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OCTOBER, NOVEMBER, AND DECEMBER 1956

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QUARTERLY REPORT
OCTOBER, NOVEMBER, AND DECEMBER 1956
METALLURGY DIVISION

ABSTRACT

Advanced Water Reactor Program - Activity 4102

Methods of producing extremely clean surfaces on rolled Zircaloy-2 strip have been investigated. It has been found that the finer abrasives, 400 mesh or finer, are more effective than coarse types because of their ability to penetrate pits and crevices more readily. Two such cleanings, with an intermediate 35 v/o HNO_3 -5 v/o HF pickle, resulted in a microscopically clean surface.

Ultrasonic inspection of the EBWR fuel plates has been completed during this quarter. Approximately 95% of the plates were found acceptable.

All subassemblies manufactured from the EBWR plates met dimensional specifications and passed 9-day corrosion tests at 290°C (550°F).

All thorium-uranium pellets for the loading of Borax-IV have been pressed, loaded into tube plates, and fabricated into subassemblies. The total number of subassemblies made was 82, of which 72 were fuel plates and 10 were blanket plates, more than sufficient for the loading. The reactor has gone critical using this loading.

Samples of two additional thorium-uranium compositions (25.6 and 12.8 w/o UO_2) have been prepared for irradiation tests in MTR.

Fast Breeder Reactor Program - Activity 4104/4580

Development of Core III for EBR-I has been started this quarter, with rigidity of the lattice being an important design factor. The core material will be enriched and natural uranium in the fuel elements and natural uranium only in the blanket elements. Both types will be clad with Zircaloy-2 by coextrusion. Development is now concentrated on the method of providing end closures.

Eddy-current inspection techniques are in development for the testing of EBR-II fuel elements for voids in the sodium bonding layer.

Casting methods and property evaluation of uranium-plutonium-fissium alloys have occupied considerable effort during the quarter. Melting was carried out at 1500°C , with pouring at 1350°C . Extrusion of U-20 w/o Pu

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base alloys containing up to 10.8 w/o fissium has been successful at a 7 to 1 reduction ratio. The expansion coefficient of 75 w/o U-20 w/o Pu-5 w/o Mo has been determined to be about $17.6 \times 10^{-6}/^{\circ}\text{C}$ for the range $25^{\circ} - 530^{\circ}\text{C}$.

Advanced Engineering and Development - Activity 4530/4540

A high speed scanning system for ultrasonic inspection of fuel plates is in development. This is expected to provide increased inspection facilities for the increased number of reactor cores scheduled for manufacture in the immediate future. An alternate method employing eddy-currents is also under development. One such instrument has been designed and successfully tested.

In the testing of uranium alloy castings, a new transmission technique (see ANL-5643) has been used to determine the location of areas of shrink and porosity.

Tests on phosphoric acid corrosion inhibitor in water have been extended to an evaluation of its use at the operating temperature for Borax-IV. No measurable corrosion rate on alloy M-388 (see ANL-5643) was noted for a test at 3.5 pH, and a rate of 0.4 mdd was measured for the test at 4.0 pH. In couples of alloy M-388 with stainless steel no signs of accelerated corrosion were observed, but a lace work of fine pits in the aluminum surface near the stainless steel was filled with a white corrosion product. No serious penetration was noted.

In superheated steam the corrosion rate of Al-5.6 w/o Ni-0.3 w/o Fe was found to be below detection limits, as compared with a rate of 0.4 mdd for Zircaloy-2. The tests were performed at 400°C and 4000 psig.

Gamma quenched and aged U-3 w/o Ti alloys disintegrated after one week in 290°C water.

Cast and quenched U-5 w/o Zr-2 w/o Ta alloy was found to be not corrosion resistant in 290°C water, but rolled and quenched, it retained corrosion resistance for a short time. Aging the rolled material destroyed the corrosion resistance.

Uranium-5 w/o zirconium-1.5 w/o niobium alloys have shown corrosion behavior independent of quenching rate, in apparent contradiction to the theory of hydrogen absorption.

Uranium-3.8 w/o silicon samples, coextruded in Zircaloy-2 tubing by Nuclear Metals, Inc., showed inconsistent corrosion results in the unirradiated condition. As irradiated, bare samples fail after short exposure to 290°C water. The effects of cladding were mixed and indeterminate.

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Samples of U-2 w/o Zr, coextruded in Zircaloy-2 by Nuclear Metals, Inc., with a diffusion heat treatment to provide a corrosion barrier, showed that such barrier does provide definite protection against small cladding defects, even after small amounts of irradiation (0.1 total atom burnup).

Irradiation tests to 0.72% total atom burnup, have been made on specimens prepared from end-pressed uranium hydride compacts. Although some specimens were cut from sides of the original compact, very little warping resulted from the irradiation. All specimens elongated in the pressing direction, in contrast to earlier data on specimens prepared from uranium powder. Swelling was observed in specimens irradiated at temperatures above 430° C.

Production, Treatment, and Properties of Materials - Activity 5410

Recrystallization studies of heavily cold rolled uranium sheet have shown that the expansion coefficients, which are considered as an indication of textural changes, increase with the volume per cent of recrystallized material, the relationship, however, is not linear. The major increase in expansion coefficient occurs following recrystallization at 400° C, annealing for 15 hours at 360° C to an extent resulting in about 30 volume per cent recrystallization was accompanied by only minor changes, if any, in the expansion coefficient. To determine whether the low temperature recrystallization can be carried to completion without a significant change in the expansion coefficient, tests are now in progress involving long time anneals at 360° C (all prior tests were confined to 15-hour anneals)

Highly depleted UF_4 for alpha uranium self-diffusion studies (U^{235} concentration - 0.03%) was obtained from Oak Ridge and arrangements made with Mallinckrodt to reduce it to metal. The metal will require purification by fused salt electrolysis to remove rather large concentrations of iron and chromium. Two more gamma phase diffusion anneals have been made with no changes in the U^{235} concentration along the length, except for random fluctuations. After considering a number of possible explanations to account for this, it is presently thought that the lack of penetration is due either to a rather low diffusion coefficient, of the order of 10^{-11} cm^2/sec , or to some sort of diffusion barrier on the surface of the specimen. A long-time diffusion experiment using a sample with a relatively thick sputtered layer is presently under way to enable us to decide which is the case.

The determination of the U-C liquidus curve by saturation has been concluded. Analyses of samples from the vicinity of the liquid-solid interface yielded an average carbon concentration of 440 ppm. The conclusion appears to be justified that saturation experiments yielded rather high values for the solubility of UC in liquid uranium, and that the data obtained by liquation represent the true liquidus curve at low carbon contents

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The development of techniques for preparing flat and parallel crystallographic faces that are thought to be suitable for high frequency ultrasonic measurements of elastic constants of alpha uranium single crystals has been completed during the past quarter. From back-reflection Laue patterns it is estimated that the strained surface layer remaining on these surfaces is approximately 1 micron thick. It is felt that this degree of surface distortion will not interfere with the ultrasonic wave measurements. Three crystals have been prepared by these techniques for measurements in the [100], [010], and [001] directions. The crystal thicknesses in these directions, which will also be the wave propagation directions, are approximately 3 to 4 mm. The measurements will be made using vibrational frequencies in the range of 50 to 75 megacycles.

The chief features of the uranium end of the uranium-ruthenium phase diagram have been mapped out as part of the program of uranium-fissium alloy properties. An alloy containing 5 w/o Ru was found to retain the body centered cubic gamma phase upon quenching from 900°C. Eleven ternary uranium-molybdenum-ruthenium alloys have been examined after heat treatment at 900°C; an extensive single phase gamma field has been found.

Sintering studies on synthetic sapphire spheres (Al_2O_3) in H_2 atmospheres at 1700° to 1900° C have disclosed that the spheres undergo considerable changes in shape in the process, approaching an hexagonal bipyramid with two basal planes. These shape changes are significant in interpreting the laws of sintering since the growth of the necks between two particles takes place between two planes inclined at a constant angle to each other. Studies are under way to determine the rate of the growth of these faces in isolated spheres and cylindrical rods; a knowledge of these rates should facilitate a more quantitative evaluation of the sintering mechanism.

The effect of vacuum heating of oxide films on zirconium and Zircaloy-2 on their corrosion behavior in 350° C water has been found to be as follows: the initial weight gain was lower but then it increased with continued intermittent vacuum heating during the corrosion test, as compared with control specimens which have not been vacuum heated. The weight gain rate returned to normal when the intermittent vacuum heating ceased. The increased oxidation rates are interpreted as due to the formation of additional defects in the oxide structure, as indicated by its conductivity increase. The initial lower gain rates are attributed to the vacuum dissolution of the initial thin film (40 to 60 Å thick) and the subsequent formation of a less permeable film; as the film grows thicker, however, it becomes more permeable. These results suggest that a resistant alloy should have an oxide whose conductivity change upon vacuum heating is very slow, as this would indicate a stable defect structure. If this view is correct, then vacuum heating could be used as a tool in the evaluation of the corrosion resistance of new alloys.

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In connection with the corrosion film resistance program the system zirconium-titanium is being studied up to 50.0 w/o Ti. Alloys containing 0.5 and 1.0 w/o Ti had very high corrosion rates at 350°C. Modifications have been made in the probe design to allow a double contact with the evaporated metal spot and to incorporate a thermocouple. For the contact spot evaporated aluminum is used, which adheres well to the oxide surface; evaporated gold was found unsatisfactory.

Alloy Theory and the Nature of Solids - Activity 5420

In studies on transition element alloy systems three new Cr_3O phases having Nb_3Sb , Ta_3Sb , and Nb_3Ge have been found. The occurrence of these phases and their lattice parameters are in conformity with the qualitative size relations formulated in the previous quarterly report. A set of linear empirical equations has been derived by means of which the lattice parameters of all known Cr_3O phases can be expressed in terms of the Goldschmidt radius of the B element. The search for equiatomic alloys of transition elements having the CsCl structure has yielded identification of this structure in the following systems: VRu, VOs, ZrOs, and possibly ZrPt and VPt.

Effects of Irradiation on Materials - Activity 5430

Radial and longitudinal distributions of neutron densities have been obtained within uranium fuel specimens, 0.25 and 0.35" in diameter, with various enrichments. Magnesium-cadmium alloys were used to duplicate the macroscopic absorption cross sections of the various degrees of enrichment. The experimentally determined radial distributions were found to agree reasonably well with theoretical calculations using various transport theory approximations.

