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QUARTERLY REPORT
JANUARY, FEBRUARY AND MARCH, 1956

METALLURGY DIVISION

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June, 1956

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For The Atomic Energy Commission

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Chief, Declassification Branch

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QUARTERLY REPORT
JANUARY, FEBRUARY AND MARCH, 1956
METALLURGY DIVISION

ABSTRACT

Advanced Water Reactor Program - Activity 4102

The EBWR loading requires a total of 888 plates. It is anticipated that approximately 1000 plates will have to be produced to obtain the number of acceptable plates required for the loading. To the end of this quarter, 568 cladding billet cores acceptable with respect to chemical composition and physical soundness had been cast; this number represents 78% of the total number of cores cast. Approximately 75% of the Zircaloy-II stock required has been rolled, and about 55% of the cladding components required have been completely finished. The anticipated number of 495 cladding billets required for the thin (0.210") natural and enriched plates have been assembled, welded, sealed, and jacketed in steel. A total of 310 cladding billets have been rolled to fuel plates; of this number, 142 have been completely finished, and the remaining 168 are in the finish processing stages.

The stability of the equipment developed for measuring the clad thickness of EBWR fuel plates has been improved by placing the phototube and the anthracene scintillator crystals in an insulated box with a temperature regulation of the order of 0.1° F.

During the past quarter 622 EBWR core castings have been inspected by the ultrasonic through-transmission technique. About 87% of the castings were found acceptable for fabrication into plates; the remainder indicated the presence of porosity, blowholes, or pipe. The sensitivity of the equipment has been improved so that a defect 1/32" in diameter or larger can be detected and recorded.

Thoria-10 w/o urania enriched pellets in an aluminum-1 w/o nickel protection tube were examined after irradiation in a water loop in CP-5 at 230° - 270° C to a calculated depletion of 3.23% of the uranium atoms. The tube was only slightly distorted, but was heavily scaled with corrosion product. Upon removal of the tube the pellets were found to be fragmented, with the lead bonding material having penetrated the fractures in some places.

Fast Power Breeder Reactor Program - Activity 4104

A composite fuel slug of an uranium-2 w/o zirconium alloy, assembled from short castings by butt welding and encased in a stainless steel protection tube, was irradiated in CP-5 to an estimated maximum burnup

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of 0.77% of total atoms. After removal of the protection tube, the slug was in five pieces, but the individual sections retained excellent dimensional stability.

A series of alpha rolled uranium-1 and 2 w/o zirconium alloys was irradiated to burnups varying from 0.031 to 0.045 total atom per cent at temperatures from 125° to 160° C. The specimens were either "as rolled" or annealed up to 96 hours at 500°, 575°, and 625° C. All specimens were observed to shorten, whether they were annealed prior to irradiation or not. The rates of shortening were usually markedly increased by a two-hour anneal; longer annealing times tended to reduce the shrinkage rates. Higher annealing temperatures tended to produce higher shrinkage rates.

Aluminum-stabilized plutonium slugs for EBR-I have been cast, machined, and jacketed in 0.020" aluminum cans according to specifications mutually agreed upon by ANL and Rocky Flats. Some of the slugs had aluminum contents exceeding the 1.24 w/o upper limit. A total of 433 standard slug assemblies, 22 experimental slug assemblies, and 17 specimens for property measurements have been made.

Mean thermal expansion coefficients of some cast plutonium alloys in the temperature range 20° to 500° C were found to be as follows:

Pu-1.4 w/o Al	$+ 15.0 \pm 0.5 (x 10^{-6}/^{\circ}\text{C})$
U-20 w/o Pu-10.8 w/o Fission Elements,	$+ 15.2 \pm 0.6 (x 10^{-6}/^{\circ}\text{C})$
U-20 w/o Pu-5 w/o Mo	$+ 20.0 (x 10^{-6}/^{\circ}\text{C})$

General Reactor Development - Activities 4530 and 4540

Twenty-four Al-1 w/o Ni alloy plates were corrosion tested up to 540 hours in the ANL-MTR high temperature water loop, with water circulating at 250° - 260° C. Half of the total number of plates were in a portion of the loop protected from the neutron flux. The in-pile plates received exposures of up to 5×10^{19} nvt fast and 5×10^{20} nvt thermal flux. For short exposures, corrosion of all plates was quite uniform, being characterized by a finely pebbled texture on the surfaces. In-pile plates exposed for longer periods tended to develop a coarser "pock-marked" texture.

