials for nuclear reactor application. When irradiated at high temperatures, these alloys, however, generally suffer damage which cannot be recovered by postirradiation treatments. The purpose of this program is to determine the effect of modified microstructures upon the irradiation stability of nickel-base alloys. These structural modifications are made by preirradiation thermal and/or mechanical treatments and are screened by tensile and stress-rupture tests and metallographic examination.

Solid-Solution Hardened Alloys

Previous reports^(1, 2) have discussed the concept of developing radiation damage resistant metals through preirradiation microstructural modification. This could be done by combinations of thermal-mechanical treatments which induce heterogeneous precipitation within the alloy structure. Control of precipitate location, volume, and type through preirradiation alloy conditioning processes could extend the useful in-reactor life of a structural component by increasing ductility while maintaining useful strength. Evidence of irradiated ductility improvement in Hastelloy X-280, solution-hardened nickel alloy, after preirradiation structural conditioning has been reported.⁽³⁾

During the last quarter, metallographic evidence was found for strain and irradiation induced changes in precipitate volume in both matrix and grain boundary areas. This is shown in the following three figures of

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1. Quarterly Progress Report, Metallurgy Research Operation, January, February, March, 1964, edited by J. J. Cadwell, HW-81269. General Electric Company, Richland, Washington. April 15, 1964.
 2. Quarterly Progress Report, Metallurgy Research Operation, April, May, June, 1964, edited by J. J. Cadwell, HW-82651. General Electric Company, Richland, Washington. July 15, 1964.
 3. Quarterly Progress Report, Metallurgy Research Operation, April, May, June, 1965, edited by J. J. Cadwell, BNWL-120. July 15, 1965.

transverse sections taken from tensile samples of Hastelloy X-280. In each case, the thermal history of the specimen, after an initial microstructural conditioning treatment, was 18 days at 540 °F, and 15 min of soaking time at 1350 °F to achieve thermal equilibrium, followed by an approximate 5 min testing time. (An Instron crosshead speed of 0.05 in./min had been used.) Figure 4.18 shows evidence of strain induced precipitation in the unirradiated condition. As contrasted with the unstressed buttonhead area of the sample, an increase in precipitate volume is seen in the stressed area in both matrix and grain boundary. Evidence for radiation (1×10^{20} nvt, $E > 1$ MeV) induced precipitation in the absence of strain was also found (Figure 4.19) in a comparison of unirradiated and irradiated buttonhead samples in the form of a fine matrix precipitate. Figure 4.18 and 4.19 show that the volume of rod-like structures remains relatively the same before and after strain or irradiation. As seen in Figure 4.20, the combined effect of strain and irradiation produces an increase in precipitate volume, which appears, at this magnification, to be primarily composed of rod-like structures.

The precipitation which appears here to be induced by strain and/or irradiation may be similar to the M_6C and an unidentified matrix phase observed in Hastelloy X by Comprelli and Wolff⁽¹⁾ after a prolonged (5075 hr at 1150 °F) exposure. They did not, however, observe a fine matrix precipitation after 5200 hr at 1050 °F. Comprelli and Lewis⁽²⁾ observed a uniform matrix precipitate along with heavy intergranular precipitation after 33 to 1025 hr exposures at 1400 °F. Electrolytic dissolution of coupons and X-ray analysis of the residues showed this (the Comprelli and Lewis) major precipitate to be of the M_6C group with a weak indication of AB_2 type Laves phase and $M_{23}C_6$ carbide.

It is interesting to note the presence in our Hastelloy X-280 micrographs of a massive, globular precipitate without a fine matrix precipitate

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1. F. A. Comprelli and U. E. Wolff. Stability of High Nickel Alloys in Superheated Steam, GEAP-4745. November 1964.
 2. F. A. Comprelli and J. E. Lewis. Microstructural Evaluation of Superheat Cladding Materials, GEAP-4751. January 1965.

FIGURE 4. 18. STRAIN-INDUCED PRECIPITATION. HEAT TREATMENT 8: 2150 °F/1 hr, A. C. ; 20% C. W. ; 1500 °F/24 hr, A. C. ALL MICROGRAPHS REDUCED 36% FOR PUBLICATION.

FIGURE 4.19. IRRADIATION-INDUCED PRECIPITATION. HEAT TREATMENT 6: 2150 °F/1 hr, A.C.; 15% C.W.; 1500 °F/24 hr, A.C. ALL MICROGRAPHS REDUCED 36% FOR PUBLICATION.

FIGURE 4. 20. COMBINED IRRADIATION- AND STRAIN-INDUCED PRECIPITATION. HEAT TREATMENT 2: 2150 °F/1hr, A. C.; 0% C. W.; 1500 °F/24 hr, A. C. ALL MICROGRAPHS REDUCED 36% FOR PUBLICATION.

in both the unstrained and unirradiated material after a 1500 °F/24 hr age followed by 1350 °F test temperature for 20 min. These observations are then contrasted with the onset of fine matrix precipitation in the 1500 °F/24 hr aged, 1350 °F tensile test material in the presence of lattice strain and/or radiation damage. Noting that other investigators found massive intergranular and fine matrix precipitation resulting from longer aging times at lower temperatures, it is logical to consider the possibility that the effect of our experimental pretreatments combined with strain and/or radiation has been to increase the rate of these precipitation reactions. We cannot, however, conclude that the grain boundary and matrix induced precipitates are identical with those triggered by thermal energy alone because the solid state reactions stimulated or caused by strain and irradiation may induce phases distinct from those thermally induced. We will attempt identification of the strain-irradiation-thermal induced microconstituents by means of microprobe analysis supported by X-ray analysis. As a final observation, platelet Widmanstatten structures are noted as a salient feature of the 1500 °F aged microstructures. These Widmanstätten platelets could be the sigma phase earlier observed in Hastelloy X aged at 1700 °F by Wheeler.⁽¹⁾ The appearance of platelets after the 1500 °F age is probably influenced by prior cold working of the material as shown in the buttonheads, Figure 4.18(a) and (b); Figure 4.20(d) shows evidence that these platelet structures also appear in unworked material after 1500 °F anneal under the influence of strain at 1350 °F and radiation.

Changes in microstructure are reflected in changes in mechanical properties. Correlations are now being made between observed microstructural changes in Hastelloy X-280 and its mechanical properties and will be discussed at length in a forthcoming topical report.

The effects of changing precipitate morphology and distribution on the high temperature creep resistance of nickel alloys in the unirradiated

1. Quarterly Progress Report, Metallurgy Research Operation, October, November, December, 1963, HW-79766. General Electric Company, Richland, Washington. January 15, 1964.

and irradiated conditions must be studied in detail. The effectiveness of preirradiation structure stabilization and the influence of changing structure on strength and creep resistance are being examined by means of the creep-rupture test. Ten Hastelloy X-280 stress-rupture specimens have been given experimental treatments and then irradiated at 540 °F to 1×10^{20} nvt ($E > 1$ MeV). Postirradiation creep-rupture tests on these specimens are now being conducted at 1350 °F in air under a stress calculated to cause fracture in 1000 hr for standard-treated, unirradiated material.

Preliminary data obtained from four samples are summarized in Table 4.10.

TABLE 4.10. CREEP-RUPTURE TESTS OF PRECONDITIONED,
IRRADIATED HASTELLOY X-280

<u>Specimen</u>	<u>Preconditioning Treatment No.</u>	<u>Rupture Life</u>
B039	1	83.5 hr, failure at buttonhead
B041	2	333.0 hr, still running
B054	4	428.0 hr, still running
B063	5	175.0 hr, failure in gage section
Treatment No. 1--2150 °F/1 hr, A.C., 0% C.W., 1000 °F/24 hr, A.C.		
Treatment No. 2--2150 °F/1 hr, A.C., 0% C.W., 1500 °F/24 hr, A.C.		
Treatment No. 4--2150 °F/1 hr, A.C., 10% C.W., 1500 °F/24 hr, A.C.		
Treatment No. 5--2150 °F/1 hr, A.C., 15% C.W., 1000 °F/24 hr, A.C.		

Application of transmission electron microscopy to the study of irradiation effects in nickel-base material could be useful in gaining understanding of radiation damage in these alloys. Techniques for preparation of thin foil samples from previously tested tensile specimens must be developed and experience in interpretation of the transmission micrographs must be gained. Initial thin foil sample preparation is under way on sections taken from four Hastelloy X-280 tensile specimens that have been given two experimental preconditioning treatments and tested at room temperature and 1350 °F. Sections were taken at the buttonhead and in the stressed zone to examine the influence of stress as well as preconditioning treatment on structure.