I. ADVANCED WATER REACTOR PROGRAM - ACTIVITY 4102

1. Cladding of Uranium-Zirconium-Niobium Alloy with Zircaloy-2

(R. E. Macherey, C. H. Bean, J. R. Lindgren)

a. Cleaning Tests on Rolled Zircaloy-2 Strip

A thorough investigation was made to obtain microscopically clean surfaces on as rolled Zircaloy strip. A wide variation, 1.9 to 6.9 mils, was noted in the thickness of the total oxide layer on 850° C rolled strip at various sections of the same piece of material. Less variation, 0.4 to 0.7 mil, existed in the thickness of oxide formed on 600° C rolling. Some crevices or fissures, which penetrated to a depth of 2.5 mils, were found in the surface of this material. Although coarser abrasives, 100 to 200 mesh, have higher apparent cleaning rates than 400 mesh and finer, the smaller particle size would be better able to penetrate the pits on the surface and the crevices described above. Cleaning tests for hot rolled strip combined initial cleaning with 100 mesh or 400 mesh grit, with a second cleaning using 400 mesh grit both with and without intermediate pickling. Tests on warm rolled strip were limited to 400 mesh grit and acid pickling.

All material used in the cleaning tests was rolled from forged and scalped Firth Sterling ingot No. FZ-249. All cleaning was done on a modified B-20 Vapor Blast machine equipped with a power-driven work carriage and three blasting guns reciprocated hydraulically. The guns were mounted with the nozzles 2" above and at an angle of 60° to the work. The gun travel was set at 2 seconds/cycle with $12\frac{1}{8}$ " long stroke. The grit concentration was maintained at 35 v/o in the water-abrasive slurry.

For 850° C rolled material, a single cleaning with 100 mesh grit at rates as low as $31\frac{1}{2}$ in.²/minute or with 400 mesh at 18 in.²/minute failed to produce clean surfaces. The specimens blasted with 100 mesh grit at $31\frac{1}{2}$ in.²/minute, and reblasted with 400 mesh grit at 27 in.²/minute, with or without intermediate pickling in 35 v/o nitric acid (specific gravity 1.42) -5 v/o hydrofluoric acid (49.2 v/o HF) solution were free from surface contamination with the exception of a few small black oxide particles in the deepest pits which were visible at 90-X. Similar microscopic specks were noted on specimens after blasting twice with 400 mesh grit at 18 in.²/minute without an intermediate pickle. With the intermediate pickle, however, double blasting with 400 mesh grit resulted in a microscopically clean surface. The optimum cleaning procedure for producing microscopically clean surfaces on 600° C rolled Zircaloy consisted of blasting with 400 mesh grit at 18 in.²/minute, pickling in 35 v/o HNO₃-5 v/o HF acid, and reblasting with 400 mesh grit at 18 in.²/minute. Since 850° C rolled material was not intended to be used as cladding component stock and would be recleaned after 600° C rolling, an absolutely clean surface was not required. Samples

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of 850° C rolled material, blasted more rapidly with 100 mesh grit at $67\frac{1}{2}$ in.²/minute, pickled, reblasted with 400 mesh grit at $67\frac{1}{2}$ in.²/minute, and rolled 50% reduction at 600° C, were thoroughly cleaned by the procedure described above for cleaning 600° C rolled strip. Strip which was cold finished from previously cleaned 850° C rolled strip was satisfactorily cleaned by degreasing and acid pickling.

b. Evaluation of EBWR Fuel Plates Rolled in Thicker Carbon Steel Cans

Sixteen EBWR fuel plates were rolled in 3" thick 1020 carbon steel cans to determine the effect of a thicker jacket on surface finish of the roll clad fuel plates and upon the dimensional uniformity of the fuel plates. The billets were assembled and rolled according to the procedures previously established for the manufacture of EBWR fuel plates. Rolling in the thicker steel cans showed a marked improvement in the surface finish of the resulting fuel plate which was smooth and free from ripples or bumps that are quite common as a result of rolling in the thinner carbon steel cans. The thicker can did improve the dimensional uniformity in the rolled plate, but with no improvement in reducing plate camber. The variation in plate width from one end to the other was reduced noticeably. Spread in over-all plate width was 34% greater than the spread in plate rolled in the $2\frac{1}{2}$ " thick steel cans.

2. Ultrasonic Tests of EBWR Fuel Plates (W. J. McGonnagle, W. N Beck)

Seventeen fuel plates were tested this quarter, completing this phase of the ultrasonic tests for EBWR. A total of 1025 fuel plates were tested in this program. Of these, 972, or about 95%, were accepted for use in sub-assemblies and 53 were considered defective.

Eight fuel plates were inadvertently welded into subassemblies prior to having been subjected to the bond test. A special two-arm probe was designed and fabricated, and the test was performed on eight plates in six assemblies. Of the plates tested in subassemblies, all were found to be adequately bonded.

3. Welding of EBWR Fuel Subassemblies (C. C. Stone, F. D. McCuaig, R. A. Noland)

The welding and corrosion testing of all of the above units has been completed and the EBWR reactor is now in operation. A total of 141 sub-assemblies were made, instead of 148 as was originally planned. No sub-assemblies exceeded the required dimensional tolerances or failed to withstand the 9-day, 290° C (550° F) pressurized water corrosion test. A final report fully describing this work is to be issued.

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4. ThO₂-UO₂ Fuel Pellets for Borax-IV (J. H. Handwerk, C. L. Hoenig, R. C. Lied)

A total of 453 kg (93.41 w/o ThO₂-6.59 w/o U₃O₈) of fuel pellets have been fabricated. These pellets were made by dry mixing the thorium and uranium powders, and then granulating the powder with addition of 2½ w/o polyvinyl alcohol and 12 w/o water. The granulated material was pressed at between 14,000 to 16,000 psi, and the pellets thus formed were fired in air to 1700° - 1750° C. The peak temperature was held for two hours before the furnace was shut off and allowed to cool to room temperature. The average geometric density of the pellets was determined to be 8.3 g/cc, while the average apparent density was found to be 9.8 g/cc. The average diameter of the fuel pellets was 0.229 ± 0.002. This tolerance was such that the pellets could be canned without grinding. Approximately 410 kg of pellets were sealed into the aluminum alloy tube plates.

5. Fabrication of Fuel and Blanket Tube-Plates for the Borax-IV Reactor (R. A. Noland, D. E. Walker, F. D. McCuaig, C. C. Stone)

All of the fuel tube-plates and blanket tube-plates for the fuel and blanket assemblies required in the core of the Borax-IV reactor have been completed. In all, 432 fuel tube-plates and 62 blanket tube-plates were made. From these, 72 fuel assemblies and 10 blanket assemblies were fabricated - enough to run the reactor plus a few spares.

The reactor has gone critical, and some of the tests for which it was intended are now being conducted. A final report describing this work in full is in preparation.

6. Thoria-Urania Bodies (J. H. Handwerk)

Irradiation samples of two additional ThO₂-UO₂ bodies were fabricated. One body had the composition 74.4 w/o ThO₂-25.6 w/o UO₂ while the second body had the composition 87.2 w/o ThO₂-12.8 w/o UO₂. Specimens which were prepared measured 0.228" to 0.231" in diameter and approximately 1½" in length. The apparent density of the 25.6 w/o UO₂ body ranged from 9.05 g/cc to 9.29 g/cc. The apparent density of the 12.8 w/o UO₂ body ranged from 9.07 to 9.23 g/cc. These samples will be submitted for irradiation in MTR.

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II. FAST POWER BREEDER PROGRAM - ACTIVITY 4104/4580

1. Fabrication of Fuel and Blanket Rods for the EBR-I, Core III Loading (R. A. Noland, C. C. Stone, F. D. McCuaig)

The core of the EBR-I reactor is to be completely rebuilt to conform with a new design intended to ensure a lattice whose component elements are unable to move relative to each other. As in previous EBR-I cores, fuel rods will occupy the central positions. These will be surrounded on all sides with natural uranium, acting as a blanket. Thus both fuel and blanket rods will be used. The external appearance and the outside dimensions of both are identical, the rods being $0.403" \pm 0.001"$ diameter by $21\frac{3}{4}"$ long (without handle). Core material is fully enriched uranium and natural uranium in the fuel elements, and natural uranium in the blanket elements. These materials are clad on their external surfaces with a $0.020"$ thick layer of Zircaloy-2, metallurgically bonded in place. Each rod has an accurately machined Zircaloy-2 locating tip at one end, and a fitting of the same material, which is drilled and tapped to receive a stainless steel handle, fixed to the opposite end. Three longitudinal fins, 0.043 to $0.047"$ high, are spaced 120° apart around the periphery of each rod for spacing purposes.

Fuel Rods. The fuel section of each fuel rod is an $0.363" \pm 0.001"$ diameter (unclad) by $8.500"$ long, highly enriched, 2 w/o Zr alloy slug clad as described. The core-containing section of the fuel rods is $0.403"$ in diameter by $19.812"$ long. It is made up of a fuel slug which is fixed between two blanket slugs to form what appears to be a single rod. A blanket slug $7.750"$ long is mounted above the fuel section; a $3.562"$ long slug is mounted below. At the present moment it has not been decided whether or not the blanket material will be alloyed with 2 w/o Zr. Thin Zircaloy-2 discs separate the fuel from the blanket slugs.

Blanket Rods. The blanket rods are identical to the fuel rods in all respects except that no enriched uranium is contained therein. Thus they consist of cylinders, $0.363"$ in diameter by $19.812"$ long, clad with $0.020"$ of Zircaloy-2, metallurgically bonded to the core.

Fabrication. Clad fuel and blanket components are expected to be made by coextruding Zircaloy-2 canned billets of the appropriate composition. It will not be possible to utilize the coextrusion process to provide integral end closures because it is necessary to fix the length dimensions of the fuel and blanket slugs to a precision of the order of a few mils. To circumvent the end effects invariably encountered in coextrusion, clad fuel sections or clad blanket sections will be extruded in long lengths which will then be cut, assembled with the proper components, and welded into completed rods. The jacket-to-jacket peripheral welds will be made without filler rod by the inert-gas tungsten-arc method. It may be necessary to

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bond the core slugs to the Zircaloy-2 separating wafer mentioned above, but no decision on this matter has as yet been made. At the moment it is also undecided as to how the spacing fins are to be attached.

2. EBR-II Bond Testing (W. J. McGonnagle, W. N. Beck)

Advance plans have been made for the automatic testing of EBR-II fuel elements for voids in the sodium layer. An eddy-current system has been designed which will furnish a warning signal when a void of objectionable size occurs. The plans call for inspection at the rate of about one fuel element per second. Tests have been made to determine a suitable material for construction of the test coil which must stand up under strong radiation fields.

3. Casting of Uranium-Fissium Alloys (R. E. Macherey, N. J. Carson, Jr.)

Foundry effort during the past quarter was directed toward service work and the casting of uranium-fissium alloys. Alloys were made for experiments concerning fabrication of alpha-gamma radioactive fuels, and irradiation of uranium-plutonium-fissium alloys. Fissium alloys containing 5, 10, and 15 w/o fissium were made.

