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METALLURGY AND CERAMICS

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Metallurgy and Ceramics

ARGONNE NATIONAL LABORATORY

P. O. Box 299

Lemont, Illinois

QUARTERLY REPORT
OCTOBER, NOVEMBER, AND DECEMBER, 1955

METALLURGY DIVISION

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June, 1956

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QUARTERLY REPORT
OCTOBER, NOVEMBER, AND DECEMBER, 1955
METALLURGY DIVISION

ABSTRACT

Advanced Water Reactor Program - Activity 4102

A total of nine clad plates, containing uranium-5 w/o zirconium-1.5 w/o niobium alloy cores and clad with Zircaloy-II, were rolled in plain carbon steel jackets, heat treated, physically evaluated, and corrosion tested. All these plates were found to be within predetermined dimensional tolerances in width, thickness, length, cladding thickness, and core distribution. Improved control of welding variables and of the length of the seal pin projecting above the end plugs resulted in the elimination of frequently observed segmented inclusions at the seal pin interfaces.

The strength of the clad-to-core bonds was found to decrease from about 80,800 psi in the as rolled condition to about 43,800 after heat treatment for dimensional stability, which consisted of heating for one-half to one hour in carbonate salt at 800° C, quenching into a carbonate salt at 640° C and holding for 24 hours, followed by air-cooling. Heating to 800° C in air and isothermally quenching in lead at 640° C showed no such bond weakening. Investigation of this effect indicated that hydrogen absorbed from the carbonate salt in amounts up to 15 ppm may have been the cause of the bond weakening.

Pickling of single plates for 10 minutes in a 35% nitric-5% hydrofluoric acid solution at 40° C generally resulted in a uniform removal of 0.005 " from all surfaces. Pickling of five plates simultaneously raised the bath temperature to 60° C with the result that most of the cladding was removed from several plates. Adequate control of the acid concentration and bath temperature will be required to insure against failures of this type.

Irradiations of specimens cut from EBWR reference alloy plates clad with various thicknesses of Zircaloy-II and quenched from 850° C indicated that the cladding can exert considerable restraint on the growth of the core material. After 0.12% uranium atom burnup, unclad specimens grew at a rate of 80 microinches/inch/ppm burnup; specimens with 0.020" cladding grew at a rate of only 16 microinches/inch/ppm burnup; specimens with 0.060" cladding showed practically no growth. It was also found that flat-rolled gamma quenched specimens of the ternary unclad reference alloy grew in length at only one-third to one-half the rate of similar round-rolled or swaged material; sidewise growth rates of the plates were 40% greater than length-wise growth rates.

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In the melting and casting of the reference core alloy for EBWR plates the most important changes occurred in mold design. The three-cavity and slab molds were discarded in favor of multicavity molds, with each cavity producing one core. One such ten-cavity mold yielded over 130 cores before failing. The molds are made of wedge-shaped graphite segments held together by top and bottom graphite rings. The mold wash was changed from magnesium zirconate only to magnesium zirconate followed by thoria; the latter increased the soundness of the castings and the stability of the wash. Using these molds the foundry can now consistently produce sound castings by alloying at 1550°C, allowing the metal to cool to 1300°C (nearly to the freezing point) in the graphite crucible, and then reheating to 1500°C and pouring.

All the facilities for the manufacture of the EBWR fuel plates have been installed and tested. Approximately 14,000 pounds of Zircaloy-II were forged from fifteen 12" diameter cast ingots to slabs approximately 3" x 9" x 12 feet. Sheet and plate stock for cladding components has been rolled from 2400 pounds of the forged slabs. Protective steel jackets for 888 cladding billets are being machined from SAE-1020 hot rolled carbon steel bars.

A total of 394 castings of the ternary reference alloy have been inspected by the ultrasonic transmission method. These results, coupled with destructive tests, led to the establishment of a standard nondestructive testing technique for acceptable castings.

An ultrasonic scanner for testing the EBWR fuel plates has been designed and built; the scanner can be used on both flat and round fuel elements.

Design changes in the EBWR subassembly required revision of the semiautomatic tungsten inert gas spot welding device designed to permit dry-box welding of the subassembly. The revisions have been made and exploratory work to establish a production procedure is now in progress.

Fast Power Breeder Reactor Program - Activity 4104

An alloy of nominal composition uranium-21 w/o plutonium-5 w/o molybdenum was found to be unworkable by rolling; preheating to 800°C or using heated rolls met with no success. Pin specimens of the above composition, 1/8" in diameter by 1-1/2" long, were successfully cast by melting in a thoria crucible and pouring into a four-cavity graphite mold. The pins are to be used as irradiation specimens to develop a plutonium-containing fuel element for EBR-II.

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General Reactor Development - Activities 4530 and 4540

Irradiations in the MTR of pressed and sintered uranium alloy specimens to about 0.40% uranium atom burnup yielded the following results:

(a) unalloyed uranium, which was end-pressed, shortened at a rate of about 25 microinches/inch/ppm burnup; (b) uranium-1.6 w/o niobium alloys and uranium-1 w/o molybdenum alloys showed small elongations, 2 to 3%; (c) an uranium-0.46 w/o silicon alloy elongated appreciably, about 22%.

An U-5w/o Zr-1.5 w/o Nb alloy sample, irradiated under restraint to a burnup of 0.19 a/o, was completely reduced to slurry in a 56-hour corrosion test in distilled water at 265°C; the preirradiation corrosion rate was 9.5 mcd at 290°C. It appears certain that radiation produces a change, perhaps similar to overaging, which reduces the corrosion resistance of this alloy independently of effects that might be attributed to surface dimensional changes.

Uranium-3.8 w/o silicon samples coextruded with Zircaloy-II cladding showed good corrosion resistance in 290°C water; the specimens were epsilonized prior to extrusion. An additional epsilonizing treatment of one week at 825°C following extrusion had no effect on the corrosion resistance of the core but did sensitize the bond line.

An uranium-3.8 w/o silicon casting, epsilonized 2-3/4 days at 800°C, fully retained its corrosion resistance in 290°C water after irradiation to 0.12 a/o burnup. Its postirradiation corrosion rate in an 86-hour test at 290°C was 0.72 mcd, as compared with 2.82 mcd prior to irradiation; the reason for the improved postirradiation corrosion resistance is not clear.

Thoria-2.5 w/o urania specimens, with or without jackets, exhibited no changes in appearance and no dimensional changes after irradiations of 0.95% total metal atom burnups in the MTR. Pellets of thoria-10 w/o UO₂, lead bonded in Al-1 w/o Ni capsules, were found to be fragmented after irradiation to a 3.16% calculated depletion of uranium atoms in a CP-5 water loop at 260° - 275°C and 760 - 810 psi.

2S aluminum containing 0.5 and 0.9 w/o nickel yielded corrosion rates of about 3.4 mg/dm²/day in distilled water at 290°C; at 150°C the corrosion rate is 0.53 mg/dm²/day (0.26 mil per year penetration). Variations in pH from 3.5 to 9 raised the corrosion rates from 2.0 mg/dm²/day to only 3.7 mg/dm²/day in 290°C water; the effect of the pH value is not nearly so great as that obtained in 2S aluminum at lower temperatures. Corrosion rates of an experimental Alcoa high strength alloy (X2219; 6.2 w/o Cu, 0.32 w/o Mn, 0.16 w/o Zr, 0.14 w/o Fe, 0.11 w/o Si) were roughly comparable to the 2S aluminum-nickel alloys. Silica additions to the solutions in concentrations of 20 to about 50 ppm were found to be detrimental.

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Aluminum-nickel test plates containing 0.5, 1, and 2 w/o nickel, corrosion tested in the MTR loop in water for 850 hours at 205° - 260° C plus 400 hours below 150° C, displayed deep, elongated, transversely oriented pits, whereas similar specimens in out-of-pile corrosion tests were characterized by shallow, large, nondirectional pits. The irradiated specimens received an estimated maximum thermal flux of 1×10^{21} nvt, and a maximum fast flux of 5×10^{19} nvt. The degree of attack appeared greater on the out-of-pile specimens.

Production, Treatment, and Properties of Materials - Activity 5410

The improved heat treatment schedule described in the previous Quarterly Report (ANL-5489) was only moderately successful in producing single crystals of suitable size for elastic constants measurements. The process yielded crystals of 0.20 to 0.22" in diameter. To obtain the required 1 cm (0.40") diameter crystals will require further adjustments in the heat treatments. In view of the difficulties encountered, the possibility is presently being studied of obtaining the elastic constants on the crystal sizes presently available using higher frequencies (of the order of 50 megacycles). The success of this method depends critically on the ability to prepare flat and parallel surfaces free from imperfections. Specimens are being prepared to try out this approach on high frequency equipment available at another laboratory.

The composition range in the uranium-zirconium-niobium ternary system has been delineated in which metastable gamma can be retained by quenching from about 900° C. Lattice parameter measurements of the retained metastable gamma indicate that increased niobium contents contract the lattice, whereas increased zirconium contents expand it. Electrical resistivity measurements of subcritically transformed ternary alloys containing a constant 2 w/o Nb indicate that at 620° C approximately 80% of the gamma has transformed, and that below 620° C only slight additional transformation occurs.