Tests of reducing agent additives indicated that H_3PO_2 at a pH of 3.4 significantly reduced the corrosion rate of an Al-0.9 w/o Ni alloy tested at 290° C. A few microscopic pits were noted on samples after more than 30 days' exposure. Tests are in progress to determine if the desirable effects can be retained at pH = 4.5.

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Production, Treatment, and Properties of Materials - Activity 5410-01

The major effort during the past quarter in the program on the measurement of the elastic constants of uranium has been devoted to the development of proper techniques to grind and polish flat, parallel, and distortion-free crystallographic faces suitable for high-frequency ultrasonic measurements. The technique tried involved the embedding of the crystal in a room-temperature setting plastic contained in a steel ring whose end faces are parallel within 0.0001" and grinding a properly oriented crystal face parallel to the reference faces of the ring. Metallographic grinding laps and a special specimen holder to maintain the axis of the mount normal to the lap were not entirely satisfactory, since difficulties were encountered in maintaining flatness of the lap. Attempts to change the alignment of the specimen holder to compensate for changes in the lap surface were not satisfactory. Other techniques for automatic grinding and polishing are under investigation.

In the problem on self-diffusion of uranium, the purification of the required highly depleted uranium has proceeded to the point where mock-up UCl_3 manufacture runs have been successfully completed and one batch of highly depleted UCl_3 has been made. A dummy material of the same chemical composition as the highly depleted uranium has been prepared which will be used for an electrolysis test run to test the feasibility of purifying the highly contaminated material by this method. An analytical procedure has been adopted for analyzing the removed diffusion layers, which involves solution of the grinding paper in HNO_3 , mixing with saturated $\text{Al}(\text{NO}_3)_3$, and extracting the uranium with acetate and water, and leaving the interfering ions in the $\text{Al}(\text{NO}_3)_3$ solution. Analysis of five duplicate samples yielded a reproducibility with a standard deviation of 1.3%, which is quite satisfactory.

The omega phase of the titanium-vanadium binary system has been found to be isostructural with the delta phase of the uranium-zirconium system. In both alloy systems the formation of these phases may be brought about by a relatively low temperature anneal of the quenched high temperature BCC phase. Both phases appear to be formed by a tripling in three directions of the small BCC unit cell; in the case of the omega phase in a Ti-15 w/o V alloy the lattice parameter of the tripled cell is approximately 1% larger than three times the parameter of the small BCC cell; in the uranium-zirconium alloys, there is a shrinkage of about 0.4%, which varies with composition.

The uranium-niobium-zirconium phase diagram has been determined up to 11 w/o Nb and 40 w/o Zr and a topical report is in preparation. X-ray diffraction patterns of a binary U-10.5 w/o Nb alloy quenched from 640°C indicated the coexistence of two gamma phases, which is in accord with the reported $\gamma_1 + \gamma_3$ two-phase region reported by Ames Laboratory from 8 to 45 w/o Nb. The course of this monotectoid has been traced into the ternary

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diagram and was found to move with decreasing temperature and increasing zirconium toward a critical point lying beyond the maximum niobium content of the alloys under investigation. At the critical point, the uranium-rich gamma phase (γ_1) and the niobium-rich gamma phase (γ_3) merge into a single gamma phase ($\gamma_{1,3}$).

In studies on the transformation kinetics of uranium-niobium alloys, a TTT curve has been determined metallographically for an uranium-4.9 w/o niobium alloy over the range 600° to 650° C.