The melting cycle consisted of heating the alloy to 1500° C, holding until all melt action ceased, and cooling to 1350° C for pouring. The crucibles used were either magnesium oxide or coated graphite. The coating for the graphite crucibles consisted of a mixture of 98 w/o thoria and 2 w/o zirconia suspended in water. The wash was applied by spraying and was dried in air at room temperature. The molds were graphite washed in the same manner as the crucibles.

To determine an appropriate pouring temperature a cooling curve was run for a 15 w/o alloy containing 0.18 w/o Zr, 0.03 w/o Nb, 8.39 w/o Mo, 4.98 w/o Ru, 0.87 w/o Rh, and 0.57 w/o Pd. Prealloyed material was charged and a washed graphite crucible was used. The crucible was insulated on all sides by 1" of zirconia brick, and on the sides and bottom by 9/16" of bubbled zirconia and another 3/8" of solid zirconia. A hollow magnesia tube was used to protect the tungsten-tantalum thermocouple. The melt was heated slowly to 1500° C and allowed to cool with the power off. A cooling curve was obtained, using a high speed Brown recorder, which had breaks at 900° and 1200° C, indicating a 300° C freezing range.

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4. Properties of Uranium-Plutonium-Fissium Alloys (L. R. Kelman, J. E. Baumrucker, H. V. Rhude)

Although present plans are to cast to finished size the EBR-II fuel pins, it was considered desirable to obtain some information about the extrudability of the fissium alloys in the event that an alternate fabrication method becomes of interest. To that end, the following uranium-plutonium alloys containing various amounts of fission product elements have been extruded.

1. U-20 w/o Pu-10.8 w/o Fs
2. U-20 w/o Pu-5.4 w/o Fs
3. U-20 w/o Pu-5.4 w/o Fs-3.6 w/o Mo
4. U-20 w/o Pu-5 w/o Mo

No difficulty was encountered with the inverse extrusion method using bare billets, a 7 to 1 reduction, and temperatures in the range 390° - 500° C. A study is being made of the thermal cycling, irradiation stability, and other properties of these alloys.

A 75 w/o U-20 w/o Pu-5 w/o Mo alloy casting was cycled several times from room temperature to 790° C in a dilatometer to study its thermal expansion and transformation characteristics. The average expansion coefficient was $15.91 \times 10^{-6}/^{\circ}\text{C}$ for the range 25° - 391° C (average of 5 cycles), and $17.61 \times 10^{-6}/^{\circ}\text{C}$ for the range 25° - 532° C (average of 4 cycles). A change in the slope of the expansion curve, indicating a solid state reaction, occurred in the region 560° - 572° C, resulting in a slight elongation of the specimen which was not recovered on cooling. This elongation continued at about the same rate for each successive cycle.

5. Irradiation of Uranium-Plutonium-Fissium Alloys (R. J. Dunworth)

Several cast pins of uranium-plutonium-fissium alloys showed excellent resistance to irradiation damage (ANL-5677). To verify these results, seven additional pins of the 70 w/o U-20 w/o Pu-10 w/o Fs alloy were cast to simulate the EBR-II injection casting method. The alloy was melted under helium at atmospheric pressure and was cast into evacuated Vycor tubes held in the melt. The pins were 1" long and 0.145" in diameter. A radiograph showed blowholes and porosity in some of the pins. The sound pins had a density of 16.9 g/cc and a hardness of 70 Rockwell A. The pins will be irradiated in the MTR facility.

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III. ADVANCED ENGINEERING AND DEVELOPMENT - ACTIVITY 4530/4540

1. Development of Ultrasonic Inspection Techniques (W. J. McGonnagle, W. N. Beck)

a. Ultrasonic "Fluoroscopy" Unit

A high speed ultrasonic scanning system is being developed and fabricated. The system utilizes two 4" x 4" crystals, one of which is a 196 segment mosaic. The crystals in the mosaic will be excited independently by row and column, at a total frame frequency of 30 frames per second. A Video sweep circuit will be synchronized with the mosaic commutator which will project a line raster on a persistent screen cathode ray tube. The impulses from the receiving ultrasonic crystal will be applied to the "Z" axis of the sweep circuit which will produce the visual image.

b. Ultrasonic Tests of Cylindrical Castings

A transmission test was conducted on 22 cylindrical uranium alloy castings. The castings measured approximately 11" in length and from 1" to 1½" in diameter. A transmission technique at an ultrasonic frequency of 1 megacycle was successfully used in the determination and location of areas of shrink and porosity.

2. Development of Eddy-Current Inspection Techniques (W. J. McGonnagle, W. N. Beck)

Development has progressed on an eddy-current instrument suitable for the measurement of cladding and plating thickness of one metal on another in a production situation. One such instrument has been designed and successfully tested. It is suitable for measurements of cladding and plating where a considerable difference in conductivity exists between the two metals, or where one of the metals is paramagnetic to a significant degree. This instrument is relatively insensitive to changes in probe-to-metal spacing, a fact which is useful in situations where a constant motion of the metal relative to the probe is required. Another such instrument which should possess greater sensitivity is being constructed.

3. High Temperature Aqueous Corrosion of Aluminum Alloys (W. E. Ruther, J. E. Draley)

a. Corrosion in Phosphoric Acid Solution

As previously reported, small additions of phosphoric acid greatly reduce the corrosion rate of alloy M-388 (0.9 w/o Ni in 1100 aluminum) at

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290° C. Two tests were performed during this quarter to evaluate this additive at the operating temperature of the Borax-IV experiment.

The tests were run at 225° C, pH 4.0 and 3.5 phosphoric acid (measured at room temperature). Considerable scatter in the amount of corrosion of individual samples was observed, because of the low corrosion rates. The pH 3.5 test (75 days) gave no measurable corrosion rate (less than 0.1 mg/dm²-day) while the pH 4.0 rate was of the order of 0.4 mdd. The intercept was below 0.1 mg/cm² for both tests (low).

A few shallow pits of about 0.06 mm diameter were noted on some samples and were absent on others. There was no correlation between length of time in test and number or size of the pits.

Corrosion couples were made by passing stainless steel bolts through a piece of aluminum alloy sheet stock. Under the microscope 40- and 80-day couple samples were quite similar in appearance. A lace work of microscopic pits in the aluminum surface near the stainless steel was filled with a white corrosion product. There was no pitting under the washers or bolt heads and only slight attack on the inside of the bolt holes in the aluminum. There was no sign of an accelerated attack on the stainless steel due to its coupling with the aluminum. When the 80-day samples were defilmed it was obvious that the lace work of pits extended further from the stainless steel for the pH 4.0 test than for the one at pH 3.5. Also, the total amount of microscopic pitting was greater for pH 4.0 exposure. There had been no serious penetration in either case.

b. Superheated Steam Test

A comparison test of ANL aluminum alloy A-203X (5.6 w/o Ni, 0.3 w/o Fe) and Zircaloy-2 was made in superheated steam. The test was performed in a small autoclave operated at 400° C and a pressure of 4000 psig. Duration of the test was 75 days.

The Zircaloy metal weight loss was estimated from the weight gain. Duplicate samples of the aluminum alloy were removed at about 15, 45, and 75 days and defilmed.

By the end of the test the adherent black oxide on the Zircaloy was turning white in spots and beginning to flake. The aluminum alloy corrosion film remained black and unchanged throughout the test. A graph of the results indicated a linear corrosion rate of about 4 mdd for the Zircaloy (intercept ~0.4 mg/cm²) and no measurable rate (less than 0.1 mdd) for the aluminum alloy (intercept 1.2 mg/cm²). This aluminum alloy would appear to be potentially useful under these high temperature conditions.

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4. Corrosion Resistant Uranium Alloys (S. Greenberg)

a. New Alloy Development

Gamma quenched samples of the U-3 w/o Ti alloy aged at 400° C for periods of 1 to 4 hours were completely disintegrated after one week at 290° C. This alloy does not have the resistance to thermal aging of the U-5 w/o Zr-1.5 w/o Nb alloy.

An ingot of U-5 w/o Zr-2 w/o Ta, prepared by N. J. Carson, Jr., of the Foundry Group, was not corrosion resistant at 290° C in the cast condition after quenching from 1070° C. The rolled and quenched material was corrosion resistant for a relatively short time. Aging the rolled and quenched material at 400° C for periods of 2 and 4 hours destroyed the corrosion resistance at 290° C (complete disintegration and a rate of 119 mcd, respectively, after 3.7 days). The results for the quenched and quenched and aged samples (400° C - 1 hour) are summarized below.

TABLE I

Aqueous Corrosion of U-5 w/o Zr-2 w/o Ta at 290° C

Test Interval (days)	Average Rate of Weight Loss During Interval (mcd)	
	Quenched from 1070° C	Quenched and Aged at 400° C - 1 Hour
3.75	16.1	14.1
6.0	31.6	230

The test was stopped after 9.75 days. Attack was nonuniform and apparently two types of oxide, one black and one reddish brown, were formed. It is apparent that the problem of homogeneity in uranium-tantalum alloys has not been solved.

Current efforts are being devoted to development of methods to produce homogeneous alloys and to explain the mechanism of corrosion resistance. Included in the latter effort are the development and interpretation of solution potential data.

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b. Uranium-5 w/o Zirconium-1.5 w/o Niobium Alloy

The study of the mechanism of corrosion resistance of this alloy is continuing. There is some evidence that rapidly quenched specimens of this alloy are single-phase structures.¹ According to our present concepts such a material would not be expected to be corrosion resistant, unless the martensitic structure has a high rate of permeation by hydrogen.

Tests on rapidly quenched (and apparently single-phase) small samples have shown corrosion behavior identical to the larger specimens previously tested. This result makes it necessary to believe either that (a) there is a submicroscopic phase present, or hydrogen diffuses readily into the martensite; or (b) our theory, requiring the absorption of hydrogen into the surface of these "good" alloys during corrosion, does not apply.

c. Uranium-3.8 w/o Silicon Alloys

Previous investigations of the corrosion behavior of the irradiated U-3.8 w/o Si alloy were limited to the cast material. However, if the material were used as a fuel element it is likely that it would be in a wrought form. In addition, the behavior of a defected clad structure is of interest.

The samples were prepared at Nuclear Metals, Inc., by heat treating at 800° C for seven days before coextrusion with Zircaloy-2 tubing. The clad rod was then cut into short lengths for test. The core was exposed at the ends of each sample. Irradiation in the MTR was done by J. H. Kittel.