All the spots on the reciprocal lattice of precession photographs from a single crystal of delta cut from a cast piece of a 41 w/o U-Zr alloy have been indexed according to the large body centered cubic cell reported earlier ($a_0 = 10.68$ Å). Laue patterns from large grains of the same alloy composition obtained by quenching from 1000° C contain very sharp spots which can be indexed according to the small gamma body centered cubic phase (a_0 approximately 3.56 Å) and a few very diffuse spots; the number and sharpness of the diffuse spots can be increased by annealing at temperatures around 200° C. The diffuse spots can be indexed as belonging to the delta phase.

The solid solubility of carbon in gamma uranium at the gamma to beta transformation temperature has been tentatively placed at about 65 ppm

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or 0.038 atom percent; an alloy containing 205 ppm carbon consisted of two phases up to 1100°C, hence the maximum solubility near the solidus temperature is below this value.

For self-diffusion studies in alpha uranium, a small quantity of highly depleted uranium (0.0334% U^{235}) has been obtained from Oak Ridge. Unfortunately, this material contains a large amount of contaminating elements (5000 ppm Fe, 200 ppm Cr, 90 ppm Ni, and 100 ppm Si) and efforts are under way to adapt the electrolytic refining technique to purify this material. The high depletion is necessary in view of the anticipated low diffusion rates in the alpha phase (maximum 660°C). In view of the scarcity and limited availability of this material, the refining experiments are being carried out on mock-up natural uranium samples. The anticipated small magnitudes of diffusion and the radioactivity of the base (depleted) uranium make the sectioning and the subsequent analysis more exacting tasks than are usually encountered in diffusion experiments. The approach currently under study calls for the use of a precision grinder (available at the Institute for the Study of Metals), dissolving the uranium from the grinding paper with HCl, analyzing for total uranium by the thiocyanate method, and analyzing for U^{235} by irradiating an aliquot of the sample and counting the ruthenium fission product.

Extruded and rolled compacts of 2S aluminum with 1 w/o, respectively, of iron, nickel, copper, graphite, and stainless steel, were corrosion tested for two days in distilled water at 290°C to note if the cathodic phases in dispersed form might not protect the aluminum against blistering attack more effectively than compound phases formed on alloying. The test, however, was inconclusive in that the blisters that formed appeared to be associated with the porosity of the compacts, rather than with the relative protective effects of the metal additives. Cathodic polarization measurements, however, indicated that good quality compacts would be more resistant to blistering attack than corresponding alloys with aluminum.

Film capacity measurements on 2S aluminum corroded in 50°C distilled water indicated considerable variations at different positions of a specimen after short exposures, but after longer exposures of 7 days, the capacitance was essentially constant for any given frequency, indicating that an equilibrium thickness has been reached. This correlates well with corrosion rate measurements, indicating a linear corrosion rate after about one week's exposure under similar conditions.

Anodizing measurement of aluminum containing about 0.15 w/o respectively, of copper, zirconium, silicon, titanium, chromium, and manganese, in 1% ammonium borate indicated that the aluminum-manganese alloy had the lowest anodizing efficiency. The corrosion rates of an aluminum alloy containing 0.5 w/o Ni and 0.3 w/o Fe with 0.15 w/o Mn added are presently under investigation.

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Alloy Theory and the Nature of Solids - Activity 5420-01

Neutron diffraction studies have corroborated the lack of Bragg reflections in a titanium-zirconium alloy containing 62 a/o Ti and 38 a/o Zr for which the calculated structure factor is zero; this results, of course, from the fact that the nuclei of these elements scatter thermal neutrons in opposite phases. Such an alloy would be useful in any device in which coherent scattering of thermal neutrons is not desired, as for example, in specimen holders for neutron diffraction studies, radiation shields for low temperature, and high temperature work with thermal neutrons, etc.

Effects of Irradiation on Materials - Activity 5430-01

The radial and longitudinal distributions of thermal neutron flux within 1.00" and 0.50" diameter uranium rods, each separated into two lengths by a graphite spacer, 0.300" and 0.100", respectively, has been measured for the regions adjacent to the spacers and in regions unaffected by the spacer. The results are summarized in graphical form in the text; a quartic equation has been found to fit the experimentally determined distributions very accurately.

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I. ADVANCED WATER REACTOR PROGRAM - ACTIVITY 4102

1. Fabrication and Evaluation of Uranium Alloy Fuel Plates

- a. Roll Clad, Modified Picture Frame Plates with Uranium-5 w/o Zirconium-1.5 w/o Niobium Alloy Cores (C. H. Bean, J. R. Lindgren, R. E. Macherey)

A total of nine integrally clad plates, Nos. 218 to 226 inclusive, with EBWR reference alloy cores and clad with Zircaloy-II, were rolled in plain carbon steel jackets, heat treated, physically evaluated, and corrosion tested. All plates were within predetermined dimensional tolerances in width, thickness, length, cladding thickness, and core distribution.

Metallographic examination of the Zircaloy-II components and of the seal pin interfaces with the end plug on rolled plate end-sections frequently showed segmented inclusions; the defects resulted from inadequate welding of the seal pin to the end plug. An investigation showed that the variables which affected the weld quality were electrode potential, length of seal pin projecting above the end plug, preheat time, amperage at which the arc was started, amperage during welding, and the time the arc was maintained. The investigation resulted in an improved procedure for making reproducible sound welds.

Examination of previously rolled and heat treated clad plates showed that the strength of the clad-to-core bonds decreased from an average of 80,800 psi in the as rolled condition to an average of 43,820 psi after heat treatment for dimensional stability. The treatment consisted of heating plates 1/2 hour to 1 hour in carbonate salt at 800° C, isothermally quenching in carbonate salt at 640° C, holding 24 hours at 640° C, and air-cooling. In heat treating tests undertaken to improve the bond strength, it was noted that the as rolled bond strength was practically unaffected when the plates were heated to 800° C in air followed by an isothermal quench in lead at 640° C. Further investigation has indicated that hydrogen absorbed from the carbonate salt in amounts up to 15 ppm may have been the cause of the weakened bonds.

All plates are rolled with 0.003" to 0.005" of excess cladding on each face. The excess is removed by vapor blasting and pickling after machining and inspection to insure a corrosion-resistant surface. Previous experience with single plates indicated that pickling for 10 minutes in a 35% nitric-5% hydrofluoric acid solution at 40° C would remove 0.005" of metal uniformly from all exposed surfaces. An exothermic reaction was found to take place while pickling a group of five plates together which raised the temperature of the bath to 60° C with the result that most of the cladding was removed from the surface of several plates. One of these plates, No. 221, failed during subsequent corrosion testing in water

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at 290°C. Measurements of the cladding thickness on this plate varied from 0.005" to 0.010" and it is probable that the failure initiated at a break in the cladding. Adequate control over acid concentration and bath temperature should prevent a repetition of this type of defect in the future.

b. Fabrication of Enriched EBWR Type Fuel Plates (C. H. Bean, J. R. Lindgren, R. E. Macherey)

A Zircaloy-II integrally clad fuel plate with uranium enriched to 1.44 w/o U^{235} was prepared for irradiation testing in MTR. Similar control plates were prepared with normal uranium in the alloy core. These plates were assembled and roll bonded using methods and equipment established for the manufacture of EBWR plates. Dimensions of billet cladding components and finished machined plates are given in Table I. Nominal cladding thickness of finished plates was $0.020" \pm 0.002"$.

TABLE I
Dimensions of Enriched Alloy Core Cladding Billet and Fuel Plate

Item	Thickness (in.)	Width (in.)	Length (in.)
Billet Core	0.803	1.630	3.134
Billet Cover Plates	0.125	2.162	4.395
Billet Side Plates	0.250	0.819	4.395
Billet End Plugs	0.819	1.662	1.000
Plate Core	0.160	1.720	15.000
Plate Over-all	0.200	2.000	17.000

c. Effects of Irradiation on Specimens Cut from EBWR Plates with Varying Cladding Thicknesses (J. H. Kittel, S. H. Paine)

To determine the restraining effect of Zircaloy-II cladding which is bonded to the U-5 w/o Zr-1.5 w/o Nb alloy core in the reference EBWR fuel plate, a series of specimens has been irradiated in the MTR with various thicknesses of cladding to 0.1% uranium atom burnup. Typical specimens before and after irradiation are shown in Figures 1 and 2. The specimens were quenched from 850°C for corrosion resistance prior to irradiation. It was found that the cladding can exert considerable restraint on the growth of the core material, as shown in Figure 3. The

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Figure 1. Appearance of a Typical Specimen Cut from an EBWR Plate Before Irradiation.

Macro 18093

2-X

Figure 2. Typical Specimen Cut from a Gamma Quenched EBWR Plate After 0.12% Uranium Atom Burnup.

Macro 18131

2-X

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Figure 3. Effect of Zircaloy-II Cladding Thickness on the Irradiation Growth Rate of Specimens Cut from a Gamma Quenched U-5 w/o Zr-1.5 w/o Nb EBWR Plate. The specimens were irradiated to 0.1% uranium atom burnup.