Precipitation-Hardened Alloys

Preirradiation structural modifications on precipitation-hardened Inconel X-750 are being examined as a companion study with the solution-hardened alloys in the nickel-base program. The first 1350 °F tensile test results on Inconel X-750 irradiated at 540 °F to approximately 1×10^{20} nvt ($E > 1$ MeV) have been obtained. The ten specimens tested had been given several selected preirradiation aging treatments ranging from underaging to overaging. Table 4.11 shows that, in general, all specimens were extremely brittle, with a ductility maximum of only approximately 1.3%. Further, preliminary examination of the data indicates a relationship between the heat treatment and tensile properties, such that both strength and ductility decreased with the degree of overaging. Two heat treatments--one, the standard treatment (manufacturer's recommended treatment) and the other, producing an extreme underaged condition--were brittle to the extent that fracture occurred at the button-headfillet. The reason for the extreme brittleness of the standard heat treated condition as compared with two near comparable treatments which produced more ductile material must be examined in depth. Similarly, the simultaneous decrease of strength and ductility with increasing degree of overage warrants detailed study. In examining the data of the three nonstandard treatments which broke normally, it is interesting to note, considering the extreme brittleness of these specimens, that excellent agreement was obtained between specimens of the same treatment in all cases. It is safe, therefore, to conclude that (1) the test equipment is functioning effectively, particularly the high temperature extensometer which has been the subject of extensive development work, and (2) the care exercised in control of specimen quality during preparation is paying dividends. Data tables summarizing this initial work on Inconel X-750 will be reported at the conclusion of unirradiated control testing now in progress.

TABLE 4.11. RESULTS OF 1350 °F TENSILE TESTS
ON IRRADIATED INCONEL X-750

Property	Heat Treatment			
	17, 10**	13	14	15
		Specimen A085-A087	Specimen A093-A095	Specimen A101-A103
U.T.S., psi	*	59,240-59,020	51,030-52,210	51,030-53,850
0.2% Y.S., psi	*	56,810-57,380	50,060-50,490	50,950-52,700
U.E., %	*	0.95-0.70	0.53-0.56	0.17-0.02
T.E., %	*	1.29-1.02	0.79-0.86	0.33-0.02

Heat Treatment 17: 2150 °F/2 hr, A.C.; 1000 °F/20 hr, A.C.

Heat Treatment 10: 2150 °F/2 hr, A.C.; 1550 °F/24 hr, A.C.; 1350 °F/20 hr, A.C.

Heat Treatment 13: 2150 °F/2 hr, A.C.; 1550 °F/24 hr, A.C.; 1000 °F/20 hr, A.C.

Heat Treatment 14: 2150 °F/2 hr, A.C.; 1550 °F/24 hr, A.C.; 1600 °F/20 hr, A.C.

Heat Treatment 15: 2150 °F/2 hr, A.C.; 1550 °F/24 hr, A.C.; 1600 °F/100 hr, A.C.

* Broke at buttonhead fillet; to be repeated

** Standard treatment for optimum high temperature creep properties

FRACTURE STUDIES - R. G. Rowe

The Effect of Irradiation on the Fracture Toughness of Annealed Zircaloy-2

Zircaloy-2 DCB specimens⁽¹⁾ irradiated at 280 °C in the G-7 Hot Water Loop of the ETR were tested to determine their fracture toughness. These data were compared with those from unirradiated specimens. The DCB specimens were machined from annealed Zircaloy-2 plate and then autoclaved at 100 psi and 425 °C for 24 hr to simulate the condition of actual reactor structural materials. The plane strain fracture toughness (expressed by the stress intensity coefficient, K_{IC}) was determined as a function of temperature and the level of neutron irradiation.

The total exposure to neutron irradiation was determined as a gradient along each specimen. Iron and aluminum-cobalt wires were used as flux monitors. The exposure gradient for each specimen is shown in Figure 4.21.

The fracture toughness, K_{IC} , of the DCB specimens oriented along a direction 90° to the rolling direction of the original plate is shown in Figure 4.22. It should be noted that all orientations are referenced to the lengthwise axis of the DCB specimen and, as such, the crack is propagating along the direction stated. Many fracture data are reported with orientations referenced to the tensile axis of the specimen which is 90° to the direction of crack propagation.

Figure 4.22 shows that neutron irradiation decreases the fracture toughness of Zircaloy-2 substantially, and that brittle behavior occurs at much higher temperatures as the level of exposure is increased.

Previous investigators^(2, 3) have not found significant changes in the fracture properties of Zircaloy-2 upon irradiation. Bement, et al.,⁽²⁾ found that annealed Zircaloy-2 irradiated to 3×10^{20} nvt at 60 °C exhibited

1. R. G. Hoagland. A Double Cantilever Beam Specimen for Determining the Plane Strain Fracture Toughness of Metals, BNWL-168. December 1965.
2. A. L. Bement, J. C. Tobin, and R. G. Hoagland. Effects of Neutron Irradiation on the Flow and Fracture of Zircaloy-2, ASTM Special Technical Publication No. 380, p. 372. 1965.
3. R. C. Aungst and L. J. Defferding. Crack Propagation Tests on Normal and Hydrided Zircaloy-2 Reactor Pressure Tubing, HW-80567. General Electric Company, Richland, Washington. August 1964.

FIGURE 4. 21. NEUTRON EXPOSURE GRADIENT ALONG ZIRCALLOY-2 DCB SPECIMENS

no appreciable shift in transition temperature from that of unirradiated material. Transition temperature studies were made on notch-bend specimens designed to obtain plane strain data. In their studies of tensile properties, it was determined that accumulation of radiation damage in Zircaloy-2 increased with increasing irradiation temperature. Thus, their fracture data at lower temperatures and exposures are entirely consistent with our data obtained from the DCB specimen irradiated at 280 °C.

FIGURE 4. 22. EFFECT OF IRRADIATION ON THE FRACTURE TOUGHNESS OF ANNEALED ZIRCALOY-2 (CRACK PROPAGATING TRANSVERSE TO ROLLING DIRECTION)

Aungst and Defferding⁽¹⁾ here at the Pacific Northwest Laboratory studied the nominal hoop stress for brittle fracture of cold-worked Zircaloy-2 pressure tubes containing premachined defects. They found

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1. R. C. Aungst and L. J. Defferding. Crack Propagation Tests on Normal and Hydrided Zircaloy-2 Reactor Pressure Tubing, HW-80567. General Electric Company, Richland, Washington. August 1964.

that tubes containing 30 to 50% cold work exhibited little or no change in their room temperature fracture properties after irradiation at 280 °C in a Hanford production reactor test loop. Although tubes exposed up to 4 yr were tested, the total integrated neutron flux was not obtainable. It is possible that the radiation damage in the tubes was offset by cold work recovery which occurred during irradiation at 280 °C. Recovery of the cold-worked structure would tend to increase the fracture toughness while radiation damage would decrease it. The net effect would be very little change in fracture properties, as observed. Further work to study the effect of prior cold work on the fracture toughness of Zircaloy-2 DCB specimens is anticipated in the not too distant future.

Although the effect of irradiation on the fracture toughness of Zircaloy-2 for cracks propagating in the rolling direction was determined, insufficient control data did not permit us to include these data in this report. It was found that the shift in fracture toughness for longitudinal specimens was almost identical to that reported for transverse cracking in Figure 4.22. It was observed, however, that anisotropy in fracture behavior decreased as the neutron exposure was increased. The plots of K_{IC} versus temperature for average exposures of 5×10^{20} nvt were almost identical for transverse and longitudinal samples. This effect will be further analyzed when complete data on unirradiated Zircaloy-2 are obtained. Specimens irradiated to higher exposures will be available for testing within the next month.

Using an analysis⁽¹⁻⁴⁾ reported in recent literature, it was possible to relate K_{IC} values obtained from the DCB specimen to critical crack

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1. J. E. Srawley and W. F. Brown, Jr. Fracture Toughness Testing, NASA Technical Memorandum TM-X-52030. June 1964.
 2. J. E. Campbell. Current Methods of Fracture Toughness Testing of High Strength Alloys with Emphasis on Plane Strain, DMIC Report No. 207. August 31, 1964.
 3. C. F. Tiffany and J. N. Masters. "Applied Fracture Mechanics," Preprint prepared for Symposium of Fracture Toughness Testing and Its Applications by the ASTM at the Annual Meeting, Chicago, Illinois. June 23-24, 1964.
 4. C. F. Tiffany and P. M. Lorenz. An Investigation of Low-Cycle Fatigue Failures Using Applied Fracture Mechanics, ML-TDR-64-53. The Boeing Company. May 1964.

depths in a tensile plate of Zircaloy-2 as a function of temperature and integrated neutron exposure. These calculations were made under the assumption that geometrical effects on K_{IC} values are negligible.