Unirradiated Samples. A few samples were corrosion tested in the unirradiated condition. Exposure was at 290° C for periods up to about 19 days. Although the samples appeared smoother than the cast material previously studied, corrosion rates remained inconsistent. Rates varied erratically from sample to sample and for the same sample from period to period. The extremes were approximately 1 and 15 mg/cm²-day (mcd), based on the exposed area of the alloy. At the end of the 19-day period some bond areas had failed while on other samples the bond area was sound. Additional heat treatment after extrusion (825° C - 7 days) resulted in increased corrosion of core and bond.

Irradiated Samples. Samples were irradiated both as clad and in the stripped condition. After irradiation the stripped samples were dark black, smooth, and lustrous. As far as physical condition is concerned, they appeared to be in the best condition of any irradiated uranium alloy that has been examined prior to corrosion testing.

¹A. E. Dwight, ANL Metallurgy Division, Private communication.

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Results of the corrosion tests follow

CE 2-1: 0.115 total a/o burnup. This sample was irradiated with clad removed. It was tested at 260°, 290°, and 315° C. Results are shown in Table II.

TABLE II

Corrosion of Irradiated U-3.8 w/o Si Alloy, Sample CE 2-1

Temperature (° C)	Time (days)	Average Rate of Weight Loss (mcd)	Comments
260	2.5	0.44	Lustrous black except for some small white spots, probably due to incomplete removal of cladding.
290	3.4	-0.27 (Weight gain)	No change in appearance.
	2.5	7.43	Sample broken into 4 large pieces. "Rate" based on weight of all pieces. Hydrogen pressure less than 25 psia.
315*	2.5	--	Sample reduced to mass of small particles. Hydrogen pressure of about 30 psi.

*Largest piece remaining after second period at 290° C was tested at 315° C.

CE 2-2: 0.115 total a/o burnup. This sample was irradiated with the Zircaloy clad on. After irradiation a 0.050" hole was drilled through the clad into the core. It was tested at 290° and 315° C

There was no change in appearance after 3.1 days at 290° C. The water was clear and apparently free of oxide or metal particles.

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It was then tested for 4 8 days at 315° C. At the end of this time the core was corroded about 1/32 " to 1/16" below the clad at each end. The clad was swollen and cracked at an identification notch at one end of the clad. There was oxide at the drilled hole but no swelling. There were many loose particles in the water but no residual hydrogen pressure.

CE 1-1: 0.098 total a/o burnup. This sample was irradiated with the Zircaloy clad removed. It was tested at 315° C for 2.9 days. At the end of the time the sample was broken into three large pieces (split in a roughly axial manner) and many small brittle pieces. The surfaces of the larger pieces were pitted. There was no residual hydrogen pressure.

CE 1-2. 0.098 total a/o burnup. This sample was irradiated with the Zircaloy clad on. The core was exposed only at the ends. It was tested at 290° and 315° C.

There was no change in appearance after 3.1 days at 290° C. The water was clear and apparently free of oxide or metal particles.

After 6.2 days at 315° C there was some oxide in the water and a small chip was cracked out of the core at the identification notch in the clad. The clad was flared out at this point. There was no residual hydrogen pressure.

After an additional 7.7 days at 315° C, the core was corroded about 1/16" below the clad at both ends. Both the core and clad were cracked at the notch in the clad and this end of the sample had swelled. There was oxide in the water and a residual hydrogen pressure of about 60 psi

CE 4-1: 0 069 total a/o burnup. This sample was irradiated with the Zircaloy clad removed. It was tested at 315° C for 10 6 days. At the end of this period it was reduced to a slurry. There was a residual hydrogen pressure of 40 psi.

CE 3-2: 0.085 total a/o burnup. This sample was irradiated with the Zircaloy clad on. After irradiation a 0 050 " hole was drilled through the clad into the core.

It was tested at 315° C for 6.6 days. At the end of this time the core was corroded about 1/16" below the clad at each end. Both core and clad were cracked at the notched end of the clad and the sample had swelled at this end. There was no swelling at the drilled hole. There was oxide in the water and a residual pressure of about 25 psi.

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Conclusions. Bare U-3 8 w/o Si alloys, after irradiation, fail after a relatively short exposure to high temperature water. The failure may not be solely the result of corrosion. The effect of partial cladding is difficult to evaluate because all clad samples were mechanically damaged in the process of identification. In order to determine the effect of cladding it would be desirable to have completely clad samples with small defects.

It is evident, based on the results of the unirradiated samples, that the lack of uniformity of these alloys is still a major problem.

d. Uranium-2 w/o Zirconium Alloys

The U-2 w/o Zr alloy is of interest because of its dimensional stability under radiation. However, it does not have aqueous corrosion resistance, even at 100° C.

Samples of the alloy were coextruded with Zircaloy-2 tubing and completely clad samples prepared by welding in plugs of Zircaloy-2 at the bored-out ends. In an effort to produce a corrosion resistant barrier layer, the samples were diffusion heat treated at 1050° ± 5° C for 2 hours and air-cooled.

To test the efficiency of the diffusion produced barrier layer, a 0.005" hole was drilled through the clad and just barely to the core (on the cylindrical surface). On some samples the hole was drilled before the diffusion heat treatment; on others, after the treatment.

The idea for the diffusion heat treatment originated at Nuclear Metals, Inc., where the samples were prepared, and the samples were tested as a service to this organization. Results follow.

Unirradiated Samples. Sample A 200 was stripped of its cladding after the diffusion heat treatment. It was corrosion tested at 290° C for 1.7 days. At the end of this time it was completely reduced to an oxide slurry.

Samples A-138 (defected after heat treatment) and A-175 (defected before heat treatment) were tested for 8.8 days at 290° C and then for an additional 13 days at 350° C. At the end of this test period there was no apparent change in the appearance of the samples, except that sample A-138 developed a white area around the drilled hole. The welded plugs were white upon receipt of the sample, presumably from prior corrosion testing.

The samples were then sectioned through the drilled hole and through the clad-core interface near the welded plugs. There was no evidence of core corrosion.

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Samples A-137 (defected after heat treatment) and A-145 (defected before heat treatment) were tested for 21.8 days at 290° C and then for 31.7 days at 350° C. At the end of this time there was no change in dimensions or appearance except for the development of a small white area around the hole in A-145.

Irradiated Samples. These samples were irradiated prior to corrosion testing (by K. F. Smith in the MTR). Burnups of approximately 0.1 total a/o were obtained

Sample A-174 (CH-1C; defected before heat treatment) was tested for 2.5 days at 290° C and then for 9.0 days at 315° C. Sample A-141 (CH-2F, defected after heat treatment) was tested for 2.6 days at 290° C and then for 9.2 days between 315° and 338° C. At the end of the given test periods there were no apparent changes in the samples.

Conclusions. The diffusion heat treatment definitely produced a protective barrier under the conditions of test. This protection is apparently unaffected by relatively small amounts of radiation. However, based on information from Nuclear Metals, Inc., the protective action of the barrier is limited to very small defects. For example, 0.016" diameter holes result in samples of widely varying lifetimes.

Testing of the samples will continue. It would be desirable to test material subjected to higher burnup.

5 Effects of Irradiation on Powder Compacts Prepared from Uranium Hydride (J. H. Kittel, S. H. Paine)

From an earlier thermal cycling investigation (ANL-5214), five compacts prepared from uranium hydride were obtained for sectioning into irradiation specimens. The compacts were 1.3" in diameter by 4" long, and were made by end-pressing uranium hydride powder, diameter 10 microns or less, under 11 tsi at 600° C. After the cycling investigation, the irradiation specimens were machined from the compacts as shown in Figure 1. Each specimen was identified by a letter, as shown in the figure, depending upon its location in the original compact.

It was anticipated that some of the irradiation specimens, particularly those taken from near the outside of the original compact, might show a tendency to warp under irradiation because of nonuniform texture. In order to investigate the feasibility of restraining any such distortion, half of the specimens were irradiated in stainless steel jackets. Jacket thicknesses were 0.005, 0.010, and 0.020", and the radial clearance between specimen and jacket was approximately 0.003". No end closures were used.

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Figure 1. Location and Identification of Irradiation Specimens Machined from Hot-Pressed Uranium Hydride Compacts.

The unclad and the jacketed specimens are described in Tables III and IV, respectively, and typical specimens after irradiation to 0.72 total atom burnup are shown in Figures 2 and 3. As shown in the tables, all specimens elongated in the pressing direction, in contrast to earlier observations on specimens prepared from uranium powder (ANL-5489, p. 27). The elongations were erratic and varied considerably in values of G_i , the rate of growth. The average growth rate of the unclad specimens and the clad specimens which could be separated from their jackets was 19 micro-inches/inch/ppm burnup.

Contrary to expectations, very little warping was found in the irradiated specimens. Those specimens which were tightly lodged in their jackets after irradiation appeared to be so as a result of an over-all diameter increase, so that the jackets provided an indication of the feasibility of restraining swelling, rather than warping. As shown in Table IV, their ability to restrain swelling was a direct function of their thickness.

TABLE III

Effect of Irradiation on Unjacketed Specimens Taken from Previously
Thermally Cycled Hot-Pressed Uranium Hydride Compacts

Specimen Number	Compact Number	Location in Compact (a)	Number of Prior Thermal Cycles (b)	Calculated Turnup (a/o)	Calculated Temp. (°C)		Length Change (%)	G _i Microin/in ppm Turnup	Diameter Change (%)	Weight Change (mg)	Density Change (%)	Hardness Change (R _A)
					Surface	Center						
AE-9	35	A	250	0.087	75	100	3.1	35	-1.4	34.8	0.21	8.8
AE-1	26	A	700	0.13	75	110	4.4	33	-1.6	1.9	0.39	8.2
AE-13	36	A	250	0.49	240	390	(c)	-	-	-	-	-
AE-17	48	A	700	0.70	320	540	6.6	9.1	19.2	1.3	-21.59	0.4
AE-14	36	E	250	0.11	80	120	5.5	49	-1.9	1.1	0.018	4.2
AE-10	35	F	250	0.43	200	340	0.79	1.8	1.1	2.0	-1.29	10.1
AE-6	31	E	250	0.44	170	280	3.8	8.5	-0.080	-0.4	-0.95	12.1
AE-18	48	B	700	0.53	220	370	4.2	7.8	1.7	2.0	-0.93	10.6
AE-2	26	F	700	0.58	250	420	4.7	7.9	0.60	-2.4	-1.19	10.2
AE-11	35	C	250	0.30	140	230	4.9	16	-0.92	1.9	-0.64	10.9
AE-15	36	C	250	0.39	180	290	4.1	10	-1.1	1.1	-0.48	9.8
AE-3	26	C	700	0.40	160	250	7.2	17	-1.0	0.5	-0.73	7.9
AE-7	31	C	250	0.64	270	450	2.0	3.1	7.6	10.0	-7.97	11.5
AE-19	48	C	700	0.64	270	460	7.8	12	2.4	2.4	-5.34	8.5
AE-8	31	D	250	0.11	70	100	3.8	34	-1.0	1.9	0.061	6.5
AE-20	48	E	700	0.27	120	180	6.8	24	-0.56	1.7	-0.25	9.8
AE-12	35	D	250	0.49	230	390	(c)	-	-	-	-	-
AE-16	36	D	250	0.64	280	470	7.8	12	6.5	-4.5	-12.10	10.9
AE-4	26	D	700	0.66	300	510	11.4	16	9.7	-2.2	-17.58	4.6

(a) The manner in which the uranium hydride compacts were sectioned for irradiation specimens is shown in Figure 1.