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present EBWR fuel plate specifications are for 0.020" of cladding, which should decrease the growth tendency of the core by a factor of about 5.

It was also found that flat-rolled, gamma quenched U-5 w/o Zr-1.5 w/o Nb alloy grows in length at only one-third to one-half the rate of similar round-rolled or swaged material. Sidewise growth rates of the flat-rolled material, however, are about 40% greater than lengthwise growth rates.

2. Manufacture of EBWR Fuel Plates

a. Melting and Casting of Uranium-5w/o Zirconium-1.5 w/o Niobium Alloys (R. E. Macherey, N. J. Carson, Jr.)

The primary concern of the foundry during the final quarter of 1955 was the production of sound castings for EBWR fuel plates. In these three months, fifty (50) melts were made with a minimum of six (6) cores per melt. At the end of this quarter sound cores were produced on a small scale production basis.

The most important changes occurred in mold design. The three-cavity and slab molds were discarded in favor of multicavity molds. These molds have several individual cavities and produce one core for each cavity. The cores are long enough (15-1/4") to allow for cropping of the piped area. The first of these molds contained eight cavities. This eight-cavity mold was later replaced by ten- and twelve-cavity molds with the cavities arranged radially about the pouring hole. The molds are made of wedge-shaped graphite segments which are held together by top and bottom graphite rings. These split type molds are easy to disassemble and therefore outlast molds previously used. One ten-cavity mold yielded over 130 cores before failing.

The problem of achieving uniform distribution of metal to the cavities has also been worked on. The most effective and reliable type of distribution head tried consists of a cup, 2-3/4" in diameter and 1-1/4" deep, with a 1/4" slot guiding the metal into each cavity. This distribution cup gives fairly uniform feeding and is not easily blocked.

The crucible selected for EBWR production is a graphite crucible having an O.D. of 14-1/2", a minimum I.D. of 12-1/2", and a maximum bottom thickness of 1-1/2". Both the sides and the bottom have a 1° taper. This crucible was chosen because of its capacity and rapid heating rate. The most satisfactory pouring hole size has been 1/2".

The mold wash was changed from magnesium zirconate only to magnesium zirconate followed by thoria. The additional coat of thoria seemed to increase the soundness of the casting and the stability of the wash. This procedure offers the possibility of using a mold more than once per washing.*

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The two furnaces used are 21" I.D. quartz tube furnaces. Using the molds and crucible described, the foundry can now consistently produce sound castings by alloying at 1500° C, allowing the metal to cool nearly to the freezing point of 1300° C in the crucible, and then reheating to 1500° C and pouring.

Castings of uniform chemical composition have been produced in virgin melts by putting the alloy below the uranium biscuit. At the present time several such melts are being analyzed.

b. Roll Cladding of EBWR Fuel Plates (R. E. Macherey,
C. H. Bean, J. R. Lindgren)

All of the facilities required for the manufacture of the EBWR fuel plates have been installed and tested. Additional material handling carts have been completed to expedite transfer of rolled plates between fabrication, inspection, and machining.

The vacuum chamber for evacuating and sealing welded billets was completed. This chamber has a removable cover from which is suspended a support plate for mounting 12 billets. A copper spacer and guide for the billets also serves as a ground connection during welding. Billets may be set up and electrodes changed and positioned outside the vacuum box. Individual electrode holders, which are insulated from and extend through the cover, receive power from a common bus bar which simplified the billet seal welding after evacuating. All welding controls may be preset and the welding arc controlled from a central panel to insure reproducible welds.

A pulpit control station was added to the 16" x 24" United Mill. This centrally located station will make it possible for a single operator to observe and perform all operations in the rolling of cladding billets from the time they leave the preheat or reheat furnace until they are returned to the furnace. This method of operation is expected to result in more efficient use of manpower, increased safety, and greater control over the uniformity of the finished product.

Because of the poor clad-to-core bond strength noted on plates heat treated in carbonate salt, the two Hevi Duty pot type furnaces were converted from salt to lead operation. A new slotted exhaust duct was installed which will remove the fumes from both pots.

A total of 14,188 pounds of Zircaloy-II was forged from fifteen 12" diameter cast ingots to slabs approximately 3" x 9" x 13'. The forged slabs were cut into convenient lengths and conditioned for rolling. Sheet and plate stock for cladding components has been rolled from 2420 pounds of the conditioned forged slabs.

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Protective steel jackets for 888 cladding billets are being machined from SAE-1020 hot rolled carbon steel bars.

c. Ultrasonic Inspection of EBWR Core Castings (W. J. McGonnagle,
W. N. Beck)

During the past quarter a total of 394 castings have been inspected using the ultrasonic (5 MC) transmission method.

The results of the ultrasonic transmission tests, coupled with destructive tests performed by the Foundry Group on the same castings, led to the establishment of a standard nondestructive testing technique for acceptable castings.

d. Bond Testing of the EBWR Fuel Plates (W. J. McGonnagle,
W. N. Beck)

An ultrasonic scanner to be used for testing the EBWR fuel plates has been designed and built; the electronic control and recording equipment have been installed. Anticipating future testing problems, the scanner and auxiliary equipment were designed and built so that both flat and round fuel elements could be tested. This equipment will be used primarily for immersed ultrasonic transmission methods; it can also be used for immersed reflection testing.

e. EBWR Subassembly Welding (C. C. Stone, F. D. McCuaig,
D. E. Walker, R. A. Noland)

Design changes in the EBWR subassembly required revision of the semi-automatic tungsten inert gas spot welding device designed to permit dry box welding of the subject subassembly. These revisions have been made and the exploratory work necessary to develop a production procedure is in progress.

II. FAST POWER BREEDER REACTOR PROGRAM - ACTIVITY 4104

1. Properties of Uranium-Plutonium-Molybdenum Alloy (J. E. Baumrucker)

An alloy of nominal composition U-21 w/o Pu-5 w/o Mo has proven unworkable by rolling; preheating to temperatures up to 800° C was tried but with no success. Alloys that had been melted a greater number of times withstood fewer passes through the rolls before breaking up. The material for rolling tests was melted and remelted in magnesia crucibles, where a certain amount of reaction between the metal and the crucible was observed. It is probable that this reaction in the molten state adversely affects the workability of the alloy by rolling.

Difficulty in casting pins, 1/8" diameter by 1-1/2" in length, of the above composition was successfully overcome by melting in a thoria crucible and pouring into a four-cavity graphite mold. These pins are being used in irradiation damage studies as part of the program to develop a plutonium-containing fuel element for EBR-II.

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III. GENERAL REACTOR DEVELOPMENT - ACTIVITIES 4530 AND 4540

1. Development of Fuel Element Materials

a. Uranium and Uranium Alloy Powder Compacts: Irradiation Effects (J. H. Kittel, S. H. Paine)

A group of alloy specimens, $1/4$ " in diameter and $3/4$ " long, made by Sylvania by side-pressing and sintering, has been irradiated in NaK-filled capsules in the MTR and examined for changes resulting from burnup. The following alloys were studied: U-0.42 w/o Si, U-1 w/o Mo, and U-1.6 w/o Nb. In addition, unalloyed hot-pressed material was included for comparison purposes. The irradiation conditions and the changes observed in the specimens are summarized in Table II. Photographs of typical specimens are shown in Figures 4 through 8.

The unalloyed material, which was end-pressed, shortened at about the same rate as that observed for other similar specimens reported previously, (ANL-5465, ANL-5489). Of the alloys investigated, the U-1.6 w/o Nb alloy was the best, followed by the U-1 w/o Mo and U-0.46 w/o Si alloys. Both the niobium and molybdenum alloys showed small elongations which seemed to be only randomly dependent on the amount of burnup they received. The silicon alloy showed large elongations as well as considerable surface roughening, and none of the specimens of this alloy could be removed from their irradiation holders.

b. Corrosion Resistance of Uranium-5 w/o Zirconium-1.5 w/o Niobium Alloy (S. Greenberg, J. E. Draley)

Hydrogen Studies: The effort to identify the form in which hydrogen is present in the U-5 w/o Zr-1.5 w/o Nb alloy has continued. A group of samples from the same casting as tested previously were heated in salt for one hour at 850°C and quenched in Wood's metal at 120°C ; they were then aged for various times in helium at 400°C and corrosion tested in water at 290°C for 24 hours. Before corrosion testing the hydrogen contents were of the order of 40 ppm; after corrosion the hydrogen contents ranged from 790 to 1200 ppm. Metallographic examination at the various stages showed only typical structures for the alloy until after corrosion testing. Micrographs taken after corrosion showed a finely dispersed phase which had never been seen before. It disappeared during removal of hydrogen in the analysis. It seems clear that alloy which has been "loaded" with hydrogen while in the gamma phase (of the order of 40 ppm H_2) absorbs hydrogen during aqueous corrosion at a rate much greater than does metal which has not been so loaded. It is only after acquiring a hydrogen content (from corrosion) much greater than has ever been obtained for "normal" alloy that the new phase has been formed.