The relationship $(a/Q)_{cr} = 0.263 K_{IC}^2 / \sigma^2$ was used to analyze semi-elliptical surface cracks in a tensile plate. The variables in this expression are:

- a = crack depth
- Q = flaw shape parameter
- K_{IC} = plane strain stress intensity coefficient
- σ = nominal applied stress.

The flaw shape parameter, Q, was determined from a plot by Tiffany, et al.,^(1,2) assuming that the shape of the crack was semicircular and that $\sigma/\sigma_{YS} = 0.8$. It was thus possible to obtain a semischematic plot of the critical crack depth for failure versus neutron exposure. This plot is shown in Figure 4.23. Restrictions imposed on the calculations were that the crack length was less than one-third of the width of the plate and that its depth was less than one-half of the thickness. It must be understood that this plot is not intended to give the reader the impression that these are accurate data for applied structures. Figure 4.23 serves to give us an idea of how critical crack depth varies with neutron exposure for Zircaloy-2. As may be seen, neutron exposure decreases the size of flaws in the material which may be safely tolerated. More detailed analysis of our data in light of these calculations is intended.

Slow Crack Propagation in High Strength Tool Steel

Investigation of stable crack propagation in D2 tool steel at loads less than that required for dynamic or unstable cracking has continued since the last report period. Experiments were performed in air over the temperature

1. C. F. Tiffany and J. N. Masters. "Applied Fracture Mechanics," Preprint prepared for Symposium of Fracture Toughness Testing and Its Applications by the ASTM at the Annual Meeting, Chicago, Illinois, June 23-24, 1964.
2. C. F. Tiffany and P. M. Lorenz. An Investigation of Low-Cycle Fatigue Failures Using Applied Fracture Mechanics, ML-TDR-64-53. The Boeing Company. May 1964.

FIGURE 4.23. EFFECT OF IRRADIATION ON CRITICAL CRACK DEPTH IN TENSILE PLATE OF ZIRCALOY-2 CONTAINING SEMI-ELLIPTICAL SURFACE CRACK. TENSILE STRESS APPLIED PARALLEL TO ROLLING DIRECTION.

range of 0 to 200 °C. It was found that the crack progressed in discrete jumps and that the time between jumps and the magnitude of each jump are both temperature and stress dependent.

The effect of the environment on the crack growth rate was investigated by performing identical tests in a vacuum of 3×10^{-6} Torr. The rate of crack propagation in the DCB specimens was followed by measuring the load decay under fixed crosshead conditions. Rates of crack growth in vacuum were substantially lower than in air. Figure 4.24 gives a schematic representation of the relative load decay rates for vacuum, argon, and air environments. Figure 4.24 was constructed for schematic purposes only, and indicates that the load had decayed continuously from the original point. Actually, each curve representing the rate of crack propagation in each environment had begun at the same level of stress field intensity, K_I , and decayed to lower levels at rates which are indicated in the figure. The load scale represents a range of approximately 10 lb at a level dependent upon the extension of the crosshead.

FIGURE 4.24. EFFECT OF ENVIRONMENT ON THE RATE OF CONTINUOUS CRACK PROPAGATION IN D2 TOOL STEEL AT 12 °C.

The first tests performed were at +12 °C to determine relative effects of the environment, but more recently a radiant heater has been constructed to heat the specimen to temperatures up to 450 °C in vacuum. In the temperature range from room temperature to 300 °C, the delay time, or time between crack jumps in a vacuum of 3×10^{-6} Torr, exhibited a strong temperature dependence. For comparable values of the stress field intensity, K_I (maintained just below K_{IC}), the delay time in vacuum varied from 4 min at 20 °C to approximately 30 sec at 300 °C. It was noticed that although the rate of crack propagation was decreased, its stress and temperature dependence in high vacuum was very similar to that in air. It is thus possible that even in high vacuum, the residual atmosphere still influences the cracking behavior.

Time did not permit the determination of crack propagation rates in an argon atmosphere as a function of temperature, but future work will be done to determine this dependence. Due to the increased frequency of crack jumps when the argon was admitted, it is thought that water vapor may have been present in the argon. This water vapor may have been introduced while backfilling the vacuum chamber with argon, or it may have been present in the bottled gas itself. Other investigators⁽¹⁻³⁾ have studied the effect of humid atmospheres on the rate of fatigue cracking in AISI 4340 and 4345 steels. They have found that very small amounts of water vapor (even that present in commercially dry bottled gas) can increase the rate of crack growth per fatigue cycle by as much as an order of magnitude.

It was noticed that the delay time between crack jumps was somewhat dependent upon the time the system had been evacuated. Tests performed immediately after the system had reached a vacuum of 5×10^{-6} Torr yielded delay times much shorter than those obtained after the system had been

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1. W. A. Van der Sluys. Effects of Repeated Loading and Moisture on the Fracture Toughness of SAE 4340 Steel, T&AM Report 245, University of Illinois. May 1963.
 2. E. P. Dahlberg. "Fatigue Crack Propagation in High Strength 4340 Steel in Humid Air," Trans. ASM, vol. 58, p. 46. 1965.
 3. C. Y. Li. U.S. Steel Corporation, Monroeville, Pa. Private Communication. 1965.

evacuated overnight. It was not determined whether this was due to a discrepancy between the vacuum in the chamber and at the ion gage or due to other factors. Heating the specimen to 300 °C for several hours after the vacuum had been obtained did not appreciably affect the delay time. If physically adsorbed gases had been responsible for this dependence upon time at vacuum, heating the specimen should have driven them off and increased the delay times. Further work will be done to look more deeply into this problem.

Two possible explanations of the effect of vacuum on cracking rates came to mind upon first looking at this problem. The first, and most evident, is that water vapor or some other atmospheric gas is being chemically adsorbed to the clean metal exposed when the crack jumps. This adsorption process would permit hydrogen or some other interstitial species to be admitted to the lattice, causing embrittlement in the highly strained region at the crack tip. The delay time between jumps would then be equal to the time required for the interstitial concentration to build up to a given level and would be temperature, pressure, and stress dependent.

Another possibility is that the rate of continuous crack propagation is controlled entirely from within the metal, and that the removal of the atmosphere permits gases which affect the delay time to be removed from the metal. By varying the thickness of the specimen and the time at vacuum, it will be possible to determine whether the loss of interstitial gases from within the metal is a controlling factor. Many other possibilities exist, and it will require further experimental work and analysis to evaluate the mechanisms operating.

It is our present thought that several possibilities are equally valid, and that the superposition of one process upon the other may be occurring. If we can isolate these processes and study them separately, it will be possible to determine the mechanics of each. Tests using controlled atmospheres and varied metallurgical conditions are anticipated in the future. By performing tests in vacuum, it will be possible to determine the effects of crack tip environment in more precise terms and to eliminate these effects to evaluate continuous cracking phenomenon which are directly governed by the material's properties.

Recent electron microscope examination of carbon replicas of the fracture surface has indicated no apparent change in the mode of fracture in vacuum and in air. No conclusions can be made from these original observations, however, until further work has been done in this area.

Fracture Toughness of Graphite DCB Specimens

Preliminary investigations have been carried out to determine the adaptability of the DCB specimen to fracture testing in graphite.* Excellent behavior was seen for specimens oriented along the extrusion direction of the graphite rod. No tests were performed for specimens oriented transverse to the extrusion direction.

Since the compliance of the DCB specimen is dependent upon both the geometry and the material from which it is constructed, graphite specimens were machined to the same dimensions as previously tested metal specimens. The only variable which was thus required to determine the compliance of the specimen was the elastic modulus, E . For the SX-5 and SGBF type graphite used, the elastic moduli were taken as 1.5×10^6 psi and 1.83×10^6 psi, respectively.

The geometry of each specimen type is reported in Table 4.12.