(b) Each thermal cycle consisted of heating from 100° to 500°C within 10 to 12 minutes followed by cooling back to 100°C within 25 to 30 minutes.

(c) Measurements could not be obtained after irradiation because the specimen was so highly distorted it was wedged in its irradiation capsule.

TABLE IV

Effect of Irradiation on Stainless Steel-Jacketed Specimens Taken from Previously Thermally Cycled Hot-Pressed Uranium Hydride Compacts.

Specimen Number	Compact Number	Location in Compact (a)	Number of Prior Thermal Cycles (b)	Jacket Wall Thickness (in)	Calculated Burnup (a/o)	Calculated Temp. (°C)			Length Change (%)	G ₁ Microin/in ppm Burnup	Diameter Change (%)	Weight Change (mg)	Density Change (%)	Hardness Change (R _A)
						Surface	Center	Jacket						
AE-35	36	C	250	0.005	0.27	140	220	135	4.7	17	-0.19 (c)	-	-	-
AE-21	26	A	700	0.005	0.28	120	180	115	6.7	23	-1.9	1.6	-0.071	7.6
AE-33	36	A	250	0.005	0.44	230	370	220	1.7	3.8	1.24 (c)	-	-	-
AE-23	26	C	700	0.005	0.48	210	340	200	2.4	4.9	0.64	3.3	-1.36	10.3
AE-34	36	B	250	0.005	0.60	270	440	260	8.8	14	1.12 (c)	-	-	-
AE-22	26	B	700	0.005	0.62	300	490	290	(d)	-	1.16 (c)	-	-	-
AE-24	26	D	700	0.005	0.64	300	500	290	18.0	26	1.65 (c)	-	-	-
AE-36	36	D	250	0.005	0.68	320	540	310	18.8	25	1.16 (c)	-	-	-
AE-28	31	D	250	0.010	0.046	55	70	55	1.2	26	-0.52	22.0	-0.058	7.6
AE-40	48	D	700	0.010	0.092	70	100	65	5.4	57	-2.2	2.5	-0.021	7.2
AE-26	31	E	250	0.010	0.27	130	190	120	2.9	11	0.0	1.5	-0.64	8.3
AE-38	48	E	700	0.010	0.43	190	300	180	8.3	19	0.11 (c)	-	-	-
AE-27	31	C	250	0.010	0.57	270	430	250	3.6	6.2	0.60 (c)	-	-	-
AE-25	31	A	250	0.010	0.65	340	550	315	7.7	11	0.21 (c)	-	-	-
AE-37	48	A	700	0.010	0.72	360	600	335	8.5	11	1.17 (c)	-	-	-
AE-29	35	A	250	0.020	0.21	140	210	130	2.9	14	0.00 (c)	-	-	-
AE-31	35	C	250	0.020	0.37	230	340	210	3.1	8.2	-0.17 (c)	-	-	-
AE-30	35	E	250	0.020	0.45	280	440	255	3.0	6.6	-0.10 (c)	-	-	-
AE-32	35	D	250	0.020	0.49	310	480	280	9.6	19	-0.20 (c)	-	-	-

(a) The manner in which the uranium hydride compacts were sectioned for irradiation specimens is shown in Figure 1.

(b) Each thermal cycle consisted of heating from 100° to 500°C within 10 to 12 minutes, followed by cooling back to 100°C within 25 to 30 minutes.

(c) The specimen could not be separated from its jacket. Diameter change is therefore the change observed in jacket diameter, rather than specimen diameter.

(d) Length measurement could not be obtained because of interference of jacket.

Figure 2. Effect of Irradiation on Unjacketed Specimens Machined from Compacts
Made from Uranium Hydride End-Pressed at 600°C.

Macro 19129

2-X

Macro 19113

2-X

Macro 19126

2-X

Burnup (a/o)

0.27

0.40

0.70

Irradiation
Temperature (°C)

180

250

540

Figure 3. Effect of Irradiation on Stainless Steel Jacketed Specimens Machined from Compacts Made from Uranium Hydride End-Pressed at 600°C.

	Macro 19135	2-X	Macro 19151	2-X	Macro 19145	2-X
Jacket Thickness (inches)	0.005		0.010		0.020	
Burnup (a/o)	0.64		0.72		0.49	
Irradiation Temperature (°C)	500		600		480	

The onset of swelling appeared to be highly dependent on irradiation temperature, as shown in Figure 4. The data shown in the figure were obtained from unclad specimens and those clad specimens which were not restrained by their jackets. It appears that the critical irradiation temperature for the beginning of swelling in uranium hydride compacts is about 430° C. It is of interest that specimen AE-17, which showed the largest density decrease, was the only specimen which showed a drop in hardness. This apparent lowering of hardness is believed to be due to the formation of a sponge-like structure, as has also been observed by British investigators.²

Figure 4. Effect of Irradiation Temperature on the Rate of Density Change in Compacts Prepared from Uranium Hydride.

²J. G. Ball, "Metallurgical Research in Nuclear Power Production," J. Inst. Metals 84, 239-250 (1956).

IV PRODUCTION, TREATMENT, AND PROPERTIES OF MATERIALS - ACTIVITY 5410

1. Recrystallization of Heavily Cold Rolled Uranium Sheet (W. R. Yario, L. T. Lloyd)

The study of recrystallization in alpha uranium at low temperatures without a texture change³ has continued with additional dilatometric measurements on samples from the room temperature rolled high purity uranium sheet. The preparation and metallography of this material was described in ANL-5623. The dilatation studies reported in ANL-5643 indicated that specimens perpendicular to the rolling direction and lying in the rolling plane (transverse) gave more consistent results than specimens parallel (longitudinal) to the rolling direction. Transverse specimens evidently are more representative of the entire sheet because they contain a greater number of bands than do longitudinal specimens, as shown by metallographic examination (Figure 5). In view of the above, the dilatation studies described below have been performed solely with transverse specimens.

Nine additional dilatation tests have been run under the same conditions as those described in ANL-5643. two for specimens annealed 15 hours at 360°C, two for samples annealed 15 hours at 380°C, four for samples annealed 15 hours at 400°C, and one for a sample annealed 15 hours at 450°C. The curves were not as consistent as those determined from the first six specimens examined, but they again showed a progressive increase in slope with increasing annealing temperature. The discrepancies observed between samples annealed at the same temperatures can probably be attributed to differences in the banded structure of the individual samples, or slight differences in the annealing treatments. The latter is indicated to be a contributing factor by the fact that when two samples were annealed together their dilatation curves were almost identical, but differed somewhat from other samples supposedly annealed at the same temperatures for the same times

After the dilatation tests, some of the specimens were examined metallographically by the procedure described in ANL-5643 to determine the volume percent recrystallization. These values are tabulated in Table V, together with an additional value determined from a 380°C annealed metallographic sample. Figure 6 graphically represents these data and the data reported in ANL-5643. The data point for the 320°C annealed sample is in doubt because the extremely small grain size makes measurements of percent recrystallization difficult. Also, the measurement is confused by the occurrence of polygonization (subgrains) in lightly deformed bands.

³ G. Cabane and J. Petit, *Revue de Metallurgie* 51 603-613 (1954).

Figure 5. Macroscopic Banding in Dilatation Specimens
Annealed at 360°C for 15 Hours.

(Macroetched in hot trichloroacetic acid)

5-a. Transverse

5-b. Longitudinal

Macro 20466 4-X

Macro 20468 4-X

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Figure 6. Effect of Annealing Temperature Upon Volume Percent Recrystallization of Heavily Cold Rolled Uranium Sheet. Constant annealing time: 15 hours.

Macro 20960

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Figure 7 is a graphic representation of the indicated texture change which occurred during recrystallization. The measure chosen is the increase in mean expansion coefficient between 200° and 300°C of annealed transverse specimens over that observed for a specimen in the cold rolled condition. The data are plotted as a function of the percent volume recrystallization. Increases in mean expansion coefficient are plotted rather than absolute values so as to avoid the need of correcting for expansion of quartz over the length of the specimen. The temperature range of 200° to 300°C was chosen to permit the referral of all samples to the same temperature range and to eliminate the difficulties encountered in initially seating the specimen in the dilatometer. Because of changes which occur in the sample due to the anisotropy of thermal expansion, reproducibility of the lower temperature portions of the dilatation curves cannot be checked by rerunning the specimen. The curve shows an increase in the mean expansion coefficient which is not a linear function of the percent recrystallization.

Samples of high purity uranium are presently being investigated for the extent of recrystallization and thermal expansion changes as a function of time for a constant annealing temperature of 360°C. This lower temperature was chosen in order to permit a clear differentiation between the two alleged types of recrystallization: one without textural changes at low temperatures, and another at about 400°C involving a texture change.

TABLE V

Percentages of Recrystallization of Heavily Cold Rolled
Uranium Sheet Annealed at Various Temperatures

Specimen Condition	Percent Recrystallized
15 hours at 360°C	26, 30
15 hours at 380°C	82, 83, 85*
15 hours at 400°C	94, 97
15 hours at 450°C	100

*Value determined from metallographic sample.

All others were measured from dilatation samples
after testing.

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Figure 7. Increase of Mean Expansion Coefficient of Uranium Sheet Between 200° and 300°C, Over That Observed for a Specimen Tested in the Cold Rolled Condition, as a Function of the Percent by Volume of Recrystallized Material.

Specimens were tested in a direction perpendicular to the rolling direction and lying in the rolling plane.

Macro 20961

0371228.0330

2. Self-Diffusion in Uranium (S. J. Rothman, L. T. Lloyd)

Refining of Highly Depleted Uranium. The highly depleted UF_4 obtained from Oak Ridge has been analyzed and was found to contain too much iron and chromium to permit the production of purified uranium by bomb reduction alone. Arrangements are being made to have the salt bomb reduced to metal; after this the uranium will be purified by fused-salt electrolysis and vacuum melting techniques.

Diffusion in the Alpha Phase. The alpha phase diffusion sample mentioned in ANL-5643 has been sectioned and analyzed. There was no change of U^{235} concentration along the specimen length, except for random fluctuations. This was expected, because the amount of U^{235} initially deposited was intentionally quite small and the sections obtained by machining were rather large.