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TABLE II
Effects of Irradiation on Uranium Powder Compacts

Spec. No.	Composition	U Atom Burnup (%)	Calc. Temp., (°C)		Length Change (%)	Growth Rate, G_i $\left(\frac{\text{microin/in}}{\text{ppm burnup}}\right)$	Diameter Change (%)	Density Decrease (%)
			Center	Surface				
BD-6-1	Uranium	0.19	95	85	- 3.10	-17	3.12	0.52
BD-5-1	Uranium	0.27	115	105	- 5.70	-22	4.00	0.64
BD-1-1	Uranium	0.32	125	115	- 5.92	-19	5.51	1.01
BD-4-1	Uranium	0.33	135	120	- 8.49	-27	5.76	0.82
BD-2-1	Uranium	0.37	140	125	- 7.46	-21	6.15	0.85
BD-3-1	Uranium	0.38	145	130	- 9.04	-25	6.16	1.02
BD-1-2	U-0.42 w/o Si	0.32	125	115	16.2	47	--	--
BD-4-2	U-0.42 w/o Si	0.33	130	115	19.8	55	--	--
BD-2-2	U-0.42 w/o Si	0.35	140	125	17.3	46	--	--
BD-3-2	U-0.42 w/o Si	0.38	145	130	--	--	--	--
BD-7-1	U-0.42 w/o Si	0.38	145	130	--	--	--	--
BD-8-1	U-0.42 w/o Si	0.40	150	135	22.2	50	--	--
BD-6-2	U-1 w/o Mo	0.18	95	85	2.76	15	5.41	3.42
BD-5-2	U-1 w/o Mo	0.27	115	105	3.41	12	5.72	5.17
BD-1-3	U-1 w/o Mo	0.33	130	115	2.84	8.5	6.75	2.31
BD-2-3	U-1 w/o Mo	0.35	140	125	3.36	9.4	5.95	4.34
BD-7-2	U-1 w/o Mo	0.38	145	130	2.56	6.7	5.06	2.08
BD-8-2	U-1 w/o Mo	0.40	150	135	2.63	6.5	5.83	2.37
BD-6-3	U-1.6 w/o Nb	0.19	95	85	1.82	9.5	0.96	1.88
BD-5-3	U-1.6 w/o Nb	0.27	115	105	2.46	9.0	2.20	3.22
BD-4-3	U-1.6 w/o Nb	0.33	135	120	2.43	7.3	3.22	4.00
BD-3-3	U-1.6 w/o Nb	0.38	140	130	3.59	9.3	3.34	5.30
BD-7-3	U-1.6 w/o Nb	0.40	150	130	2.49	6.2	1.16	1.68
BD-8-3	U-1.6 w/o Nb	0.40	150	135	1.78	4.4	1.00	1.25

A horizontal strip of a black and white photograph showing a textured, possibly metallic or mineral, surface. The central part of the strip is dark and appears to have a fine, granular texture, while the edges are lighter and more uniform. The strip is set against a light, mottled background.

2-X

2-X

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Figure 6. End View of a Pressed and Sintered U-0.42 w/o Si Alloy Specimen After 0.32% Uranium Atom Burnup at a Calculated Temperature of 125°C.

The specimen was so badly distorted that it could not be removed from the holder in which it was irradiated.

Macro 18210

2-X

Figure 7. Pressed and Sintered U-1 w/o Mo Alloy Specimen After 0.40% Uranium Atom Burnup at a Calculated Temperature of 150°C.

Macro 18231

2-X

Figure 8. Pressed and Sintered U-1.6 w/o Nb Alloy Specimen After 0.40% Uranium Atom Burnup at a Calculated Temperature of 150°C.

Macro 18232

2-X

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Effect of Irradiation: One sample of the same alloy, irradiated under restraint (essentially zero growth) to a burnup of 0.19 a/o was tested in degassed, distilled water at 265° C for 56 hours. For the first 48 hours the correspondence between pressure and temperature indicated no rapid corrosion. During the last eight hours of test the pressure gradually increased to about 100 psi above saturation pressure. When the autoclave cooled to approximately room temperature, there was a residual pressure approaching 100 psia; the sample was completely reduced to slurry. This sample had been gamma quenched and aged at 400° C for two hours. Pre-irradiation corrosion rate was 9.5 mcd at 290° C.

It appears certain that radiation produces a change, perhaps similar to overaging, which reduces the corrosion resistance of the material independently of gross dimensional changes. It is possible that the sample was overaged during the course of irradiation, since the calculated center temperature was 335° C (not much below the temperature at which overaging would be expected to occur).

c. Uranium-3.8 w/o Silicon Alloy (S. Greenberg, J. E. Draley)

Samples of an U-3.8 w/o Si alloy, coextruded with Zircaloy-II cladding, were received from Nuclear Metals, Inc.; the alloy had been epsilonized before extrusion. Samples from two extrusions were tested in degassed, distilled water at 290° C. Duplicate samples were given an additional epsilonizing treatment of one week at 825° C to determine the effect of such treatment on the corrosion behavior of core and bond in water at 290° C. No effect on the corrosion of the core alloy was observed: all samples showed good corrosion resistance. However, the additional time at the epsilonizing temperature sensitized the bond line which was severely attacked.

Effect of Irradiation on Corrosion: A casting prepared and heat treated 2.75 days at 800° C by Nuclear Metals, Inc., was irradiated to a burnup of 0.12 a/o. Preirradiation corrosion tests at 265° C (Nuclear Metals) and 290° C gave corrosion rates of 1.00 and 2.82 mcd, respectively. After irradiation, the sample was retested at the above temperatures with the following results:

265° C (112 hours) - 0.28 mcd

290° C (86 hours) - 0.72 mcd

The lower corrosion rate is probably due, at least in part, to the inability to remove loose oxide as completely in a remote operation as in ordinary corrosion tests; it is not likely, however, that this alone could account for the considerable increase in corrosion resistance. Regardless of the explanation, the alloy retained its corrosion resistance after irradiation

NO DATA

d. Urania-Thoria Fuel Bodies

Irradiations in MTR (J. H. Kittel, S. H. Paine)

A group of ceramic specimens, 1/4" in diameter and 3/4" long, with the composition ThO_2 -2.5 w/o UO_2 , made by J. H. Handwerk, has been irradiated in NaK-filled capsules in the MTR. Some of the specimens were irradiated with no jacketing; others were jacketed in stainless steel or zirconium. Irradiations were made at calculated maximum temperatures ranging up to 485°C, and to total metal atom burnups ranging up to 0.95% (36% U atom burnup).

Photographs of typical specimens are shown in Figures 9 and 10. The specimens were unchanged in appearance as a result of the irradiation they received. Dimensional changes, if any, were less than 0.001". The exceptional dimensional stability of these specimens is in contrast to UO_2 specimens which fractured badly when irradiated to lower burnups, as described in a previous report (ANL-5489).

The good performance of these specimens may be due, in part at least, to the fact that they contained about 10% porosity prior to irradiation. The voids in the material may act favorably in taking up volume expansions resulting from fission product formation before cracking stresses develop.

Irradiations in CP-5 (F. L. Brown, S. H. Paine)

A capsule containing ThO_2 -10% UO_2 cylindrical pellets was examined following 3.16% calculated depletion of uranium atoms in a water loop in CP-5 reactor. Irradiation was at 500° - 520° F (260° - 275° C) and 760 - 810 psi. The capsule as received was severely distorted and a transverse crack in the Al-1% Ni tube clearly exposed the lead bonding in the annulus between specimen and tube, as shown in Figure 11. The outlines of the individual specimens within the tube were apparent, and it appeared as though the capsule had enlarged in some way and then collapsed, wrapping itself intimately about the specimens (also shown in Figure 11).

After partial solution of the capsule in caustic, the pellets were disclosed to be fragmented, but otherwise unaffected (see Figure 12), a condition typical of pellets previously examined which had been irradiated in Zircaloy or stainless steel capsules.

e. High Temperature Corrosion-Resistant Aluminum Alloys
(W. E. Ruther)

Additional corrosion rate determinations have been completed for 2S aluminum-nickel alloys and for alloy X2219 (experimental Alcoa high strength alloy). The results are presented in Table III. Group I shows that the corrosion rates of the two alloy castings used are essentially identical (independent of the nickel content).

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Figure 9. Unjacketed ThO_2 -2.5 w/o UO_2 Specimen After 0.88% Burnup of the Total Metal Atoms at a Calculated Temperature of 450°C .

The appearance of the specimen was unchanged as a result of the irradiation it received.

Macro 18098

2-X

Figure 10. Jacketed ThO_2 -2.5 w/o UO_2 Specimen After 0.95% Burnup of the Total Metal Atoms at a Calculated Temperature of 485°C .

The dimensions of the jacket were not changed by the irradiation exposure.

Macro 16769

2-X

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Figure 11. Al-1 w/o Ni Alloy Capsule Collapsed About Specimens with Lead Alloy Exposed in Crack Between Two Pellets.

Macro 18383

4-X

Figure 12. Fragmented Pellets of ThO_2 -10 w/o UO_2 Exposed After Capsule Was Partially Dissolved in Caustic.