TABLE 4.12

<u>Graphite Type</u>	<u>L</u>	<u>h</u>	<u>b</u>	<u>w</u>	<u>Co</u>
SGBF	7	1	0.500	0.200	2
SX-5	7	0.500	0.250	0.110	2

The variables reported correspond to standard dimensions of the DCB specimen as previously adopted.⁽¹⁾

The fracture toughness of the graphite was then determined using the same force-energy relationships which were derived for use with metal DCB specimens. No error should be introduced by changing the material

* Work was carried out in cooperation with the Graphite Research and Development Unit at Pacific Northwest Laboratory.

1. R. G. Hoagland. A Double Cantilever Beam Specimen for Determining the Plane Strain Fracture Toughness of Metals, BNWL-168. December 1965.

of the specimen. The fracture toughness (K_{IC}) of the graphite is shown in Figure 4.25. It can be seen that the two types of graphite used exhibited slightly different levels of K_{IC} , but that both indicated an increase in K_{IC} with increasing crack length. The fracture toughness of graphite is much lower than that of most metals, as would be expected.

The reason for the difference in the dependence of K_{IC} with crack length for aluminum and graphite was not established. Further work will be required to understand more about the fracture toughness behavior of graphite.

This preliminary work has demonstrated the effectiveness of the DCB specimen in testing brittle engineering materials other than metals. It appears that graphite is one of these materials for which this specimen is ideally suited.

FIGURE 4. 25. FRACTURE TOUGHNESS (K_{IC}) VERSUS CRACK LENGTH FOR SGBF AND SX-5 TYPE GRAPHITE COMPARED TO 7075-T6 ALUMINUM

CHEMICAL METALLURGY UNIT

ENVIRONMENTAL EFFECTS

In-Reactor Corrosion of Zirconium Alloys - A. B. Johnson, Jr.

The irradiations discussed in this report were undertaken to correlate with previous exposures^(1,2) of Zircaloy coupons in the G-7 loop of the Engineering Test Reactor (ETR) at the National Reactor Testing Station. It is therefore first appropriate to briefly review the foregoing G-7 loop results.

Previous experience with Zircaloy corrosion specimens in the G-7 loop indicated:

- Order of magnitude increases in corrosion rates for Zircaloy-2 in high oxygen (~1 ppm) water
- Lower in-reactor oxidation rates for Zircaloy-2, Zircaloy-4, Zircaloy-2 (low nickel) and Zr-3Nb-1Sn in low-oxygen (<0.1 ppm) water, with indications of a lower susceptibility of Zr-3Nb-1Sn and heavily cold worked Zircaloy-2 toward accelerated oxidation
- No significant effect of flux on the fraction of corrosion product hydrogen.

Since Zircaloy-4, Zircaloy-2 (low nickel) and Zr-3Nb-1Sn alloys were not previously exposed in the high-oxygen environment, a two-cycle exposure was undertaken to look for alloy effects on in-flux oxidation.

Effects of prefilming and heavy cold work (86%) were investigated in the two-cycle exposure. Samples also were exposed to the loop coolant ~1 sec (position A) and ~1 min (position B) from the flux to investigate possible differences in the reactivity of the coolant at the two positions. These samples served as zero-flux controls for comparison with the in-flux samples. A diagram of the loop is reported elsewhere.⁽²⁾ The conditions

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1. W. A. Burns and H. P. Maffei. Neutron Irradiation and Cold Work Effects on Zircaloy-2 Corrosion and Hydrogen Pickup - An Interim Report, HW-76636. General Electric Company, Richland, Washington. December, 1962.
 2. W. A. Burns. Effects of Fast Neutron Irradiation, Fabrication History and Water Oxygen on the Environmental Behavior of Zirconium Alloys, BNWL-88. February, 1965.

of exposure were:

Temperature: 530 °F, bulk outlet temperature

pH: 10 (LiOH)

Oxygen: ~1 ppm

		<u>>1 MeV</u>	<u>Thermal</u>
Neutron Flux:	Quadrant 197	1.9×10^{13} nv	7.7×10^{13} nv
	Quadrant 198	1.6×10^{14} nv	4.8×10^{14} nv
Exposure:	48 full power days 36 days at temperature		
	Quadrant 197:	7.8×10^{19} nvt	
	Quadrant 198:	6.6×10^{20} nvt	
Cs ¹³⁸ :	4×10^5 dis/min/ml		
ETR Cycles:	73 and 74		

The zirconium alloy specimens used in this study were from the same sample stock as those used in previous ETR G-7 loop exposures. The specimens measured 3 3/8 in. in length and 1 in. in width. They were mill cut from 0.050, 0.040, and 0.030 in. thick plate. The coupons weigh 10 to 17 g and have surface areas of ~0.45 dm². Details of specimen history are given elsewhere.⁽¹⁾ Final conditions are summarized below.

NPR Zircaloy-2 [from New Production Reactor (NPR) tube stock]	- Exposed in annealed and heavily cold worked conditions. Cold rolled to 0.050 in., 86% cold work. Annealed specimens were heated in vacuum 8 hr. at 1400 °F.
Zircaloy-4 and Low Nickel Zircaloy-2	- Exposed in annealed condition only. Cold rolled to 0.030 in. Vacuum annealed 1 hr at 1400 °F.
Zr-3Nb-1Sn	- Exposed in annealed condition only. Cold rolled to 0.040 in., with intermediate anneals at 1400 to 1475 °F. Vacuum annealed at 1070 °F for 24 hr.
Zircaloy-2, 6515 Plate	- Exposed in cold worked condition only. Annealed at 1550 °F - 40% cold work, with intermediate anneals, 1 hr. at 1380 °F.

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1. W. A. Burns. Effects of Fast Neutron Irradiation, Fabrication History and Water Oxygen on the Environmental Behavior of Zirconium Alloys, BNWL-88. February, 1965.

The specimens were pretreated by vapor blasting and etching in a hydrofluoric-nitric acid bath to remove 1 mil per surface. Samples were exposed in pairs, one etched, one preautoclaved. Preautoclaved films, 7 to 8.2 mg/dm², were formed at 572 °F for 48 hr in refreshed demineralized water at pH 6.

Prior to exposure, specimens were weighed on a microbalance. Following exposure, out-of-flux coupons were weighed on the same microbalance. In-flux coupons were weighed on an in-cell automatic balance. Balances were cross-checked by periodic weighing of a reference standard.

The coupons were exposed in two quadrants having identical sample loadings but placed at different flux levels.

Following the G-7 loop exposure, the samples underwent examination at Pacific Northwest Laboratory.

Upon removal from the quadrants, the samples had a greasy film, apparently from the milling operation. The film was readily removed with carbon tetrachloride, revealing a gray-black nonflaking oxide. Following initial sample weighings, two of the in-flux coupons were subjected to decontamination treatments in alkaline permanganate and ammonium citrate solutions at ~ 95 °C; the samples were exposed 1 hr in each solution. There was no change in weight or appearance of the samples as a result of the decontamination procedure.

The samples exposed at out-of-flux positions A and B were weighed, monitored for beta-gamma and alpha activity, and decontaminated by the procedure described above. Oxides on all out-of-flux samples had the normal shiny, black appearance.

Results

Results of the G-7 loop in-flux exposure are summarized in Table 5.1. The corresponding out-of-flux loop data are shown in Table 5.2.