In basic corrosion studies, an 1100 Al-0.9 w/o Ni alloy sample corroded for two days in water at 290° C analyzed less than 0.1 ppm H_2 after removal of the corrosion coating. An 1100 aluminum sample, similarly corroded, and with the corrosion coating removed, was found to contain 7.3 ppm H_2 , as compared with an initial H_2 content of only 0.6 ppm in the uncorroded stock. A series of 1100 aluminum samples given the same corrosion treatment, upon etching away various thicknesses of metal with a dilute HNO_3 -HF mixture, yielded hydrogen analyses which indicate that the corrosion hydrogen is apparently held within a few tenths of a millimeter from the surface, producing high local hydrogen concentration. These results clearly demonstrate the role of hydrogen penetration in the high temperature water corrosion of aluminum.

To study the relative cathodic protection effects of second phase intermetallic compounds in aluminum, the following intermetallic compounds were corrosion tested in 290° C water: $FeAl_3$, $NiAl_3$, $FeNiAl_9$, and $CuAl_2$. The penetration rates, however, were not large enough or different enough to explain the large differences in the corrosion behavior of some of the alloys containing these compounds. Nor were the cathodic polarization curves in degassed distilled water at 290° C significantly different for any of the compounds. However, the open circuit potential measured against corroded 347 stainless steel was -0.08 volts for the $NiAl_3$ and near -0.37 volts for the other compounds, indicating the $NiAl_3$ to be by far the most efficient cathode. These results do not offer any explanation for the need of a small amount of iron in the low aluminum-nickel alloys; the explanation based on the distribution characteristics of the second phase is still preferred.

In studies on the corrosion mechanism of zirconium, the extent to which oxide films dissolve on heating in a vacuum was measured by visual comparison of the interference colors. Oxide films of various thicknesses were obtained by anodizing in KOH. The rates of dissolution were studied as a function of time and temperature in the range 450° to 600° C. The amount of oxide dissolved at a given temperature was found to be a linear function of time; the rate of dissolution was constant and was independent of film thickness. A plot of dissolution rate ($\text{\AA}$ per unit time) vs. $\frac{1}{t}$ yielded a straight line, indicating a linear law of film dissolution. The disappearance of the oxide represents a uniform reduction at the metal-oxide interface, which would require a transfer of O^- from the oxide to the metal along with

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a simultaneous transfer of electrons from the metal to the oxide. As a result of these processes, the metal-oxide interface moves outward. The controlling factor may be either oxygen or electron mobility; the former process is much more likely since the electrical conductivity of the oxide becomes appreciable after short times even at relatively low temperatures.

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I. ADVANCED WATER REACTOR PROGRAM - ACTIVITY 4102

1. Manufacturing of EBWR Fuel Plates (R. E. Macherey, C. H. Bean, N. J. Carson, Jr.)

The manufacture of the fuel plates for the Experimental Boiling Water Reactor was started in the first quarter of 1956. The reactor loading requires a total of 888 plates. The plates are of two thicknesses and of two enrichments (0.7 w/o and 1.44 w/o U^{235}), as shown in Table I. The dimensions of the plates are presented in Table II. It is anticipated that approximately 1000 plates will have to be produced to obtain the number of acceptable plates required for the loading.

TABLE I

Fuel Plates Required for Loading of the EBWR

Plate Thickness (in.)	Number Required	
	Natural	Enriched
0.273	108	336
0.210	108	336

TABLE II

Dimensions of EBWR Fuel Plates

	Thickness (in.)	Width (in.)	Length (in.)
Fuel Plate (0.273")	0.273 $\begin{smallmatrix} + 0.006 \\ - 0.000 \end{smallmatrix}$	3.625 $\begin{smallmatrix} + 0.000 \\ - 0.005 \end{smallmatrix}$	54 $\pm 1/64$
Fuel Plate Core (0.273")*	0.233 $\begin{smallmatrix} + 0.012 \\ - 0.004 \end{smallmatrix}$	3.310 ± 0.030	51 $\pm 1/4$
Fuel Plate (0.210")	0.210 $\begin{smallmatrix} + 0.000 \\ - 0.006 \end{smallmatrix}$	3.625 $\begin{smallmatrix} + 0.000 \\ - 0.005 \end{smallmatrix}$	54 $\pm 1/64$
Fuel Plate Core (0.210")*	0.170 $\begin{smallmatrix} + 0.006 \\ - 0.008 \end{smallmatrix}$	3.310 ± 0.030	51 $\pm 1/4$

*Core is located symmetrically in plate.