Macro 18388

4-X

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TABLE III

Corrosion of Aluminum Alloys at Elevated Temperatures

Alloy		Conditions	Rate of Metal Corrosion After Initial Period (mg/dm ² -day)	Estimated Intercept (mg/cm ²)
I	M388 (2S + 0.9 w/o Ni)	290° C Distilled H ₂ O	3.3	0.9
	A124 (2S + 0.5 w/o Ni)	290° C Distilled H ₂ O	3.4	0.8
II	M388	150° C Distilled H ₂ O	0.53	0.2
	M388	200° C Distilled H ₂ O	1.2	0.3
	A124	250° C Distilled H ₂ O	2.3	0.5
	A124	290° C Distilled H ₂ O	3.4	0.8
III	A124	290° C pH 3.5 (H ₂ SO ₄)	2.0	0.4
	A124	290° C pH 6 (No additive)	3.4	0.8
	M388	290° C pH 9 (NH ₄ OH)	3.7	1.2
IV	X2219 (6.2 w/o Cu, 0.32 w/o Mn, 0.16 w/o Zr, 0.14 w/o Fe, 0.11 w/o Si)	250° C Distilled H ₂ O	1.7*	0.5
	X2219	290° C Distilled H ₂ O	3.5*	1.1

*Rate incorrect and low due to incomplete removal of oxide coating.

Group II shows the variation of corrosion with temperature. Both rate and intercept increase with increasing temperature. The rates are low; for example, at 150° C a penetration of about 0.26 mil per year is indicated.

In Group III is shown the variation of corrosion with pH at constant temperature. The spread is not nearly as great as that obtained with 2S aluminum at lower temperatures (i.e., 7.6 mdd at pH 8.5 and 0.7 mdd at pH 3.5; 200° C).

Group IV lists the results obtained with alloy X2219. This alloy tended to pit uniformly over the surface. Oxide remained in these pits after stripping and the rates calculated are low. The rates are roughly comparable to the Al24 alloy.

Two short tests were run with silica additions. In the first, 20 ppm SiO_2 was passed through the solution autoclave (as Na_2SiO_3) with the pH adjusted to about 8 (H_2SO_4). The M388 samples exposed to this solution at 290° C could not be effectively stripped of their adherent corrosion product so an accurate rate could not be determined. From the data available it was obvious that the corrosion rate was several times greater than in distilled water.

Another test was run in small autoclaves with soluble silica obtained in different fashions. For the first solution, the soluble silica was obtained by dissolving technical silica powder in water at 350° C. This solution was then allowed to stand at room temperature and diluted to 52 ppm SiO_2 . Another solution was made up of $\text{Na}_2\text{SiO}_3 + \text{H}_2\text{SO}_4$ to give the equivalent amount of H_2SiO_3 at elevated temperatures. This solution analyzed 42 ppm SiO_2 .

Samples of M388 were suspended in each of these solutions and the weight gain curves at 290° C were obtained. The solution was not severely depleted by the short duration of the test periods. The lowest effluent analyzed 32 ppm after a 3.5-day test period. A plot of the weight gains gave 8 mdd for the silicic acid and 11 mdd for the $\text{Na}_2\text{SiO}_3 \cdot \text{H}_2\text{SO}_4$ solution. If the usual assumptions are made, these values yield corrosion rates of 6 mdd and 9 mdd, respectively. A comparison with the distilled water rate of 3.3 mdd indicates that in this concentration silica is detrimental. C. Wohlberg, Reactor Engineering Division, has obtained results indicating some inhibition by silica but only at high concentrations (~1000 ppm).

f. Examination of Aluminum-Nickel Alloy Plates from Reactor Engineering Division Corrosion Test in the MTR Loop
(F. L. Brown, S. H. Paine)

Nine aluminum-nickel alloy corrosion test plates were macro-examined for the Reactor Engineering Division Test Nos. MTR-W6 (in-pile) and MTR-W6E (out-of-pile). Nominal compositions of the alloys were aluminum with 0.5, 1, and 2 w/o nickel. Two plates of each alloy (6 total) were tested in-pile and one plate of each alloy was tested in the out-of-pile portion of the loop. The in-pile cartridge was irradiated in water for a period of 850 hours at 400° - 500° F (205° - 260° C) and 400 hours below 300° F (150° C). In addition, the plates were exposed to 400° - 500° F (205° - 260° C) water for 75 hours out of the irradiation zone. Maximum thermal flux was estimated as 1×10^{21} nvt, maximum fast flux as 5×10^{19} nvt.

Examination disclosed no great variation in the appearance of the corroded surfaces among the in-pile or among the out-of-pile plates. However, a large difference was noted between the irradiated group and the nonirradiated group. The irradiated plates displayed deep, elongated, transversely oriented pits, whereas the out-of-pile plates were characterized by shallow, large, nondirectional pits. The degree of attack appeared greater on the out-of-pile specimens, confirming Reactor Engineering Division pre- and postirradiation weight measurements. Typical stereo-photos are shown in Figures 13 and 14.

2. Development of Structural, Shielding and Control Rod Materials

a. Preparation of Rare Earth Ceramic Bodies (J. H. Handwerk)

The high density $\text{Sm}_2\text{O}_3\text{-Gd}_2\text{O}_3$ powder was found to react with water, and the reaction was accompanied by a severe swelling in the powder. It is evident that sintering the $\text{Sm}_2\text{O}_3\text{-Gd}_2\text{O}_3$ will not stabilize these mixed oxides. The effect of small additions of such materials as magnesia, alumina, calcia and silica is being studied in order to stabilize the $\text{Sm}_2\text{O}_3\text{-Gd}_2\text{O}_3$ in water.

Figure 13. Al-1 w/o Ni Plate Showing Typical Corrosion Under Irradiation.

Macro 18173

7-X

Figure 14. Al-1 w/o Ni Plate Showing Typical Out-of-Pile Corrosion.

Macro 18181

7-X

IV. PRODUCTION, TREATMENT, AND PROPERTIES OF MATERIALS - ACTIVITY 5410-01

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

The fabrication schedule described in ANL-5489 proved moderately successful for preparing alpha uranium single crystals from large diameter rods by the grain coarsening method. A number of 0.20 to 0.22" diameter single crystals have been obtained from 0.350" diameter specimens which were produced from 0.765" diameter rods by this schedule. Further variations in processing are necessary, however, to obtain single crystals of larger diameters. The single crystal diameter is restricted by the formation of other coarse grains in the peripheral areas of the cross section. Experiments are being made to determine whether this can be eliminated by varying the distribution of grain growth inhibitor in the specimens.

Although large single crystals of the order of 1 cm diameter are desirable for determining the elastic constants by ultrasonic wave velocities of frequencies in the order of 10 megacycles, the possibility is presently being studied of obtaining such data on the single crystal sizes presently available using higher frequencies. To obtain accurate and reliable data it is necessary that the minimum specimen dimensions be approximately ten times the ultrasonic wave lengths. The specimens must contain two flat, parallel faces to which the wave transducer and detector can be attached, and the flat faces must be crystal planes suitably chosen so that the fundamental elastic constants can be simply derived from the velocity data. The specimens which can be prepared from the 0.20" diameter single crystals will be of such dimensions that ultrasonic waves of approximately 50 megacycles will be necessary. The equipment for producing and detecting such high frequency waves has been developed at another laboratory* and arrangements have been made to try out this equipment to determine the feasibility of obtaining the velocity data from the small size crystals presently available.

The success of the high frequency method depends critically on the condition of the specimen surfaces and the single crystal perfection. As indicated above, surfaces through which the waves enter the crystal and which reflect the waves must be flat and parallel within close tolerances.** An automatic grinding procedure is now being developed to be used for preparing surfaces on any desired crystal plane. The mechanical grinding, however, introduces crystal imperfections at these surfaces; and a means for removing the imperfect surface without losing the surface flatness is necessary. The presently used metallographic electropolish is not suitable; other electrolytes will be tried.

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*Bell Telephone Laboratories

**Estimated within 0.0001".

Our present program is to continue with attempts to produce larger single crystals, but at the same time to prepare from the available specimens the largest crystals possible to try out the applicability of the high frequency equipment.

2. Uranium Corner of the Uranium-Zirconium-Niobium Phase Diagram (A. E. Dwight)

The composition range in which the gamma phase can be retained in a metastable state by quenching from approximately 900°C into water is summarized in Figure 15. Below the dashed line the quenched structure existing at room temperature is martensitic in appearance, and is shown by X-ray diffraction to be alpha plus gamma. Above the dashed line the structure existing at room temperature appears to be 100% retained metastable gamma on the basis of microstructure and etching characteristics. X-ray diffraction patterns on compositions above the dashed line yielded strong gamma patterns along with weak zirconium lines. For compositions near the line, a range exists in which a water quench may or may not retain metastable gamma, depending upon the cooling rate for a particular specimen. In the binary uranium-niobium system, the 4.9 and 6 w/o Nb alloys appear to be affected by quenching conditions or specimen size.