In-Reactor Oxidation Rates. Weight gain data for in-flux coupons and etched out-of-flux coupons are plotted in Figure 5.1. Data for preautoclaved in-flux specimens were modified by subtracting the prefilm weight

TABLE 5.1. IN-FLUX OXIDATION OF ZIRCONIUM ALLOYS IN THE G-7 ETR LOOP

Specimen Material	Condition	Surface Preparation	Total Weight Gain, ^(a) mg/dm ²	In-Reactor Weight Gain, mg/dm ²	$\frac{\Delta W \text{ In-Flux}}{\Delta W \text{ Out-of-Flux}}$
Quadrant 197: 36 days at 530 °F(c); ~1 ppm O ₂ ; 1.9 x 10 ¹³ nv; 7.8 x 10 ¹⁹ nvt					
Zry-2 6515	40% CW	Preautoclaved	55.2	47.1	4.9
Zry-2 6515	40% CW	Etched		46.9	(b)
Zry-2 NPR	86% CW	Preautoclaved	66.7	58.5	6.6
Zry-2 NPR	86% CW	Etched		30.0	3.2
Zry-2 NPR	Annealed	Preautoclaved	48.8	41.0	3.9
Zry-2 NPR	Annealed	Etched		39.4	3.5
Zry-2 low Ni	Annealed	Preautoclaved	47.5	39.9	4.1
Zry-2 low Ni	Annealed	Etched		39.4	3.7
Zry-4	Annealed	Preautoclaved	47.4	39.9	(b)
Zry-4	Annealed	Etched		36.6	3.6
Zr-3Nb-1Sn	Annealed	Preautoclaved	29.6	21.9	2.9
Zr-3Nb-1Sn	Annealed	Etched		21.3	1.7
Quadrant 198: 36 days at 555 °F(c); ~1 ppm O ₂ ; 1.6 x 10 ¹⁴ nv; 6.6 x 10 ²⁰ nvt					
Zry-2 6515	40% CW	Preautoclaved	108.0	101.1	9.5
Zry-2 6515	40% CW	Etched		101.0	(b)
Zry-2 NPR	86% CW	Preautoclaved	70.0	61.9	6.9
Zry-2 NPR	86% CW	Etched		61.6	6.7
Zry-2 NPR	Annealed	Preautoclaved	65.8	57.9	5.3
Zry-2 NPR	Annealed	Etched		57.8	6.7
Zry-2 low Ni	Annealed	Preautoclaved	68.9	61.4	6.0
Zry-2 low Ni	Annealed	Etched		158.2	14.8
Zry-4	Annealed	Preautoclaved	52.9	45.9	(b)
Zry-4	Annealed	Etched		59.2	5.7
Zr-3Nb-1Sn	Annealed	Preautoclaved	56.4	49.6	4.5
Zr-3Nb-1Sn	Annealed	Etched		37.1	3.6

(a) Prefilm + in-reactor weight gains

(b) No corresponding out-of-flux weight gain

(c) Estimated sample temperatures based on previous loop calibrations;
loop water inlet temperature 515 °F, loop water exit temperature, 530 °F

TABLE 5.2. OUT-OF-FLUX OXIDATION OF ZIRCONIUM ALLOYS IN THE ETR G-7 LOOP

Specimen Material	Condition	Surface Preparation	Preautoclave Weight Gain, mg/dm ²	Total Weight Gain, mg/dm ²
<u>Position A: ~1 sec Out-of-Flux; 530 °F</u>				
Zry-2 6515		Preautoclaved	7.1	11.3
Zry-2 NPR	Annealed	Etched	-	11.4
Zry-2 NPR	Annealed	Preautoclaved	9.0	12.5
Zry-2 NPR	86% CW	Etched	-	9.3
Zry-2 NPR	86% CW	Preautoclaved	8.2	10.3
Zry-2 NPR	86% CW	Preautoclaved	8.2	10.3
Zry-2 low Ni	Annealed	Etched	-	10.7
Zry-2 low Ni	Annealed	Preautoclaved	8.6	11.5
Zry-4	Annealed	Etched	-	10.3
Zr-3Nb-1Sn	Annealed	Etched	-	10.3
Zr-3Nb-1Sn	Annealed	Preautoclaved	7.9	12.5
Zry-2 NPR	86% CW	Etched	-	9.2
Zry-2 NPR	86% CW	Preautoclaved	7.0	9.9
<u>Position B: ~1 min Out-of-Flux; ~510 °F</u>				
Zry-2 6515		Etched		Fretted
Zry-2 NPR	Annealed	Etched		11.0
Zry-2 NPR	86% CW	Etched		Fretted
Zry-2 low Ni	Annealed	Etched		Fretted
Zry-4	Annealed	Etched		10.6
Zr-3Nb-1Sn	Annealed	Etched		9.0*

* Mild fretting was observed around one mount hole.

gain. Points plotted in Figure 5.1 were obtained by averaging the weight gains on corresponding pairs of etched and preautoclaved samples (corrected for prefilm weight).

Out-of-flux weight gain data for etched specimens of the alloys are grouped about the line for 550 °F water. The data fall 1 to 3 mg/dm² above values at 530 °F obtained by interpolation of data reported by Kass.⁽¹⁾

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1. S. D. Kass. Curves Describing the Corrosion and Hydrogen Absorption Behavior of the Zircalloys, WAPD-CM(RM)-4419. Westinghouse Electric Corporation, December, 1963.

FIGURE 5.1. COMPARISON OF IN-FLUX WEIGHT GAINS ON ZIRCONIUM ALLOYS WITH OUT-OF-FLUX AND OUT-OF-REACTOR DATA FOR ZIRCALOY-2

1. B. Lustman and F. Kerze. The Metallurgy of Zirconium, National Nuclear Energy Series, Division 7. McGraw-Hill Book Company, Inc., New York, N.Y., vol. 4, p. 633. 1955
2. W. A. Burns. Effects of Fast Neutron Irradiation, Fabrication History and Water Oxygen on the Environmental Behavior of Zirconium Alloys, BNWL-88. February, 1965.

It is clear that the in-flux coupons underwent accelerated oxidation. Most of the points fall near the line for 750 °F steam, in agreement with previous observations by W. A. Burns for Zircaloy-2 exposed to G-7 loop water containing oxygen.⁽¹⁾ Ratios of weight gains, in-flux/out-of-flux, for the various alloy and flux combinations are shown in the last column of Table 5.1.

In general, agreement between pairs of samples is excellent, although anomalies appear, particularly for the cold worked NPR Zircaloy-2 from Quadrant 197 and the etched Zircaloy-2 (low nickel) specimen in Quadrant 198. The latter sample was not included in Figure 5.1. The anomalies eventually will be investigated by metallography to see if the weight gain discrepancies are confirmed.

Effect of Flux. In-reactor weight gains for the alloys are plotted as a function of fast flux in Figure 5.2. In all cases, the oxidation rate was higher at the higher flux. The slopes of the lines are similar for all alloys except the Zircaloy-2 6515 alloy, for which the slope is considerably higher. Previous G-7 loop experience resulted in higher weight gains for cold worked 6515 Zircaloy-2 compared to cold worked NPR Zircaloy-2.⁽¹⁾ However, the acceleration of the 6515 Zircaloy-2 coupons in Quadrant 198 is unexpectedly high compared to NPR Zircaloy-2 coupons in the same quadrant.

Effect of Alloy. The radiation-induced oxidation of the Zr-3Nb-1Sn alloy was clearly lower at both flux levels, compared to the other alloys. This result is in agreement with comparisons between in-flux behavior of Zr-3Nb-1Sn and Zircaloy-2 conducted in the FRG-1 reactor.⁽²⁾ However, in opposition to the FRG-1 tests, which were conducted in steam at 400 °C, samples exposed in the ETR G-7 loop did not show oxide spalling.

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1. W. A. Burns. Effects of Fast Neutron Irradiation, Fabrication History and Water Oxygen on the Environmental Behavior of Zirconium Alloys, BNWL-88. February, 1965.
 2. W. Jung-Konig, H. Richter, W. Spalthoff, and E. Starke. Studies on the Influence of Neutron Irradiation on the Properties of Zr-Nb3-Sn1, Final Report, U.S.-EURATOM Joint Research and Development Program, EUREC-1249. October, 1964.

FIGURE 5.2. EFFECTS OF FLUX AND ALLOY ON THE IN-REACTOR OXIDATION OF ZIRCONIUM ALLOYS, EXPOSED IN THE ETR G-7 LOOP, AT 530 °F, ~1 ppm O₂

The Zircaloy-2 6515 samples exposed at the higher flux showed significantly higher oxidation rates than those of the other alloys. However, the samples exposed at the lower flux were grouped closely with the other alloys.

Effect of Prefilming. The effect of prefilming is demonstrated on the bar graph, Figure 5.3, showing the individual samples grouped according to alloy. H and L refer to high and low flux. Dashed bars refer to etched coupons and solid bars to preautoclaved coupons. The lateral marks indicate the fraction of the film formed in preautoclaving. For seven of the twelve pairs of etched/preautoclaved specimens, there is close agreement between in-reactor weight gains when the preautoclave weight gain

is subtracted. Two pairs showed a higher oxidation rate for the prefilmed sample and three pairs showed a higher rate for the etched sample. Where the weight gains of a pair of samples differ, the corresponding pair at the other flux position shows no deviation. The fact that the deviations are not systematic supports the conclusion that prefilming did not influence the in-flux oxidation rate at the level of exposure of these tests.