Diffusion in the Gamma Phase. Two more gamma phase diffusion runs have been finished, #3 at 922°C for 39 hours, and #4 at 967°C for 24 hours. There were no changes in the U^{235} concentration along the length of either specimen, except for random fluctuations. The sputtered layer on #4 remained unoxidized and adherent through the diffusion anneal, while the sputtered layer on #3 was somewhat oxidized and had flaked off in places. There was some UO_2 , USi_3 , and USi_2 in the bottom of the quartz tube in which #3 had been annealed. Both samples exhibited surface roughening of about 10^{-2} cm, probably brought about by phase transformations.

Five possible reasons for the constancy of the U^{235} concentration were given in ANL-5643. These were: (a) the U^{235} is not deposited during sputtering; (b) it oxidizes and spalls off during the diffusion anneal; (c) it spalls off due to the phase transformations; (d) it gets lost during machining, and (e) it is homogeneously redistributed throughout the specimen. The last implies a D value of the order of $10^{-2} \text{ cm}^2/\text{second}$, which is unlikely, and consideration of the two samples described above eliminates all the others but "d." The sputtered layer is probably lost as follows: before sectioning (following annealing) the sample is turned to remove the U^{235} which was sputtered on the cylindrical surface of the sample. To make the new axis of the specimen accurately perpendicular to the original interface, the sample is turned between brass pads. The U^{235} layer is probably scraped off in this process. If that be the case then it must have been on the specimen during the diffusion anneal, yet there has been no penetration. Therefore, either the diffusion coefficient at these temperatures ($T/T_m = 0.888$) is of the order of $10^{-11} \text{ cm}^2/\text{second}$ which is rather low, but not out of the question (D for thorium at $T/T_m = 0.888$ is about $4 \times 10^{-8} \text{ cm}^2/\text{second}$), or there is some sort of diffusion barrier on the surface of the specimen. A long-time diffusion experiment using a sample with a relatively thick sputtered layer should enable us to decide which is the case. Such an experiment is now under way.

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A diffusion coefficient of 10^{-11} cm²/second cannot be measured if the original interface of the specimen undergoes distortions of 10^{-2} cm. The roughening due to the phase transformations must therefore be eliminated. We have succeeded in doing this in one preliminary experiment by heating the sample very slowly in the alpha region and across the phase transformations.

3. Uranium-Carbon Alloys (B. Blumenthal)

a. Liquidus Curve

The experimental work on the determination of the liquidus curve by saturation was concluded by adding a 24-hour melt to the 2-, 4-, and 8-hour melts at 1200°C reported in ANL-5643. The complete data are listed in Table VI and plotted in Figure 8.

TABLE VI

Diffusion of Carbon into Molten Uranium

Layer* Number	C Content in ppm by Weight After Indicated Time at 1200°C			
	2 Hrs (B 706)	4 Hrs (B 707)	8 Hrs (B 708)	24 Hrs (B 713)
0	226, 199	457, 433	321, 464	532, 445
1	127, 144	-	-	389, 418
2	90, 96	210, 192	261, 205, 181	320, 327
3	47, 48	70, 88, 81	140, 96	173, 226
4	53, 44	31, 37	57, 84, 65	196, 195
5	46, 48	35, 33	24, 24	129, 136
6	47, 39	27, 25	25, 19	84, 115
7	-	-	-	124, 127
8	-	-	-	41, 106, 75
C Content of Original Metal	34	24	36	57

*Each layer represents a thickness of approximately 0.20". Samples of layer 0 were prepared from the immediate vicinity of the top carbide layer.

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Figure 8. Diffusion of Carbon into Molten Uranium at 1200°C.

Macro 21000

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Diffusion of carbon into liquid uranium occurs at a slow rate and the equilibrium concentration occurs near the liquid-solid interface. Analyses of samples prepared from the vicinity of this interface yielded carbon concentrations of 390 to 530 ppm by weight with an average of 440 ppm. This value is closer to the 300 ppm limit obtained by liquation at 1200°C (ANL-5423) than to the 700 ppm obtained in the early saturation experiments (ANL-5465). Although UC forms a distinct layer on top of molten uranium, no precise line of separation exists between the two phases. Both mix in a limited manner making it difficult to exclude UC particles in a sample taken from the immediate vicinity of the top layer. Therefore, such samples will have a higher carbon content than is actually held in solution at temperature.

The conclusion appears to be justified that all saturation experiments produce rather high values for the solubility of UC in liquid uranium and that the data obtained by liquation represent the true liquidus curve of the uranium-carbon alloys of low carbon content. As shown in Figure 9, the liquidus curve is continuous with that derived from earlier investigations of high carbon alloys.

Figure 9. Liquidus Curve of the High Uranium End of the Uranium-Carbon System.

Macro 21001

0370201030

b ^v Decarburization

Two more decarburization experiments were performed both at slightly increased rates of argon gas flow. The temperature of the last unit of the gas purification train, a furnace containing uranium turnings, was lowered from 850° to 750°C. This had the effect of increasing the residual nitrogen content of the argon gas without affecting its oxygen content.

A material with 85 ppm carbon was used in one experiment (B-695-B), and high purity uranium (B-714) with 30 ppm carbon in another. In experiment B-695-B the material was 600°C rolled rod; it became warped during the decarburization heat treatment which resulted in the gradient of the oxide and nitride coat being dissimilar on opposite sides of the specimen. The slightly convex side, facing the gas stream, was dull and obviously more heavily coated than the somewhat protected, slightly concave side, the top end of which was, in fact, quite bright. To minimize warpage, the other specimen was 300°C rolled with increasing reductions between anneals at decreasing annealing temperatures. This rod showed little distortion after heat treatment for 2 weeks at 950°C.

X-ray diffraction patterns (number I through V from the lower end) were taken at different heights, 3/4" apart, by the method described in ANL-5643. The patterns yielded the following information. As in the sample described in ANL-5643, the UO_2 reflections decreased in intensity from the lower end upward and disappeared completely at the center portion of the specimen. The oxide layer actually decreased in thickness and eventually disappeared completely which confirms the fact that the oxygen content of the gas was consumed as it passed along the specimen. The pattern from the top end (No. V) contained alpha uranium reflections, showing that the gas contamination was used up and the thickness of the residual surface film was extremely thin. Not all of the possible uranium reflections were found, and the relative intensities of the observed reflections differed considerably from those of fine grained randomly oriented material. For example, in a randomly oriented, fine grained alpha uranium sample the intensity of the (111) reflection should be greater than that of the combined (044) and (244) reflections. In the present case the converse was found. The same applied to the relative intensities of other alpha uranium reflections, which indicated that the specimens were coarse grained. Since only a very few grains were covered by the X-ray beam, their chance orientation determined the relative intensities of diffraction pattern.

A similar phenomenon of reversed relative intensities was observed for the reflections of the U(CN) phase. For randomly oriented material one finds the intensity of the (222) reflection to be less than that of the (311) reflection. These normal relative intensities are reversed in the patterns of positions IV and V. This is probably an orientation effect that

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becomes more pronounced as the surface film gets thinner and its coherency relationship to the orientation of the underlying original gamma uranium grains becomes important. The previously observed shift in the lattice parameter was not confirmed.

It is worth noting that the presence of the thin U(CN) surface film had an effect on the oxidation resistance of uranium; it retarded greatly the oxidation of the metal on storage in air.

4. Preparation of Alpha Uranium Single Crystals for Elastic Constants Studies (E. S. Fisher, L. T. Lloyd)

The development of techniques for preparing flat and parallel crystallographic faces that would be suitable for high frequency ultrasonic measurements of elastic constants of alpha uranium single crystals has been completed during this quarter. The grinding and lapping procedures were partially described in ANL-5643. The final stages of specimen preparation consist of alternately lapping and electropolishing as follows: after the surfaces are made parallel to each other and to a predetermined crystal plane by lapping with 14 micron diamond paste, the strained surface layer is completely removed by electropolishing in phosphoric acid electrolyte for approximately 1-1/2 hours. The convex surface, thus produced, is made flat again by lapping with 3 micron diamond paste. The resultant strained surface layer is removed by electropolishing for approximately 20 minutes. This slightly convex surface is finally lapped with 1 micron diamond paste until interference fringes, observed by optical flats, are straight and equally spaced.

Because electropolishing to remove a strained surface layer diminishes the previous surface flatness, it would be advantageous, if possible, to dispense with this operation after the final lapping step. Back-reflection Laue patterns from 1 micron lapped surfaces indicate that the strained layer may be sufficiently thin so as not to interfere with ultrasonic wave velocity measurements. X-ray patterns, using Cu target radiation, from 14 micron and 3 micron lapped surfaces, showed only the Debye-Scherrer rings due to diffraction of Cu K_{α} by the crystallites in the surface layer; however, the patterns from the 1 micron lapped surfaces contain both the crystallite diffraction and the Laue pattern from the underlying crystal. The intensity of the Laue spots is estimated to be 1/4 the intensity of the incident beam; from this it is calculated that the strained surface layer thickness is approximately 1 micron. Initial attempts at wave velocity measurements will be made on the final lapped surface.

Three uranium single crystal specimens are being prepared by these techniques for measurements in the [100], [010], and [001] directions. The two specimens for measurements in the [100] and [001] directions have

rectangular flat surfaces of approximately 4 by 6 mm perpendicular to the measuring direction; they are close to 3 mm in thickness. The specimen surfaces perpendicular to the [010] direction are elliptical in shape with 4 and 6 mm minor and major axes; the specimen thickness is approximately 4 mm.

For elastic constants measurements, attempts will be made to determine the resonance frequencies of pure longitudinal and shear modes of vibrations with propagation directions along the three principal axes*. It is hoped that the specimen dimensions will be satisfactory for propagation of undistorted wave fronts using vibrational frequencies in the range of 50 to 75 megacycles. Assuming the resonance frequencies can be measured, the velocities of the wave can be evaluated from the specimen thickness and the number of wave lengths in the wave path (the harmonic number of the resonant waves).

The relationship between the wave velocities and the elastic constants is expressed by the equation:⁽⁴⁾

$$V = \sqrt{\frac{q}{d}}$$

where V = wave velocity, q = stiffness factor, and d = density.

The stiffness factor, which is calculated from measured values of V and d , is some function of the nine fundamental elastic stiffness constants of the alpha uranium crystal.** The complexity of this function depends on

*In longitudinal waves the atoms vibrate in the direction of propagation; for shear waves the atoms vibrate normal to the propagation direction.

(4) Cady, Walter, Piezoelectricity, McGraw Hill Book Co., Inc., New York, 1946, page 55.