Lattice parameter measurements on the retained metastable gamma alloys were only approximate, but showed a rough trend as follows: increase niobium content contracts the ternary lattice parameter, whereas increased zirconium content expands it; this is the same trend as that of the binary uranium-niobium and uranium-zirconium systems. The effect of solute elements on the gamma lattice parameter appears to be related to the critical cooling rate for retention of metastable gamma, and to the transformation time in which gamma decomposes under isothermal conditions. Niobium and, as has been shown elsewhere, molybdenum strongly contract the lattice parameter and retard the subcritical transformation rates; zirconium, on the other hand, expands the lattice and has only a slight retarding effect on the transformation rate.

Electrical resistivity measurements have been continued on the high uranium alloys containing a constant 2 w/o Nb. Data are shown in Figure 16. Specimens were heated into the gamma range, transformed by the interrupted quench method, and water quenched. Resistivity was measured at room temperature by the potential drop method. The data, together with metallographic evidence, indicate that at 620°C approximately 80% of the gamma had transformed, and that below 620°C, only slight additional transformation occurs.

Figure 15. Phases Present in Uranium-Zirconium-Niobium Alloys Quenched from 900°C.

Macro 18411

Figure 16. Electrical Resistivity at Room Temperature of Uranium-Zirconium-Niobium Alloys Isothermally Transformed for 24 Hours at Indicated Temperatures.

Macro 18410

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3. The Delta Phase in Uranium-Zirconium Alloys (M. H. Mueller, L. Heaton)

As reported previously,¹ X-ray diffraction evidence obtained from the delta phase indicated that this phase is cubic with an approximate a_0 of 10.68 Å. This conclusion was based on the symmetry of a number of Laue photographs, rotation, and equi-inclination Weissenberg patterns. More recently, all of the spots on Laue patterns mentioned above have been successfully indexed according to this same cubic cell. All of the hkl indices, as determined, have $h^2 + k^2 + l^2 = 6n$. This sum has a numerical range from 12 to 684, which is in agreement with the much smaller range of 6 to 186 calculated previously from the powder diffraction data obtained with copper radiation. The assigned indices on the Laue patterns have also been found to be compatible with the θ angles observed and with the wave length distribution expected from a tungsten target tube operating at 40 KV.

Precession photographs have also been obtained from a single crystal of delta carefully cut from a cast piece of approximately 41 w/o U-Zr alloy. All of the spots observed to date in the reciprocal lattice have also been indexed according to this cubic cell.

Several large crystals of the 41 w/o U-Zr alloy have been obtained by quenching from 1000°C. The Laue patterns from these crystals show very sharp spots which can be indexed according to the small, gamma body centered cubic phase with a_0 of approximately 3.56 Å; in addition there are a few very diffuse spots. The number and sharpness of these diffuse spots can be increased by annealing at temperatures around 200°C, which would indicate that the gamma phase may transform gradually, probably by an ordering process, to the delta phase. Rotation photographs from these partially transformed crystals also show both sharp and diffuse spots. The sharp spots on the 0 and third layer lines can be accounted for by the same small body centered unit cell and the diffuse spots which appear on the other layer lines can be indexed by the delta phase which is the tripled gamma unit cell.

As mentioned previously,¹ some of the lines in powder photographs of the delta phase are displaced in a regular way corresponding to a slight increase in the a_0 . It has also been found that, for a given composition, approximately 46 w/o Zr-U, for example, some of the diffraction lines showed a displacement at room temperature, but at approximately 525°C all lines appeared in the expected position for this large, body centered cubic phase. Possible causes of this seemingly anisotropic behavior are being investigated.

Preliminary X-ray diffraction results indicate that the delta phase may be quite closely related to the omega phase found in many of the titanium alloys, such as titanium-vanadium and titanium-chromium.

¹M. H. Mueller, "The Delta Phase in the Uranium-Zirconium System" Acta Crystallographica, December, 1955.

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4. The High Uranium End of the Uranium-Carbon System (B. Blumenthal)

Figure 17 represents the data obtained to date on the solubility limit of carbon in gamma uranium as determined by metallographic examination of annealed and water quenched high purity uranium-carbon alloys. The light circles indicate absence of UC inclusions, the dark circles their presence. These inclusions are light grey with rounded contours and are observed after careful hand polishing and a 3-second electrolytic polish in a phosphoric acid bath. A longer electropolish destroys their identity by either rendering them black, possibly by oxidation to UO_2 , or by dissolving them and leaving a cavity. Care was taken to differentiate between occasional dark grey UO_2 inclusions and the residual carbides.

In evaluating these data it must be borne in mind that the solubility of carbon at the lower temperatures is very small and that the errors caused by nonuniformity of ingot composition, sampling, and analytical methods are larger than would appear from the plot of the data. For instance, the analytical data that were reported for an alloy with an average carbon content of 62 ppm were: 64, 54, (30), 66, 63, and 61 ppm; the values for an alloy with an average of 70 ppm were: 68, 80, 71, 67, 65, and 67 ppm. Since metallographic examination correlates structure and true carbon content, a plot which shows structure versus average carbon content may contain occasional inconsistencies. The carbon solubility at the gamma to beta transformation is about 65 ppm or 0.038 atomic percent; an alloy with 205 ppm carbon consisted of two phases up to 1100°C , hence the maximum solubility near the solidus temperature is below this value.

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

The problem of self-diffusion in alpha uranium was mentioned in ANL-5257 and the methods for producing cylindrical U^{238} - U^{235} diffusion couples were described in ANL-5382. Since the diffusion temperature in the alpha phase is limited to a maximum of 660°C , the diffusion coefficients will probably be very small, and normal or slightly depleted uranium contains enough U^{235} to make the measurement of small diffusion coefficients almost impossible. The layer in which the concentration changes would be so thin and the quantity of U^{235} diffusing, relative to that initially present, would be so small that accurate measurements of change in U^{235} are unlikely. Our present phase of the problem, therefore, concerns itself with the preparation of highly depleted uranium.

A small quantity of uranium containing 0.0334 w/o U^{235} has been obtained from the electromagnetic separations plant at Oak Ridge. Unfortunately, this material contains a large amount of contaminating elements (5000 ppm Fe, 200 ppm Cr, 90 ppm Ni, 100 ppm Si) and must be purified in order to be usable. There are enough impurities present to

Figure 17. Solubility of Carbon in Gamma Uranium.

Macro 18409

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cause the appearance of a second phase, which would make the diffusion coefficients meaningless. Efforts are presently under way to adapt the electrolytic refining techniques (including the preparation of UCl_3) described by Noland and Marzano² to purify this material.

Our first efforts in this direction called for making a limited amount of UCl_3 , using as much of the metal as possible for the anode. During the mock-up experiments using natural uranium two Vycor cells broke, probably due to alkali metal attack; the alkali metals were liberated at the cathode because of the low uranium concentration in the salt. Using an Hastelloy "C" cell, the crystals obtained analyzed high in chromium (100 ppm). We are presently making more UCl_3 and doing further mock-up electrolyses in a Vycor cell.

Further studies of the sputtering process have shown that, without changing the geometry developed by Weil (ANL-5382), we can produce a uniform plane sputtered layer. The machining problems associated with unidirectional diffusion are rather simpler than the ones associated with a cylindrical geometry.

The anticipated small magnitude of the diffusion coefficient makes the sectioning of the diffusion specimens an exacting task. A precision grinder on the University of Illinois model³ will be used. Professor N.H. Nachtrieb of the Institute for the Study of Metals has almost completed the construction of such a machine, and has been so kind as to offer us its use.

The radioactivity of the "base" (depleted) uranium makes the analysis rather more tortuous than usually encountered in similar studies. The approach currently under study calls for dissolving the uranium from the grinding paper with HCl , analyzing for total uranium spectrophotometrically by the thiocyanate method,⁴ and analyzing for U^{235} by irradiating an aliquot of the sample, and separating and counting the ruthenium fission product.⁵

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²C. Marzano and R. A. Noland, "Electrolytic Refining of Uranium," ANL-5102.

³H. Letaw, Jr., L. Slifkin, and W. Portnoy, "A Precision Grinding Machine for Diffusion Studies," Rev. Sci. Inst. 25, 865 (1954).

⁴C. Crouthamel and C. Johnson, "Spectrophotometric Determination of Uranium by Thiocyanate Method in Acetone Medium," Anal. Chem. 24, 1780 (1952).

⁵R. Larsen, "Analytical Methods for Laboratory Use," based on L. E. Glendenin, "Improved Determination of Ruthenium Activity in Fission," Radiochemical Studies: The Fission Products, Book 3, NNES, 1951.

6. Thermal Conductivity Apparatus for Uranium (K. F. Smith)

Equipment for the measurement of thermal conductivity of uranium at elevated temperatures has been constructed and a successful test has been completed to 500° C.

The essential features of the apparatus are shown in Figure 18, and mechanical details are available on Argonne Drawing CS-2079. The principle of operation which was originally introduced by Shelton and VanDusen (Research Paper 668, Bureau of Standards Journal of Research 12, 429, 1934) is of a comparison type.