FIGURE 5.3. IN-FLUX WEIGHT GAINS ON ZIRCONIUM ALLOYS IN THE ETR G-7 LOOP

Comparison of Oxidation at Two Out-of-Flux Positions. A previous brief exposure in the G-7 loop at positions ~ 1 sec (position A) and ~ 1 min (position B) from the flux showed indications of faster oxidation rate at the

position nearer the flux.⁽¹⁾ In the current test, samples of the alloys tested in-flux were also exposed at the two positions. At position A, samples were exposed in the etched and autoclaved conditions; at position B only etched samples were exposed. Fretting corrosion occurring around the mounts in position B obscured the weight gain on three of the six samples. Comparisons of the three remaining samples with corresponding etched samples in position A (data from Table 5.2) are shown below:

	Position A	Position B
Zircaloy-2 NPR, annealed	11.4 mg/dm ²	11.0 mg/dm ²
Zircaloy-4	10.3 mg/dm ²	10.6 mg/dm ²
Zr-3Nb-1Sn	10.3 mg/dm ²	9.0 mg/dm ²

The low value for the Zr-3Nb-1Sn coupon in position B is likely the result of a small fretted area observed around one mount hole. Otherwise the comparisons indicate no significant difference in oxidation rate at the two positions. Weight gains on etched and preautoclaved specimens in position A appear to be internally consistent to within experimental error. While the out-of-flux results for Zircaloy-2 and Zircaloy-4 are generally higher than results reported by Kass,⁽²⁾ the differences do not appear to be sufficiently large to interpret as a coolant-induced acceleration of oxidation.

Comparison of Surface Activity at Out-of-Flux Positions. The samples from the two out-of-flux positions were counted for beta-gamma and alpha activity before and after decontamination treatments. Prior to decontamination, samples from position A read 11.5 to 21 mR/hr at 4 in. Samples from position B read 2 to 5 mR/hr. In both cases the activity was primarily beta. Alpha activity was 50 to 250 dis/min/cm² on position A samples and 80 to 200 dis/min/cm² on position B samples prior to decontamination. Therefore, there was no difference in alpha activity deposited

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1. W. A. Burns. Effects of Fast Neutron Irradiation, Fabrication History and Water Oxygen on the Environmental Behavior of Zirconium Alloys, BNWL-88. February, 1965.
 2. S. D. Kass. Curves Describing the Corrosion and Hydrogen Absorption Behavior of the Zircalloys, WAPD-CM(RM)-4419, Westinghouse Electric Corporation, December, 1963.

at the two positions. The beta-gamma activity on a stainless steel spacer in the position A sample holder was 150 mR/hr, with an alpha count of 300 dis/min/cm².

Decontamination (three cycles in alkaline permanganate and ammonium citrate) of the Zircaloy specimens reduced the beta-gamma activity by a factor of 3 on position A coupons and by a factor of 2 on position B samples. The alpha activity was reduced by approximately a factor of 2 by the three-cycle decontamination.

Weight losses from the decontamination were 1 to 21 mg/dm² for position A samples and 2 to 10 mg/dm² for position B samples. The sample surfaces became more lustrous after decontamination. Otherwise, the presence of the removable deposit was not obvious.

Gamma scans of the decontamination solutions showed Co⁶⁰, Co⁵⁸, Fe⁵⁹, Zn⁶⁵, Mn⁵⁴, Zr⁹⁵/Nb⁹⁵, and Cr⁵¹. Fission products were absent.

Discussion

In the context of previous experiments, the tests reported here:

- Add to the evidence of enhanced in-reactor oxidation of zirconium alloys in an oxygen-bearing coolant
- Support previous G-7 loop results showing in-reactor oxidation rates typical of out-of-reactor rates at temperatures ~200 °F above the loop coolant temperature
- Indicate a lower susceptibility of the Zr-3Nb-1Sn alloy toward flux-induced oxidation
- Support previous G-7 loop results indicating increased oxidation as the flux increases
- Indicate no systematic effect of prefilming on the in-reactor weight gain
- Indicate no significant accelerated corrosion by irradiated loop coolant at out-of-flux positions ~1 sec and ~1 min from the core. This observation is in disagreement with indications in a previous

test that accelerated oxidation occurred in the position ~ 1 sec out-of-flux. We do not have an explanation for the enhanced oxidation observed in the first test.

The explanation of enhanced in-reactor oxidation is obviously vitally concerned with where the rate control resides in the oxidation process. If the popular concept of control by anion diffusion through the oxide film is accepted, then an oxide damage mechanism appears logical. On the other hand, if coolant chemistry effects are real, this implies at least partial control at or near the oxide/coolant interface. A mechanism has been proposed which takes into account coolant chemistry and heat flux.⁽¹⁾ However, it is not yet clear what coolant species must be taken into account in the mechanism and how in-flux oxidation rates vary with concentrations of various species in the coolant.

1. W. K. Anderson. A Theory of the Effect of Heat Flux and Temperature on the In-Pile Corrosion Rate of Zirconium Alloys, TID-17974. 1963.

ATR GAS LOOP SUPPORT

Corrosion Studies - L. A. Charlot and R. E. Westerman

Oxidation of nichrome heater components of the ATR loop has been assumed to occur at rates comparable to those found for the oxidation of Hastelloy X-280 and Haynes alloy 25.⁽¹⁾ A series of isothermal tests on nichrome at temperatures above 1000 °C and pressures between 140 μ and 85 Torr oxygen have been conducted to compare nichrome oxidation to the oxidation of the other superalloys.

The Hastelloy and Haynes alloys have been found to oxidize according to a parabolic rate law. The kinetics of nichrome oxidation can be best described by a cubic rate expression, i.e., $W^3 = kt$. Average rate constants calculated from 7000-min exposures, for the oxidation of nichrome are:

1020 °C, 140 μ replenished O ₂	$k = 2.8 \times 10^{-5} \text{ (mg/cm}^2\text{)}^3/\text{min}$
1020 °C, 25 Torr static O ₂	$k = 3.8 \times 10^{-5}$
1020 °C, 85 Torr static O ₂	$k = 4.6 \times 10^{-5}$
1120 °C, 140 μ replenished O ₂	$k = 1.7 \times 10^{-4}$

At 1220 °C in 140 μ replenished O₂, the nichrome sample oxidized to the extent of 1 mg/cm² in 2500 min. The sample then started losing weight. At this temperature, weight loss would be due to the evaporation of the chrome oxide. In general, nichrome is more oxidation resistant than either the Hastelloy or Haynes alloy.

The scale retained by the nichrome sample on cooling was found to consist of both chromium and nickel oxides. The postoxidation microstructure of the samples tested showed grain growth and void areas. The void areas near the metal-oxide interface are similar to those found in the other superalloys. Intergranular penetration or subsurface oxidation was not found in any of the samples tested.

1. L. Charlot and R. E. Westerman. High Temperature Corrosion of Candidate ATR Structural Materials, BNWL-100. September, 1965.

Dynamic Materials Test Apparatus - R. A. Thiede and R. E. Westerman

On the basis of static-system tests, it has been shown that the high-temperature evaporation of superalloys in vacuo can result in as much metal loss as oxidation in low-pressure oxygen.⁽¹⁾ The effect of pressurized, flowing inert gas on evaporation rates has heretofore not been presented. Ten successful tests have been conducted in flowing ultra-pure helium at 300 psi and 2050 °F at linear flow velocities to 500 ft/sec. Six of the tests have been conducted using samples of Hastelloy X, four with samples of Haynes 25. Average test duration has been approximately 80 hr.

The results of the tests are shown in Figure 5.4. Though considerable data scatter exists, it is evident that presence of the pressurized gas inhibits evaporation, even at 500 ft/sec linear flow, compared to vacuum data. Also, the data indicate that decreasing the flow rate decreases the evaporation rate. It is not felt that any other conclusions, such as a comparison of the evaporation rates of the two alloys, are warranted at the present time.

1. L. Charlot and R. E. Westerman. High Temperature Corrosion of Candidate ATR Structural Materials, BNWL-100. September, 1965.

FIGURE 5.4. RELATIONSHIP BETWEEN SUPERALLOY EVAPORATION AND LINEAR VELOCITY OF ULTRAPURE HELIUM AT 300 psi AND 2050 °F

PRP MATERIALS DEVELOPMENT

Corrosion of PRTR Zircaloy-2 Process Tube - H. P. Maffei and B. Griggs

Investigation of the oxide thickness on sections of a discharged PRTR Zircaloy-2 process tube is in progress. Oxide thickness investigations on previously discharged process tubes have been reported. (1, 2) The process tube currently under study had been in service from startup of PRTR until August 7, 1965. During this period of time, the tube was operating at a temperature of 400 °F (204 °C) or more for approximately 620 days. Plugs, 1/4 in. diam, were removed from the process tube for examination at various distances along its length. The plugs were mounted, polished metallographically, and measurements taken of the oxide thickness.