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The manufacturing practice for the fuel plates may be divided into five separate steps as follows:

- a. Uranium Alloy Core Processing
- b. Zircaloy-II Cladding Component Processing
- c. Cladding Billet Assembly
- d. Roll Bonding and Heat Treatment of Plates
- e. Final Machining, Cleaning, and Inspection of Plates

A flow sheet depicting the detailed operations in each step of manufacture is presented in Figure 1.

a. Uranium Alloy Core Processing

The uranium alloy containing nominally 5 w/o Zr and 1.5 w/o Nb is being produced by dissolving the alloying elements in molten uranium. Uranium biscuit, zirconium sponge, and niobium pressed powder are the charge constituents. Melting is done in graphite crucibles 14-1/2" O.D. x 12-1/2" I.D. x 14" deep, with a bottom thickness of 1-1/2". A pouring hole 1/2" in diameter is provided in the center of the bottom of each crucible, and a graphite stopper rod 3/4" in diameter is used for sealing the pouring hole during melting.

The high temperature required for the solution of the niobium alloy addition coupled with the increase in the activity of the melt resulting from the zirconium addition causes rapid attack upon an unprotected graphite crucible. The high concentration of carbon resulting from this practice promotes the segregation and loss of the zirconium alloy addition. To protect the graphite crucible and stopper rod as well as the mold, a duplex ceramic coating is applied. The first coat, applied by brushing, is magnesium zirconate supplied by Titanium Alloy Manufacturing Company. This $\text{MgO} \cdot \text{ZrO}_2$ coating adheres tightly to the graphite and serves as an excellent base for the second coating. The second coat is thoria applied atop the $\text{MgO} \cdot \text{ZrO}_2$ by spraying. The thoria, -325 mesh, is sprayed as a water suspension. Because of the high temperatures employed, the magnesium zirconate is attacked by the melt, causing this wash to fail as a protective coating. The addition of the thoria coating reduces the rate of attack to a point where the coating will provide complete protection in a majority of the heats.

The charging of the melt constituents is an important aspect of the foundry practice. In order that the alloying additions go into solution readily, they must be placed at the bottom of the crucible. In addition, the uranium must be supported above the alloy level so that the alloy is not compacted by the heavy weight of uranium. For this purpose the uranium charge is supported above the alloy level by means of prealloyed uranium blocks which rest on the crucible bottom.

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Figure 1
MANUFACTURE OF FUEL PLATES FOR THE EXPERIMENTAL BOILING WATER REACTOR - FLOW SHEET

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The melting is done by induction in a vacuum ranging from 2 to 10 microns. The melting cycle consists of superheating to 1550° C for solution of the alloying elements, dropping the melt temperature to 1300° C to permit outgassing of the melt, and raising the temperature to 1475° C for pouring. The heat time is approximately 4-1/2 hours.

The melt is poured into a multicavity mold by means of a distributor. In this way several individual billet cores can be cast from a single large heat. Two sizes of mold cavities are being used: one, for the 0.210" thick plates, is 0.925" x 3.280" cross section x 15" deep; the other, for the 0.273" thick plates, is 1.285" x 3.315" cross section x 15" deep. The mold for the thin plate cores contains 12 cavities while the mold for the thick plate core contains 10 cavities. The charge weights required to fill the 12-cavity and 10-cavity molds are 148 and 170 kg, respectively. The cavities are cut in individual wedge-shaped sections of graphite which are held together top and bottom by tapered compression rings. The outside dimensions of the mold are 12-3/4" diameter x 17" high. The distributor which feeds the metal simultaneously into all mold cavities is shown in Figure 2, which also shows the disassembled mold and the crucible. The distributor fits the top counter-bore leak tight so as to be self-regulating; that is, when one cavity fills before the others, flow is stopped in this cavity and the other cavities continue to fill.