In Figure 18, heat supplied by a Nichrome heater at the upper end of the uranium specimen flows downward through the specimen and through an Inconel standard, which was calibrated by the United States Bureau of Standards, to a heat sink below. A Hastelloy B rod at the bottom provides a steep temperature gradient to prevent excessive temperatures at the base of the apparatus. To prevent heat losses by radiation from the sides of the specimen, a split guard tube surrounds the central assembly. The guard tube is heated by separate Nichrome-wound heaters located near the extreme ends of the specimen and standard. They are supplemented by a central heater which is used to equalize the gradients in the guard tube so that they conform with the individual gradients in the specimen and standard. The portion of the guard tube opposite the Inconel standard is made of nickel, which is a good heat conducting material compared to the stainless steel opposite the specimen. As a result of this arrangement of the guard materials it is never necessary to apply cooling at the central location to balance gradients; a heater alone is sufficient.

Calibrated thermocouples are placed on specimen and standard at locations suitable to compare the gradients associated with the two materials, but far enough from contact surfaces to avoid end effects. Opposite each of the above thermocouples a corresponding thermocouple is placed on the inside surface of the guard tube for the purpose of matching temperatures of the guard to the specimen and standard.

When such temperature matching has been achieved under conditions of temperature equilibrium, the thermal conductivities of specimen and standard are inversely proportional to their measured temperature gradients. Conductivities of both specimen and standard are assumed to be referred to their respective mean temperatures.

The success of this type of thermal conductivity apparatus is contingent upon good thermal contacts from one material to another. In this case the guard tube components were welded together in series, using transition zones whenever necessary. The contact of specimen to standard was effected by a pressure connection assisted by an interposed foil of soft copper previously dipped in molten Wood's metal. The upper contact of the uranium specimen and the lower contact of the Inconel standard were pressure contacts of 12 to 15 microinch ground finishes.

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Figure 18. Essential Features of Thermal Conductivity Unit.

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Since uranium at elevated temperatures reacts with oxygen readily, it is necessary to perform these measurements in a vacuum of 10^{-5} to 10^{-6} mm of mercury. The resulting auxiliary system to the main unit is shown in block layout form in Figure 19. The DC power source is highly desirable to avoid interaction between heater and thermocouple leads without cumbersome electrical shielding. The Brown-Rubicon potentiometer is self-balancing, allowing rapid and precise temperature determination. The vacuum system is characterized by an absence of shutoff valves, which helps to maintain a simple leak-free system. The cooling system features a stabilizing unit copied from the Bureau of Standards which consists of running the closed system of cooling water through a coil immersed in pentane (BP approximately 33°C). The pentane is exhausted into a condensing stack to prevent its loss into the room.

An aluminum block is employed as a multiple reference junction for the thermocouples. A thermometer measures the temperature of the aluminum block with sufficient precision for use in differential temperature work such as this.

Figure 20 shows results of a proof run using uranium of the composition shown in Table IV. The test was performed on a specimen, 2 cm in diameter by 15 cm in length, which was machined from cast metal.

TABLE IV.

Analysis of Uranium Used for Thermal
Conductivity Measurements*

Element	ppm by Weight	Element	ppm by Weight
C	229 - 295	Mn	4
Al	7	Na	5
Cr	3	Ni	20
Cu	2	Pb	2
Fe	30	Si	30
Mg	2		

*All other elements are below limits of spectrographic detection.

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Figure 19. Block Layout of Thermal Conductivity Unit and Auxiliary Equipment.

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Figure 20. Thermal Conductivity of Reactor Grade Uranium.

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7. Corrosion Mechanism of Aluminum at Elevated Temperatures (W. E. Ruther, C. A. Youngdahl, J. E. Draley)

Mixed Powder Compacts: Compacts of mixed powders of 2S aluminum plus 1 w/o, respectively, of iron, nickel, copper, graphite and stainless steel were extruded to see if the cathodic phases, incorporated in this manner, would protect the aluminum against the penetrating type of corrosion which is typical for 2S aluminum in water at elevated temperatures. It was anticipated that the compacts might be even better than alloys, since it is believed that the added materials in dispersed form are, in some cases, more efficient cathodes than the compounds formed in alloying.

The alloys were rolled and tested for 2 days in distilled water at 290°C. All samples had blisters ranging from a few microscopic ones to complete conversion to oxide. The type of blisters noted and their stringer-like formation suggest initial voids in the compacts which were elongated in extrusion and rolling. The differences noted between compacts appeared to be associated more with their porosity than with the relative protective effects of the metal additives.

Electrochemical measurements were then made to corroborate the expected corrosion behavior of these compacts. The cathodic polarization of rods of steel, stainless steels 347 and 304, nickel, copper, and graphite was measured at 300°C in distilled water. A preliminary aging of the specimen for 16 hours in water at 300°C preceded each measurement. The results are shown in the accompanying table.

TABLE V.
Cathodic Polarization of Metals
at 300°C in Distilled Water

Material	Open Circuit Potential (volt)*	ΔE for 100 $\mu a/cm^2$ (volt)
Nickel	-0.275	-0.200
SS-304	-0.340	-0.215
SS-347	-0.385	-0.235
CR Steel	-0.490	-0.240
Copper	-0.460	-0.420
Graphite	-0.745	-0.645

*Measured using corroded stainless steel autoclave as reference electrode.

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The changes in potential, caused by cathodic current, are strikingly less than for aluminum, and significantly less than those for the corresponding eutectics with aluminum for which this property has been determined, (see Quarterly Report ANL-5489). It would hence be deduced that good quality compacts would be more resistant to blistering attack than corresponding alloys with aluminum.

Capacity Measurements: The film capacity of 2S aluminum corroded in 50°C distilled water was measured in a $\text{HBO}_3 + \text{NH}_3$ solution at 20°C as a function of corrosion exposure. The experiment was performed to attempt to demonstrate the existence of a barrier layer and to study its growth as a function of time. The corroded specimen is considered to have a thin, relatively impervious layer which limits the corrosion rate. This layer acts as a dielectric between the metal on one side and a porous oxide filled with an electrolyte on the other. This naturally requires a complex electrical analogy. A study of these circuits has been made by Van Geel⁶ and is not considered pertinent to this preliminary study.

Three positions, each 1 cm² in area, were tried on each specimen. For the shorter corrosion exposures the three positions showed considerable variation in capacity. For the longer exposure there was essentially no difference. This implies that the initial growth of the film was not uniform. Unfortunately, as might be expected from the complex nature of the system, the capacitance measured was dependent on frequency. For any given frequency (0.2, 5, and 20 kc) the capacitance was essentially constant after 7 days' exposure, indicating equilibrium had been reached. The equilibrium values were approximately 10% of the values obtained for one-day exposure.

A rough estimate of the thickness of the barrier layer may be made from the formula used by Dekker and Urquhart:⁷

$$b_t \simeq \frac{\epsilon A}{4 \pi C} \quad \text{take } \epsilon \text{ (dielectric constant)} \simeq 8 \text{ (estimated; based on } \beta \text{ Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O)}$$

$$A = 1 \text{ cm}^2$$

$$C \text{ (capacitance)} = 9 \times 10^{+3} \text{ stat farads}$$

$$b_t \simeq 7 \times 10^{-5} \text{ cm}$$

This is considerably thicker than the values usually supposed for a film of this nature formed in air or boric acid solution ($\sim 10^{-7}$ cm). The use of capacity measurements where complex coatings are formed on the metal

⁶ Van Geel, W. Ch., "Halbleiter Probleme Vol. I" Vieweg and Sohn, p. 299-310, Braunschweig, 1954.

⁷ Dekker, A. T. and Helen Urquhart, Can. J. Res. 28, 541-550 (1950).

is limited to a qualitative picture. In this case the capacity measurements indicated an equilibrium thickness had been reached by one week. This correlates well with corrosion rate measurements, since an equilibrium thickness would account for the linear corrosion rate with time noted after about one week's exposure under similar conditions.

Film Conductivity - Aluminum: Several types of experiments were performed in an effort to measure the electronic conductivity of the oxide film on aluminum alloys and to correlate these measurements with corrosion behavior. The reason for interest in the conductivity is based on the hydrogen-blister corrosion hypothesis. The competing reactions for the cathodic corrosion process are presumed to be proton diffusion inward from the solution to the metal and electronic diffusion outward. The proton diffusion results in hydrogen formation beneath the barrier layer with consequent damage. If the film conductivity is increased, the electronic diffusion should be favored at the expense of the proton diffusion, and the hydrogen damage should be reduced.

The measurement of electronic conductivity of aluminum oxide on aluminum is moderately difficult because of its excellent insulating properties. A method of circumventing the difficulties for a relative measurement is to measure the efficiency of formation of an anodic film. The greater the electronic conductivity, the lower the efficiency of formation, since in this case the electronic conductivity is competing with the anode process.

With the objective of decreasing corrosion hydrogen damage, alloys containing about 0.15 w/o of various metal additives were made. The castings were solution heat treated 4 hours at 650°C and water quenched. The samples were then electropolished and anodized in purified 1% ammonium borate using 0.5 ma/cm² (platinum cathode). Sample weights were not taken since the relative formation efficiency was compared with high purity aluminum. There were slight variations in the slopes of the potential vs. time curves for individual specimens, but the average value from start to sparking was chosen for comparison. The results are summarized in Table VI.