The oxide thicknesses converted to equivalent weight gains are shown in Table 5.3. It can be seen that the highest weight gains are associated with the samples receiving the highest flux intensities. The inside diameter oxide thickness is equivalent to a weight gain of 108 mg/dm², which is a factor of 5 higher than sample number 1 which saw virtually no neutron exposure. The large differences in weight gains between the inside and outside surfaces of the process tube cannot be conclusively explained by preliminary results of the investigation. Alpha emitting contamination has been found on the inside surface of the process tube. Investigations are being conducted to determine what type of alpha emitter is present and to what extent.

Typical metallographic cross sections from this process tube are shown in Figure 5.5.

-
1. Quarterly Progress Report, Metallurgy Research Section, April, May, June, 1964, edited by J. J. Cadwell, HW-82651. General Electric Company, Richland, Washington. July 15, 1964.
 2. Quarterly Progress Report, Metallurgy Research Section, July, August, September, 1964, edited by J. J. Cadwell, HW-84281. General Electric Company, Richland, Washington. October 15, 1964.

TABLE 5.3. OXIDE THICKNESS MEASUREMENTS ON PRTR PROCESS TUBE 6074

Sample Number	Distance from Inlet End, ft	Approximate Flux Intensity, nv (>1 MeV)	Weight Gains, mg/dm ²		Net* In-Reactor Weight Gain	
			Calculated from Oxide Thickness		ID	OD
			Inside Surface	Outside Surface		
1	15	$<1 \times 10^5$	36	21	20	5
2	13 3/4	1×10^{13}	64	28	48	12
3	12 1/2	5×10^{13}	63	35	47	19
4	11	8×10^{13}	124	37	108	21
5	9 3/4	8×10^{13}	124	42	108	26
8	5 3/4	5×10^{13}	61	38	45	22
9	4 1/2	1×10^{13}	42	24	26	8

* Assuming an original autoclave film on the process tube equivalent to a weight gain of 16 mg/dm²

5.18

BNWL-207

←ZrO₂→
←Zry-2→

ID

OD

15 ft

11 ft

0.01
mm

ID

OD

13 3/4 ft

9 3/4 ft

ID

OD

12 1/2 ft

4 1/2 ft

FIGURE 5.5. TYPICAL OXIDE THICKNESSES ON INSIDE AND OUTSIDE DIAMETERS OF PROCESS TUBE 6074 AT VARIOUS DISTANCES FROM INLET END

MATERIALS ENGINEERING UNIT

PRTR PRESSURE TUBES - M. C. Fraser

The PRTR pressure tubes were fabricated from Zircaloy-2 ingots by a forging-hot extrusion-tube reduction process. These tubes have a unique shape, one end is flanged and the other tapers to a reduced diameter. They also have a unique microstructure distribution; there is an annealed region between the taper and the flange, the remainder cold worked. The ability of these tubes to sustain the imposed PRTR system loads with ever increasing neutron exposure has been a subject of study and testing since reactor start-up. The following paragraphs describe the study and testing done during the last quarter year.

Properties of Irradiated PRTR Pressure Tubes

An experiment was performed to determine if a temperature of 550 °F would cause significant annealing of irradiation damage. An annealing-aging reaction was indicated by the data obtained.

The ring type specimens used in the test were cut from an irradiated PRTR tube. The tube had received a total neutron exposure of 5×10^{20} fast nvt at a temperature between 185 and 276 °F. After being held for one, two, three, or four thousand hours in a neutral atmosphere and at a temperature of 550 °F, the rings were tensile tested.

The data obtained were load-elongation curves plus initial and final cross-section areas. The maximum load sustained by each specimen varied with cross-section area; and after taking the ratios of maximum load to cross-section area, the unit maximum loads were found to vary with annealing time at 550 °F. This effect is shown in Figure 6. 1.

The first 1000-hr at 550 °F reduced the maximum unit load from 107,750 to 104,400 psi. At greater than 1000 hr, aging of the alloy was indicated by an increase in maximum unit load. At 4000 hr, the maximum unit load was 111,500 psi. This is $3 \frac{1}{2}\%$ greater than at the start of testing and about 7% above the 1000 hr value.

FIGURE 6. 1. EFFECT OF 550 °F-INERT ATMOSPHERE ON MAXIMUM UNIT LOAD OF RING SPECIMENS TAKEN FROM IRRADIATED PRTR ZIRCALOY-2 PRESSURE TUBE. RING SPECIMENS EXPOSURE, 5×10^{20} Fast nvt ($E > 1\text{MeV}$)

The data suggest that irradiated Zircaloy-2 tube strength reduction from recovery from irradiation damage by annealing is overridden by strength enhancement from aging for extended 550 °F heat treatment.

PRTR Zircaloy-2 pressure tube number 6095 failed during performance of an experiment with the PRTR fuel element rupture facility. After removal of the tube from PRTR, the ruptured portion was cut from the tube and transferred to Radiometallurgy for study. A report⁽¹⁾ of this study was written. The essence of the study was in photomicrographs of the microstructure near the rupture. They showed that the cold worked

1. M. C. Fraser. Metallurgy of Failure of PRTR Tube Number 6095, BNWL-CC-386. December 8, 1965.

grains adjacent to the opening in the tube had been heated at least to alpha-beta transition temperatures. For Zircaloy-2 this requires a temperature within the range 1480 to 1770 °F.⁽¹⁾ The photomicrographs also showed a region of recrystallized grains between the beta treated region and the unaffected cold worked grains region. Figure 6.2 shows these photomicrographs and a sketch of the metallographic specimen. The heat treated areas are indicated.

Figure 6.3 shows the influence of temperature upon burst strength of PRTR Zircaloy-2 tube specimens up to temperatures of 600 to 800 °F. It also shows the recorded temperature of incipient failure of a tube specimen during performance of a simulation of 6095's rupture.⁽²⁾ These data suggest that at the temperature indicated by the microstructure the strength of the hot spot on tube 6095 was insufficient to contain PRTR operating pressure.

Figure 6.4 shows the failure region.

-
1. Zirconium Highlights, WAPD-ZH-7. May, 1958.
 2. P. J. Pankaskie and T. E. Michaels. Monthly Progress Report, Battelle-Northwest Studies Executed for the USAEC-AECL Cooperative Program, October, 1965, p. 4, BNWC-27 10.

FIGURE 6. 2. LONGITUDINAL CROSS SECTION OF PRTR TUBE 6095 SHOWING MICROSTRUCTURE REGIONS DISCUSSED IN TEXT. (The diagram is about 90 times larger than the actual specimen. The magnification of the photomicrographs is about 225X; and they were taken using polarized light.)

FIGURE 6. 3. INFLUENCE OF TEMPERATURE ON STRENGTH OF PRTR ZIRCALOY-2 TUBE SPECIMENS

FIGURE 6. 4. PRTR TUBE 6095 FAILURE REGION. MAGNIFICATION $\sim 1.05X$

USAEC-AECL COOPERATIVE PROGRAM

Zr-Nb Pressure Tubing - P. J. Pankaskie

The general objective of this program is to evaluate Zr-2.5 Nb as a pressure tube material with reference to the tests and reactor experience that has been obtained on Zircaloy-2 pressure tubes. Crack propagation tests were continued on tubes both in the cold worked and hydrided to 250 to 300 ppm condition. The results are shown in Table 6. 1.