The mold is split for easy removal of the castings. The cavities are machined such that 0.030" per face is provided for grinding to thickness and 0.040" per side is provided for grinding to width. Excess length in the castings is provided for removal of shrinkage pipe and chemical samples. All heavy scrap is recycled.

The specifications for the composition range of the alloy are 1.26 to 1.74 w/o Nb and 3.5 to 6.5 w/o Zr. These specifications were established from nuclear considerations. The range of zirconium content, however, must be held much closer because of rolling characteristics of the alloy. The low and high limits on zirconium content have been set at 4.5 and 5.5 w/o.

After removal from the mold, the castings are sawed to rough length, and chemical samples are taken from top and bottom of two of the cores. The cores are then ground to finished thickness and width to remove mold marks which interfere with the supersonic testing which follows.

The cores are inspected for soundness by a supersonic through-transmission technique, using a standard to preset the equipment. Sound cores are held for chemical analyses check, and unsound cores are recycled.

Cores which are sound and within the chemical specifications are machined to length by milling. Dimensions of the cladding billet cores for the two sizes of billets are given in Figure 3.

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Figure 2. Coated Graphite Mold and Crucible Used in Producing Uranium Alloy Cores for the EBWR.

Crucible, cover, and stopper rod grouped at right. Mold partially disassembled shown at left. Mold bottom plugs shown in front of mold. Distributor in position at top center of mold.

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Figure 3. EBWR Cladding Billet Assembly and Dimensions.

CLADDING BILLET DIMENSIONS		
	THIN BILLET (210 Plate)	THICK BILLET (273 Plate)
A	11.828" ± 0.010"	11.802" ± 0.010"
B	3.667" ± 0.003"	3.695" ± 0.003"
C	0.126" ± 0.002"	0.126" ± 0.002"
D	0.850" ± 0.002"	1.205" ± 0.002"
E	0.251" ± 0.002"	0.251" ± 0.002"
F	10.440" ± 0.010"	10.300" ± 0.010"
G	3.115" ± 0.003"	3.133" ± 0.003"
H	0.833" ± 0.002"	1.181" ± 0.002"
I	3.177" ± 0.003"	3.195" ± 0.003"
J	1.062" ± 0.003"	1.250" ± 0.005"
K	0.850" ± 0.002"	1.205" ± 0.002"

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Vapor degreasing, wet abrasive blast cleaning to remove oxidation, blast washing with water, distilled water rinse, absolute alcohol rinse, and vacuum drying and storage readies these uranium alloy billet cores for assembly.

b. Zircaloy-II Cladding Component Processing

The Zircaloy-II stock from which the cladding components are made is purchased from commercial producers in the form of double arc melted ingot produced by the consumable electrode process. Most of the ingots are 12" in diameter, weighing about 1000 pounds. Ingots are conditioned by turning when received.

Initially the Zircaloy-II ingots are forged at approximately 925° C to slabs 3" x 9" cross section x 13' long. Ingots are heated in a gas fired furnace, and forging is done as rapidly as possible on a 4000-pound steam hammer.

The forged slabs are then cut into 13" lengths suitable for rolling, and approximately 1/16" is removed from the two faces by machining to remove ingot and forging defects. The blocks are inspected for surface defects using the Dycheck method (Turco Products, Inc.). Unsound blocks are remachined for removal of defects; in some of the material it is impossible to remove all defects.

Following scalping and inspection, the blocks are hot rolled at 850° C to an appropriate thickness for finishing. The material for end plugs is rolled to 1-5/16" and 1-3/8" for thin and thick billets, respectively (see Figure 3 for end plug dimensions). This stock is machined all over so that no further rolling is necessary. The stock for the cover plates and side plates is hot rolled to 50% oversize in thickness.