** The stiffness constants are the coefficients of the strains in the generalized form of Hooke's law which for orthorhombic crystals can be expressed, using matrix subscripts, as:

$$S_{xx} = C_{11}s_{xx} + C_{12}s_{yy} + C_{13}s_{zz}$$

$$S_{yy} = C_{12}s_{xx} + C_{22}s_{yy} + C_{23}s_{zz}$$

$$S_{zz} = C_{13}s_{xx} + C_{23}s_{yy} + C_{33}s_{zz}$$

$$S_{yz} = 0 + 0 + 0 + C_{44}s_{yz}$$

$$S_{xz} = 0 + 0 + 0 + 0 + C_{55}s_{xz}$$

$$S_{xy} = 0 + 0 + 0 + 0 + 0 + C_{66}s_{xy}$$

where: S_{xx} is a component of force in the x direction acting in the x direction, etc.

S_{yz} is a component of force in the y direction acting in the z direction, etc.

s_{xx} , s_{yy} , s_{zz} are extentional components of strain, and

s_{yz} , s_{xz} , s_{xy} are shearing strains.

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the orientation of wave front direction and vibration directions contributing to the propagated wave front. When longitudinal or shear waves are separately propagated in the principal crystal directions, it can be shown from elastic theory that the stiffness factors involve only one of the fundamental constants. For longitudinal wave propagation along the [100], [010] and [001] axes, $q = C_{11}$, C_{22} , and C_{33} , respectively. For shear waves propagated in the [100] direction with vibration direction along the [010] axis, $q = C_{66}$; for vibration direction along the [001] axis, $q = C_{55}$. Similarly, measurements of C_{44} and cross checks of C_{44} , C_{55} , and C_{66} are obtained from properly oriented shear waves propagated along the [010] and [001] axes, respectively.

The cross constants C_{12} , C_{13} , and C_{23} cannot be evaluated using the simply oriented flat surfaces since they are not contained in the stiffness factors governing the velocity of longitudinal or shear waves. It will be necessary then to prepare three other specimens with differently oriented flat surfaces. These orientations will be specifically chosen* so that the q factors for wave fronts parallel to these surfaces will be simple functions involving the previously determined constants and the individual cross constants.

5. Uranium-Fissium Alloys (A. E. Dwight)

The features of the binary uranium-ruthenium phase diagram that have been determined during the past quarter are shown in Figure 10. It was found that an alloy containing 5 w/o Ru could be quenched from 900°C to retain the body centered cubic gamma phase with a lattice parameter of 3.46 Å, indicating that ruthenium as a solute is nearly as effective as molybdenum in contracting the lattice parameter of gamma uranium. The crystal structure of U_2Ru (18 w/o Ru) is under investigation.

The lattice parameter of gamma uranium-molybdenum alloys as a function of molybdenum content is being determined.

Eleven ternary uranium-molybdenum-ruthenium alloys have been prepared and examined after heat treatment at 900°C and an extensive single phase gamma field has been found.

*The equations of Christoffel used for obtaining q in terms of the elastic constants when direction cosines are known are discussed in Reference 4, p. 104.

6. Sintering of Ceramic Materials (L. L. Abernethy, G. C. Kuczynski*)

Sintering studies have been made of Al_2O_3 in the temperature range of $1700^\circ\text{--}1900^\circ\text{C}$. Thirty-mil Linde synthetic sapphire spheres (alpha corundum), ground from very pure single crystals, were used in these experiments. During heating in H_2 or He atmospheres, in tungsten or molybdenum heaters, the sapphire spheres underwent considerable change in shape, beginning with the appearance on each bead of a six-pointed star which developed into three great circles (Figure 11), and after longer times the spheres approached the shape of an hexagonal bipyramid, with two basal planes (Figure 12). These observations are significant in interpreting the laws of sintering inasmuch as the growth of the neck in these cases takes place between two planes inclined at a constant angle to each other. The general equation $X^n \sim t$, where X is the diameter of the neck between two particles, still holds, but the numerical values of the exponent n

*University of Notre Dame; consultant to ANL Metallurgy Division

Figure 11. Thirty-Mil Synthetic Sapphire Spheres After Heating for One Hour at 1785°C in Molybdenum Heater and Helium Atmosphere.

Micro 20959

140-X

Figure 12. Thirty-Mil Synthetic Sapphire Spheres After Heating for One Hour at 1800°C in Tungsten Heater and H_2 Atmosphere.

Macro 21621

45-X

03712281030

corresponding to various transport mechanisms would be different than those for materials where no changes in shape take place:

- n = 1 Viscous flow
- n = 2 Evaporation and condensation
- n = 3 Volume diffusion
- n = 4 Surface diffusion

An attempt has been made to determine this exponent n experimentally, by heating single rows of sapphire spheres at 1810°, 1860°, 1910°, and 1960°C and subsequently measuring the interface diameters between adjacent particles. (No appreciable sintering was observed below 1810°C.) The obtained results appear to be somewhat erratic. The most frequently observed exponent was $n = 2$, which would indicate that the transport mechanism is through the vapor phase. In all these cases the hexagonal axis of at least one of the sintered particles was perpendicular, or nearly so, to the interface. In two cases, when the hexagonal axes were parallel to the interfaces, n was found to be close to 5, suggesting that volume diffusion may be operative; in this case the vicinity of the neck is spherical. The mechanism of sintering of highly anisotropic crystals obviously involves the development of crystal faces as well as the growth of "necks" or interfaces.

A study is now being made of the rate of growth of these faces on isolated spheres and cylindrical rods of Al_2O_3 . A knowledge of the rate for the development of the crystalline faces will facilitate a more quantitative evaluation of the sintering mechanism.

7. Corrosion Mechanisms of Zirconium (R. D. Misch, F. H. Gunzel)

a. Changes in Corrosion Produced by Vacuum Heating

Introduction. Previous work has established that the corrosion oxide film has low electrical conductivity at room temperature and at 400°C. The conductivity is sufficiently low to be a controlling factor in the corrosion process. The conductivity is dependent on the history of the film and increases with time of heating in vacuum. This latter effect was studied to determine whether the corrosion rate is affected by this change in the film. The procedure and results are described below.

Experimental. Eight specimens of zirconium and eight of Zircaloy-2 were prepared by machining and etching in HF-HNO_3 solution. The specimens were then arranged in pairs and corrosion tested in water

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at 350°C. The specimens were removed and weighed after 16-hour test periods. Two sets of specimens were heated in vacuum (10^{-5} mm Hg or better) for 1 minute at 600°C before testing and during each interval out of test. The procedure, which applied both to zirconium and Zircaloy-2, is summarized in Table VII.

TABLE VII

Description of Experimental Procedure

Specimen Numbers	Treatment
7, 8	These were vacuum heated prior to testing and also each time after weighing the specimens (up to 320 hours).
5, 6	These were tested in the same autoclave as Nos. 7 and 8 but were never vacuum heated.
3, 4	These were vacuum heated with Nos. 7 and 8 but not corrosion tested until vacuum heating was discontinued.
1, 2	These were corrosion tested in the same autoclave as Nos. 3 and 4 and were never vacuum heated.

Specimens 3 and 4 were not put into test until the vacuum heating was discontinued while Nos. 5, 6, 7, 8 were continued in test. Consequently the test time was longer on the latter specimens. Specimens 7 and 8 were weighed before and after heating, and slight weight changes of 0 to 5 micrograms/cm² were found. These were negligible in comparison with the weight gains which were of the order of milligrams/cm².

Results. The data are shown in Figures 13, 14 and 15 for zirconium and Figures 16, 17 and 18 for Zircaloy-2. Figures 13 and 16 represent the effect of vacuum heating which was carried out up to and including 320 hours and then stopped. Figures 14, 15, 17 and 18 show the controls. The effects of vacuum heating are evident from comparison of these data.

Discussion. Vacuum heating had two effects. The weight gain was lower initially and then higher than the controls. The lower initial weight gain can be attributed to the vacuum heating which preceded corrosion testing. The difference is between an as-etched surface and a surface where the very thin oxide has been dissolved by subsequent vacuum heating.

037028.000

Figure 13. Weight gains of four specimens of arc-melted zirconium, corrosion tested simultaneously in water at 350°C . Nos. 7 and 8 were heated at 600°C for 1 min. at the time of each weighing up to and including 320 hrs. (also prior to testing). Heating was discontinued after this point. Specimen Nos. 5 and 6 were not heated.

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Figure 14. Weight gains on arc-melted zirconium specimens No. 1 and No. 2, Corrosion tested simultaneously with Nos. 3 and 4 in water at 350°C .

Figure 15. Weight gains on arc-melted zirconium, specimens No. 3 and No. 4, heated simultaneously with Nos. 7 and 8, but corrosion tested only after the vacuum heating had ended.

Figure 10. Weight gains of four Zircaloy-2 specimens, corrosion tested simultaneously in water at 350°C . Nos. 7 and 8 were heated at 600°C for 1 min. at the time of each weighing up to and including 320 hrs. (also prior to testing). Heating was discontinued after this point. Specimen Nos. 5 and 6 were not heated.

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Figure 17. Weight gains on Zircaloy-2 specimens No. 1 and 2, Corrosion tested simultaneously with Nos. 3 and 4 in Water at 350°C.

Figure 18. Weight gains on Zircaloy-2, specimens No. 3 and 4, Heated simultaneously with Nos. 7 and 8, but corrosion tested only after the vacuum heating had ended.

037128.030

A lower corrosion rate was not noted when vacuum heating was started after a 16-hour corrosion film was already on the surface. With continued vacuum heating the corrosion rate increases and the heated curve intersects the control curve. After terminating vacuum heating (320 hours) the weight gain curve leveled off. The heated specimens (7, 8) of both zirconium and Zircaloy-2 were turning white at the end of the test. The curve for Zircaloy-2 showed evidence of flaking (weight loss) while the zirconium curves did not.

The controls indicate that the vacuum heating must act on the oxide film since any metallurgical effects should also show up on specimens 3 and 4. In both zirconium and Zircaloy-2 the preliminary vacuum heating given to specimens 3 and 4 did not produce as low a plateau as showed up on specimens 7 and 8. This suggests that several vacuum heatings with the corrosion film on the surface may be optimum to produce a low weight gain.

In comparing the two metals, the effect of vacuum heating was more pronounced in Zircaloy-2. Both metals showed a diminution of corrosion rate after vacuum heating was ended. It is concluded that the heating effect is temporary and gradually disappears in the autoclave. This can be explained by assuming that the concentration gradient in the oxide is changed by vacuum heating and then restored in the autoclave.

As already mentioned, the factor of film dissolution must be considered in evaluating these data. In a previous report dissolution of the oxide on zirconium was found to increase rapidly with temperature. At 600°C the rate was 100 Å/minute. After heating 20 times the film should have decreased in thickness by 2000 Å. This corresponds to approximately 3 mg/dm² of oxygen which would enter the metal during heating. This quantity is negligible in comparison with the other changes in weight.