TABLE 6. 1. CRACK PROPAGATION DATA FOR Zr-2.5 wt% Nb ALLOY

Specimen Identification	Specimen Condition	Test Temp., °C	Slot Length, in.	Hoop Stress at Failure, psi	Crack Length at Failure
30-9	30% CW and Hydrided	25	1/2	76,500	Brittle crack propagated full length of test piece
30-7	30% CW and Hydrided	25	1 1/2	31,400	Brittle crack propagated full length of test piece
30-10	30% CW and Hydrided	25	2 1/2	28,000	Brittle crack propagated full length of test piece
30-9	30% CW and Hydrided	150	1 1/2	27,300	Brittle crack propagated full length of test piece
60-9	60% CW and Hydrided	25	2 1/2	8,300	Brittle crack propagated full length of test piece
30-17	30% CW and Hydrided	25	4	33,300	Brittle crack propagated full length of test piece
60-17	60% CW and Nonhydrided	25	4	26,600	No crack propagation
30-18	30% CW and Nonhydrided	0	No slot	142,500	Brittle, line crack for a about 4 in. which terminated at each end into two branching cracks which propagated to the end fitting. No shear lip on all crack surfaces
60-19	60% CW and Nonhydrided	0	1 1/2	53,000	Crack propagated about 2 in. either side of slot
60-18	60% CW	0	1/2	116,700	Crack propagated nearly full length. 45° shear lip on all crack surfaces
60-6 ^(a)	60% CW and Nonhydrided	-23	1/2	73,500	Brittle behavior, crack propagated full length of test piece

(a) This specimen was initially tested at 300 °C and could not be ruptured at this temperature with the crack sealing materials available.

The above data show that substantial levels of hydrogen (i. e., 250 to 300 ppm) result in brittle behavior at least to 150 °C. The effect on hoop stress at failure, however, does not appear to be entirely consistent. In an attempt to find the basis for this behavior, these test pieces were sectioned for metallographic examination. Photomicrographs of samples from the tubes reveal uniform hydriding except for a thin hydride case on the exterior surface. This case is machined off before testing. Orientation of the hydrides is similar to that observed in Zircaloy-2. Near the inside surface the poles of the hydride plates are oriented radially, as illustrated in Figure 6.5 (a and b), and in the interior of the tube wall the plate orientation is more random when reviewed on a transverse section. From these photomicrographs there does not appear to be a hydride level or distribution difference to account for the variations in hoop stress at failure. Further testing of hydrided specimens will be done.

Some differences in the temperature at which brittle failure occurs have been observed for the 30% and 60% cold worked conditions. Based on the few tests now complete, it appears that "brittle" temperature for the 60% cold worked material is lower than for the 30% cold worked material. The 60% cold worked condition was produced by two cold drawing operations providing for a 30% reduction in each step. The 30% cold worked condition was produced by identical reductions but the material was given an annealing treatment between the two cold reduction steps. Figures 6.6 and 6.7 show the microstructure and hydride impurity of the two materials. The grain structure of the 60% cold worked material is appreciably finer; however, this microstructural difference does not appear to exert any effect on ultimate tensile and burst strengths as compared to the 30% cold worked condition. Hence, it now appears that the difference in hydride impurity level is responsible for the observed differences in brittle fracture temperature. Further testing of these materials will continue.

Also tested was a specimen made up of equal length of Zircaloy-2 and Zr-2.5 wt% Nb alloy tubing which AECL had joined by butt welding. The Zircaloy-2 piece was 3.25 in. ID x 0.160 in. wall and the Zr-Nb piece

(a)

250X

(b)

250X

FIGURE 6.5. (a) TRANSVERSE SECTION OF Zr-2.5 wt% Nb TUBE HYDRIDED TO 250-300 ppm. (This section near inside surface illustrates radial orientations of poles of the platelets.) (b) LONGITUDINAL SECTION OF ABOVE SPECIMEN

FIGURE 6.6. PHOTOMICROGRAPHS OF 30% COLD WORKED Zr-2.5 wt% Nb ALLOY TUBING. (The top photo is a bright field view and shows the typical level of hydride impurity estimated to be about 30 ppm.)

FIGURE 6. 7. PHOTOMICROGRAPHS OF 60% COLD WORKED Zr-2.5 wt% Nb ALLOY TUBING. (The top photo is a bright field view and shows the typically low level of hydride impurity estimated to be less than 10 ppm.)

was 3.25 in. ID x 0.095 in. wall. A 1/8 in. deep x 1 in. long slot located about 2 in. from the welded joint was milled in the outside surface of the Zircaloy-2 section. Pressurizing the test piece initiated brittle failure in the Zircaloy-2 section at a hoop stress of 52,000 psi; the brittle crack propagated only a short distance through the weld and was arrested in the Zr-Nb alloy section.

GAS LOOP DEVELOPMENT

The model gas loop is a 2000 °F, 500 lb/hr flow, helium recirculating loop that is approximately a one-tenth model of the ATR Helium Loop that is designed for installation in the Advanced Test Reactor (ATR) at Idaho Falls. The ATR loop will be used for irradiation damage studies on refractory metals and with some modifications could be used to irradiate fuel samples. One important function of the model loop is to support the design of the ATR loop. This function is nearly complete except for the gas heater which is in the design phase. The heater design represents a significant departure from the commercial practice, therefore, a similar type of heater is being built for the model loop. Other work in support of the ATR this quarter has involved bench tests on a mock-up of a seal between the in-core 347 SS pressure tube of the ATR Helium Loop and the columbium sleeve liner for this tube.

Columbium Sleeve Leak Test - L. J. Defferding

The specimen train and the 2000 °F helium in the test section of the ATR Gas Loop will be separated from the in-reactor pressure tube of the loop by a replaceable columbium sleeve heat shield. A labyrinth seal at the top of the sleeve must reduce helium flow in the annulus between the liner and the pressure tube to 25 lb/hr or less at a sleeve temperature of 2000 °F and a pressure drop of 30 psi, otherwise heat loss to the water jacket surrounding the pressure tube would be excessive. The nominal diametral clearance between the sleeve and the seal that was tested previously was 0.010 in. as compared to a design clearance of 0.020 ± 0.010 in. Tests were run by varying the sleeve temperature to as much as 1000 °F. A pressure drop of 35 psi at 1000 °F and a flow through the seal of 8.9 lb/hr extrapolates to 30 psi, 2000 °F and 5 lb/hr, respectively.

Tests were completed on a second sleeve with an average diametral clearance of 0.025 in. The maximum average sleeve temperature that could be obtained with the present equipment was 1670 °F. The extrapolation of the leakage curve to 2000 °F indicates a flow of 30 lb/hr with a pressure drop of 25 psi for this sleeve. This would indicate the sleeve should have a maximum clearance of about 0.020 in. in order to meet the leakage flow requirements.

Model Loop - L. J. Defferding

Disassembly of the model loop has been started. All the shroud piping and the primary pipe that is not required for installation with the new model heater is being removed. The present heater that is in the loop will be removed and stored without disassembly. The Haynes 25 and Hastelloy X primary piping will be tested to determine the effect of operation at elevated temperature on the mechanical properties.

Model Gas Loop Heater and Piping Modifications - R. J. Evans

Final assembly is now in progress on the model gas loop heater designed to incorporate and investigate essential details of a compact two-stage, concentric heater being designed for the ATR Gas Loop. Major design features of this heater are described in previous Quarterly Reports. (1-4)

The assembly of the first stage of the heater was completed. This assembly consisted of a series of nichrome tubular type heating elements that are inserted into close fitting holes in a stack of alumina rings. Each tube is roll fitted against a nickel connector, by using an expanding mandrel type tool, and then welded to form a seal weld between the end of the tube and the connector. Test results on full size specimens indicate this method of attaching the tube to connector will result in a diffusion bond at operating conditions. This entire assembly with pressure taps and thermocouples has been inserted into a welded, cobalt base metal liner that will be used to direct the flow of gas through this stage of the heater.

The tubular molybdenum heating elements in the second stage of the heater form a series electrical circuit the same as the nichrome tubes in the first stage of the heater. In order to minimize connector heat losses, a thermally stable, tight fit between tubes and connectors is required. The molybdenum tubes, however, are not amenable to roll-fitting as were the nichrome tubes. The fit selected as most practical was a locking taper with a seal weld on the end of the tube. The molybdenum connectors and tubes have been machined and are now being assembled.

-
1. Quarterly Progress Report, Metallurgy Research Section, October, November, December, 1964, edited by J. J. Cadwell, HW-84573. General Electric Company, Richland, Washington, January 15, 1965.
 2. Quarterly Progress Report, Metallurgy Research Section, January, February, March, 1965, edited by J. J. Cadwell, BNWL-79. April 15, 1965.
 3. Quarterly Progress Report, Metallurgy Research Section, April, May, June, 1965, edited by J. J. Cadwell, BNWL-120. July 15, 1965.
 4. Quarterly Progress Report, Metallurgy Research Section, July, August, September, 1965, edited by J. J. Cadwell, BNWL-166. October 15, 1965.

The primary piping for the revision of the model gas loop is being prefabricated with water jackets and foil insulation into three subassemblies. This will reduce the final assembly when the model heater is completed.

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