The alloy containing manganese showed the lowest anodizing efficiency, so a new alloy was made of Al-0.5 w/o Ni-0.3 w/o Fe-0.15 w/o Mn. The corrosion rate over a 3 to 14 day period was 10% less than the M388 reference alloy in 290°C distilled water, but the intercept of the corrosion curve was greater. This value is based on only two samples and a larger melt will be made to supply enough samples for an accurate corrosion rate determination in the solution autoclaves. In addition, the metallurgy of the alloys made is not the same, so that having all additives at 0.15 w/o is possibly quite unfair. Further consideration of this factor is planned. Perhaps new alloys will be made in which the additives can be shown to be dissolved in the aluminum.

TABLE VI.

Relative Film-Forming Efficiency

Alloy	Anodizing Efficiency* (% of High Purity Value)	Sparking Voltage (volts)
High Purity	100	460
Al-0.16% Cu	99	460
Al-0.17% Zr	99	467
Al-0.13% Si	91	460
Al-0.34% Ti	90	470
Al-0.14% Cr	89	490
Al-0.17% Mn	68	480

*100% = high purity aluminum; values obtained from slope of potential vs. time curve.

8. Mechanism of the Aqueous Corrosion of Zirconium (R. D. Misch, F. Gunzel)

The work of the past quarter on the electrical conductivity properties of zirconium oxide films has dealt with measurements at room temperature in air and at 450°C in vacuum. Several techniques have been employed to measure conductivity at room temperature but reliable data are difficult to obtain. Thin films are subject to electrical breakthrough which produces a low resistance.

If the contact area is diminished, the sensitivity of the method goes down, but the probability of contacting a uniform film increases. By use of a wire probe, the breakthrough voltage was measured on anodic films and found to lie close to the voltage of formation. This behavior is similar to observations by other investigators on aluminum and tantalum.

At 450°C in vacuum, a wire probe was used to measure the changes in conductivity with time. The current may be expressed as:

$$i - i_0 = t^b e^{-cS}$$

where i = current

t = time

S = thickness

i_0 , b and c are constants.

This conductivity change is not a consequence of film dissolution (by oxygen diffusion into the metal) since the latter rate has been shown to be too low to account for the magnitude of the effect. Further work will endeavor to relate these effects quantitatively to corrosion processes.

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V. ALLOY THEORY AND THE NATURE OF SOLIDS - ACTIVITY 5420-01

1. Neutron Diffraction Study of the Titanium-Zirconium System (S. S. Sidhu, L. Heaton)

Titanium and zirconium metals crystallize in close-packed hexagonal structures with the following lattice parameters:

$$\text{Ti: } a_0 = 2.952 \text{ \AA}, c_0 = 4.689 \text{ \AA}, \text{ and } C = 1.588$$

$$\text{Zr: } a_0 = 3.223 \text{ \AA}, c_0 = 5.123 \text{ \AA}, \text{ and } C = 1.590$$

The unit cell of each structure contains 2 atoms, A_1 at (000) and A_2 at $(1/3, 2/3, 1/2)$. The nearest distance of approach of atoms is 2.897 Å in the titanium lattice and 3.168 Å in the zirconium lattice. These distances differ by less than 10 per cent. The valency of both elements is essentially the same. They are completely miscible in each other and form a continuous series of substitutional solid solutions.

In Figure 21 are given the X-ray diffraction patterns of the two metals and a typical solid solution of the two. Figure 22 shows the neutron diffraction patterns of the same samples. The Bragg reflections are obtained in all three patterns taken with X-rays, but not in those taken with neutrons. This is due to the fact that the nuclei of these elements scatter thermal neutrons in opposite phases, the nuclear scattering amplitude for titanium (f_{Ti}) being -0.38×10^{-12} cm and for zirconium (f_{Zr}), $+0.62 \times 10^{-12}$ cm.

The intensity of a Bragg reflection for a given set of parallel planes in a crystalline substance is given by the expression:

$$I_{hkl} \propto \frac{|F|^2 m}{\sin^2 \theta \cos \theta} \quad (1)$$

where hkl are the Miller indices; m , the multiplicity factor; $1/\sin^2 \theta \cos \theta$, the Lorentz factor; and F , the structure factor. The latter is calculated from the expression:

$$F_{hkl} = \sum_n f_n e^{2\pi i (hu + kv + lw)} \quad (2)$$

in which f_n is the scattering amplitude and u, v, w , the fractional coordinates of atoms in the unit cell. When the u, v, w values for A_1 and A_2 atoms are substituted in expression (2), it becomes:

$$F_{hkl} = f_n \left\{ 1 + e^{2\pi i [(h+2k)/3 + l/2]} \right\} \quad (3)$$

Figure 21. X-Ray Diffraction Patterns of Zr, 60 a/o Ti
40 a/o Zr and Ti, Filtered CuK α Radiation.

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Figure 22. Neutron Diffraction Patterns of Zr, 60 a/o Ti₀
40 a/o Zr and Ti Neutron Wavelength $\lambda = 1.01 \text{ \AA}$.

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Now, if in a random substitutional solid solution of the two metals 62 per cent of all sites, A_1 and A_2 , are occupied by titanium atoms and 38 per cent by zirconium atoms, then:

$$F_{hkl} = \left\{ 0.62 f_{\text{Ti}} + 0.38 f_{\text{Zr}} \right\} \left\{ 1 + e^{2\pi i} [(h + 2k)/3 + l/2] \right\} \quad (4)$$

and by substituting the values of f_{Ti} and f_{Zr} in (4) one obtains:

$$F_{hkl} = 10^{-12} \left\{ 0.62 (-0.38) + 0.38 (0.62) \right\} \left\{ 1 + e^{2\pi i} [(h + 2k)/3 + l/2] \right\} = 0$$

Therefore, the structure factor F of a random substitutional solid solution of titanium and zirconium metals containing 62 atomic per cent titanium and 38 atomic per cent zirconium or the solid solutions approaching this composition must be negligible. There should be no Bragg reflections in the neutron diffraction pattern of such an alloy. As shown in Figure 22, this indeed is the case.

The nuclei of metallic elements⁸ that are known at present to have negative scattering amplitudes are:

Element	f (10^{-12} cm)
Li	-0.18
Li ⁷	-0.25
Ti	-0.38
V	-0.048
Mn	-0.37
Ni ⁶²	-0.87
Sm ¹⁵²	-0.50

They may be combined, either as solvents or solute atoms, with other nuclei that possess positive scattering amplitudes to develop alloys that give zero structure factors for Bragg reflections. For example, nuclear scattering amplitude of nickel for thermal neutrons is 1.03×10^{-12} cm. An "isotopic alloy" may be developed by dissolving 45.9 atomic per cent of Ni⁶² in nickel. The condition that must be fulfilled, however, is that these alloys must be random substitutional solid solutions of the solvent and the solute atoms.

These alloys are extremely useful in constructing any device in which coherent scattering of thermal neutrons is not desired. For example, specimen holders for neutron diffraction studies, radiation shields for low temperature as well as high temperature work with thermal neutrons, etc., may be constructed.

⁸Bacon, G. E., Neutron Diffraction, Oxford, London (1955).

VI. EFFECTS OF IRRADIATION ON MATERIALS - ACTIVITY 5430-011. Neutron Flux Distribution and Wilkins Effect in Irradiation Specimens
(F. R. Taraba, S. H. Paine)

The radial and longitudinal distribution of thermal neutron flux within 1.00" and 0.50" diameter uranium rods, each separated into two lengths by a graphite spacer (0.300" and 0.100", respectively), has been measured for the regions adjacent to the spacers. The neutron flux distribution at the ends of the rods remote from the spacer and in regions unaffected by the spacer or rod ends has also been measured. The technique used is described briefly in a previous Quarterly Report (ANL-5489).

Figures 23 and 24 give the radial distributions of thermal neutron flux for a few locations within a 1.00" and 0.50" diameter natural uranium rod. The bottom curves are for the unperturbed regions of the rods, the center curves are for the rod faces next to the graphite spacers, and the upper curves are for the rod faces distant from the spacers. Each series of curves has been normalized to unit neutron flux on the rod axis for an unperturbed section of the rod.

Figures 25 and 26 give the longitudinal distributions of average cross sectional neutron flux for the above rods and spacers. The upper curves are for the rod ends adjacent to the graphite spacers and the lower curves are for the other ends. The lower curves are essentially those which would result for a very large or infinite graphite spacer. Each curve is normalized to unit average cross sectional flux at the rod faces.

The curves of Figures 23 and 24 have been obtained by a least squares analysis of the data obtained from a large number of foils and samples. It has been found that a quartic function can be made to fit the experimentally determined distributions very accurately.

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Figure 24. Radial Distribution of Thermal Neutron Flux in a 0.50" Diameter Uranium Rod.

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Figure 26. Longitudinal Distribution of Average Cross Sectional Thermal Neutron Flux in a 0.50" Diameter Uranium Rod.