When vacuum heating is applied to an as-etched specimen, the thin oxide film (40 to 60 Å in thickness) should be dissolved. A new film can then form when air is admitted to the vacuum chamber. The new film must be less permeable than the old although no compositional change would be expected. Possibly the oxide grains which form in this case are of a different type. With thicker films the tendency is always to produce a more permeable oxide. It is unlikely that any sintering of the oxide film can take place at 600°C. The effect on corrosion is attributed to additional defects in the oxide film as indicated by the conductivity increase. Such defects are created more easily in Zircaloy-2 than in zirconium as shown by the corrosion curves.

It is believed that a resistant alloy should have an oxide in which the conductivity change upon heating is very slow. This would

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indicate that the oxide had a very stable defect structure. If this viewpoint is correct, then vacuum heating could be used to evaluate new alloys for corrosion resistance.

b. Electrical Resistance of the Oxide Film

In connection with the film resistance program the alloy system zirconium-titanium is being studied. Alloys have been made to the following compositions: 0.01, 0.05, 0.1, 0.5, 1.0 and 50.0 w/o Ti. The 0.5 and 1.0 w/o alloys have very high corrosion rates and cannot be measured conveniently at 350°C. It is necessary to lower the test temperature to 250°C to produce a conveniently measurable corrosion rate. If possible, a dark coherent oxide will be produced on all of the alloy combinations to permit film resistivity to be measured.

The measurement of film resistance at room temperature has brought to light a number of different problems. These are partly a function of the very high resistance, 10^8 to 10^{11} ohms, and other factors involving the evaporated metal spot and the probe. The major difficulties caused by the high resistance are the time for the circuit to reach a stable value and the sensitivity to A.C. pickup.

At the present time contact is being made by evaporated aluminum which adheres well to the oxide surface; evaporated gold does not. Erratic results were obtained with gold and were attributed to peeling of the film. The aluminum film is less easily damaged.

The probe design has been changed to allow a double contact with the spot as well as to incorporate a thermocouple. By this means the contact of the platinum wire with the aluminum surface is checked and temperature is measured with minimum handling of the specimen.

It is believed desirable to evaporate aluminum as soon as possible after removing specimens from the autoclave. Contact is made by grinding the reverse side of the specimen which then rests on a conducting support. This subjects the film to as little mechanical strain as possible, as would be caused, for example, by a clamp. Figure 19 illustrates the latest arrangement for measurement. Shielding will be provided in the future by the metal vacuum system and the wire cage of a bell jar. The contact wire is the only one that must be shielded. The thermocouple is as close to the contact wire as possible.

c. Zirconium Alloys

Studies of corrosion resistance are being made on zirconium alloys containing additives which form +3 cations of favorable size for substitutional solution in ZrO_2 . The reason for this study is that the

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Figure 19. Schematic of the method of contacting the evaporated aluminum spot on a corrosion specimen.

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additives iron, chromium and nickel in Zircaloy-2 should influence the stoichiometry of ZrO_2 by reason of their cation valencies below +4. However, the role of these additives may be twofold in the light of the theory of hydrogen damage to the film. According to this view, iron, chromium and nickel can catalyze the evolution of cathodic hydrogen at sites away from the metal-oxide interface. These elements are present in Zircaloy-2 in excess of their solid solubility in zirconium. The theory of hydrogen damage has explained many aspects of aluminum corrosion in high temperature water.

To avoid this complexity one may employ elements also producing cation of valency less than 4 but which do not form cathodic phases. In the present study the elements of particular interest are scandium and yttrium. These elements have favorable ionic radii for substitution in the ZrO_2 lattice.

Thus far, zirconium alloys have been made containing scandium and yttrium, both alone and in combination with other elements. The use of other elements is important since there is very little data on the interaction of additives in the ZrO_2 film. It is felt that binary systems should not be the sole criterion of the desirability of an alloying element.

Evidence for the above view has been found in this investigation for both scandium and yttrium. Each of these elements has been combined in various mol ratios with other elements to make alloys containing 1 w/o of additive. The large majority of these alloys exhibited lower corrosion resistance than the parent zirconium crystal bar. No alloy was significantly better than pure zirconium. Alloys with comparable corrosion resistance require a long time for evaluation in 300°C water and some of these tests are still under way. Steam tests at 400°C are also being carried out on a limited number of specimens. Controls are being made up for the more interesting ternary combinations. These consist of zirconium alloys containing an equivalent percent of only one of the ternary additives. A compilation will be presented when the necessary comparisons have been made.

8. Corrosion Mechanism of Aluminum at Elevated Temperatures (W. E. Ruther)

Very little data exist concerning the pH of partially ionized acids at elevated temperatures. Work on corrosion mechanism has been hampered by the inability to evaluate the relative effects of pH and the corresponding anion for the various acids. Experiments have therefore been started to alleviate this difficulty. An autoclave has been modified to permit one insulated electrical connection and a method of introducing

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hydrogen gas at elevated temperatures. The equipment was similar to that described by Choudbury (Master's thesis, Columbia 1952) for his attempt to measure the platinum (H_2) half-cell vs. a silver-silver chloride electrode.

Attempts to duplicate his measurements have resulted in the reduction of silver ion by the hydrogen gas at the platinized platinum. This effect was also noted with silver iodide (much less soluble than silver chloride). This deposition ruins the platinum as a hydrogen electrode.

Another experiment is scheduled using separate chambers for the two electrodes connected by a very fine capillary tube.

9. Solution Potentials of Aluminum in Dilute Aqueous Solutions (F. E. DeBoer)

Preliminary to studying the detailed polarization behavior of aluminum, a program has been under way to measure the steady state potential and the polarizing characteristics of a number of metals in boiling distilled water. To date an experimental survey has been made of the following metals: aluminum, gold, graphite, cadmium, nickel, iron, germanium, magnesium, antimony, titanium, uranium, zirconium, U-7% Ti, U-3% Ni, U-5% Zr-1.5% Nb. It now appears that the steady state potentials and the changes in potential due to the passage of anodic currents to the samples have been satisfactorily measured. However, there is considerable doubt concerning the reliability of the cathodic polarization curves. Small leakage currents in the measuring circuit are suspected to have been causing errors. When this difficulty has been overcome, the data will be reported in detail.

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V. ALLOY THEORY AND THE NATURE OF SOLIDS - ACTIVITY 5420

1. Intermediate Phases in Transition Metal Systems (M. W. Nevitt)

Progress in the study of the Cr_3O type structure can be summarized as follows:

1. Three new Cr_3O phases having nominal compositions Nb_3Sb , Ta_3Sb , and Nb_3Ge have been found. The occurrence of these A_3B phases and the values of their lattice parameters are in conformity with the qualitative atomic size relations cited in the last progress report.
2. A set of linear empirical equations has been derived by means of which the lattice parameters of all known Cr_3O phases can be expressed in terms of the Goldschmidt radius of the B element. The theoretical significance of this relation is being studied.
3. The structure found for the nominal composition Cr_3Bi , which was tentatively described in the last progress report as a tetragonal modification of the Cr_3O structure, has also been found in alloys whose nominal compositions are V_3Bi , Nb_3Bi , W_3Bi . An analysis of this structure is under way.

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

The search for equiatomic alloys of transition elements having the CsCl structure has been continued. Systems in which the CsCl structure was found are: VRu, VOs, and ZrOs, and possibly ZrPt and VPt. Systems in which the CsCl structure was not found are: TiPd, ZrMn, ZrRe, ZrFe, ZrPd, HfMn, HfRe, VMn, VFe, VCo, VIr, NbMn, NbRe, NbRu, NbOs, NbRh, NbIr, NbPd, and NbPt.

It was noted that four equiatomic alloys, ZrRh, ZrIr, HfRh and HfIr, gave very similar diffraction patterns, whose structure is as yet unknown.

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VI. EFFECTS OF IRRADIATION ON MATERIALS - ACTIVITY 5430

1. Neutron Flux Distribution and Wilkins Effect in Irradiation Specimens
(F. R. Taraba, S. H. Paine)

The experimental work on the distribution of thermal neutrons within enriched fuel specimens during irradiation has been nearly completed. Radial and longitudinal distributions of neutron densities within uranium fuel specimens of various diameters and enrichments have been obtained. Magnesium-cadmium alloys were used to duplicate the macroscopic absorption cross sections of the various enriched fuel materials considered. Theoretical calculations of the radial distribution of neutrons within heavily absorbing rods have also been made using various transport theory approximations and were found to agree reasonably well with the experimentally determined radial distributions. Figures 20 and 21 show the theoretically determined radial distributions of neutrons within a 0.25 and 0.353" diameter fuel specimen containing 0.71, 5, 10, and 20 w/o U^{235} (balance U^{238}). Experimental data points are also shown in the figures. Figures 22 and 23 give the ratios of the average to surface and axial to surface neutron density for uranium fuel specimens of various diameters and enrichments. Figure 24 gives the ratios of the average to surface neutron density for rods of various macroscopic absorption cross sections and diameters.

An exact mathematical solution to the problem of finding the perturbed neutron distribution in the region of the spacer separating two fuel specimens is very difficult to obtain. However, an approximate solution has been obtained and is still in the process of being programmed for machine computation. Calculations of the Wilkins Effect in enriched fuel materials have also been made and are in reasonably good agreement with observed results. Table VIII shows the experimentally observed Wilkins Effects for fuel specimens of 5 and 20 w/o U^{235} .

The experimental data are at present being analyzed to determine a satisfactory expression for the longitudinal distribution of neutrons in the above-mentioned fuel specimens.

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Figure 20. RADIAL DISTRIBUTION OF NEUTRON DENSITY
WITHIN A .250 INCH DIAMETER URANIUM
ROD OF VARIOUS U²³⁵ ENRICHMENTS

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Figure 21. RADIAL DISTRIBUTION OF NEUTRON DENSITY
WITHIN A .353 INCH DIAMETER URANIUM
ROD OF VARIOUS U²³⁵ ENRICHMENTS

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Figure 24. Ratio of Average To Surface Neutron Flux Versus Macroscopic Absorption Cross Section For Various Diameter Rods

TABLE VIII

Wilkins Effects in Enriched Fuel Specimens

Diameter of Rod (inches)	Enrichment (w/o U^{235})	Graphite Spacer (inches)	Wilkins Effect
0.250	5	0.05	1.13
		very large	1.25
	20	0.05	1.50
		very large	2.10
0.353	5	0.05	1.15
		0.10	1.29
		very large	1.50
	20	0.05	1.60
		0.10	2.02
		0.20	2.50
		very large	2.88

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