The hot rolling is followed by an absolute removal of surface contamination. This operation is performed in a Vapor Blast Machine equipped for automatic operation. Blasting is done by driving a water suspension of 100 mesh Al_2O_3 onto the work by high velocity air by means of a suitable gun. Completeness of cleaning is assured by extensive although not complete microscopic inspection. Plates that do not clean up thoroughly are recycled. The cleaning rate on the 9" wide sheet is 5"/minute.

After the wet abrasive blasting operation, the plates are pickled in 35% concentrated HNO_3 and 5% concentrated HF to uncover minor surface defects. Minor defects are removed by grinding with carbide burrs.

The final rolling operation is carried out at approximately 600° C. This 600° C rolling has replaced cold rolling because the reduction possible at room temperature is so low (approximately 10%) that minor surface irregularities resulting from hot rolling are not removed. At

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600° C the reduction possible is considerably greater than at room temperature; and the atmospheric contamination that results at this temperature (providing heating time is kept within reason) is very thin and tightly adherent. This contamination does not mar the surface finish of the rolled plate as does the voluminous products formed at the higher rolling temperature. The cover plate stock for all billets is rolled to $0.127'' \pm 0.002''$; the side plate stock is rolled to $0.252'' \pm 0.002''$.

A second wet abrasive blasting operation follows the 600° C rolling. The complete removal of all traces of contamination is absolutely essential to successful bonding during the fuel plate rolling which follows. The blasting is done with 400 mesh Al_2O_3 in another automatic machine. Microscopic examination is done to provide reasonable assurance of cleanliness.

After the abrasive blast cleaning, cladding components are sheared. The cover plates are sheared to final length and oversize in width to allow for machining. The side plates are sheared oversize in width and length for machining to these two final dimensions. Final width dimensions of the cover plates are developed by straddle milling. The side plates are planed or straddle milled to width and milled to length. Degreasing follows the machining operations.

The cladding components after machining and degreasing are prepared for billet assembly by acid pickling in boiling concentrated HNO_3 with 1% concentrated HF added. Approximately 2 mils are removed from the thickness of the cover and side plate components; about 1 mil is removed from the end plugs. The final pickling brings the components to the dimensions shown in Figure 3. Acid is removed in four separate water rinses. Formation of water stains on the plates is prevented by a final rinse in distilled water before drying. Drying is accomplished in an oven operating at 150° C. Components are then stored until used.

The final billet sealing operation (closing the purge opening) requires the use of a seal pin and an electrode made of Zircaloy-II. These items are produced by forging an ingot to 1-1/2" diameter bar at 925° C. The 1-1/2" diameter bar is rolled to 7/8" diameter at 850° C for electrodes; the seal pins (see Figure 3) are produced by hot rolling to 3/8" diameter and finishing to 1/4" diameter by swaging. Seal pin design is developed by turning.

c. Cladding Billet Processing

For the rolling billet assembly the core and clad components are placed in their respective positions and pressed together by a pressure of 50 tons applied normal to the cover plates and 4 tons applied normal to the side plates by means of water cooled, copper alloy platens. The equipment used is shown in Figure 4.

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Figure 4. Equipment Used for Pressing, Purging, and Welding Zircaloy-II Cladding Components Around Uranium Alloy Billet Core.

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Argon purge tube extends from near end of billet shown between vertical and horizontal press platens.
Inert gas arc welding torches shown in welding position.

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Air is removed from inside of the billet by purging with argon while the components are under reduced pressure to permit escape of the air and purge gas. Following purging, full pressure is applied and all seams in the Zircaloy-II are closed by the inert gas arc welding method without the addition of filler rod. Weld penetration is approximately $1/16"$. At this time the billet is completely sealed with the exception of the purge opening.

The sealing operation is completed by evacuation and welding of a seal pin. The billets in groups of twelve are placed in the fixture shown in Figure 5, and are inserted into the vacuum and welding chamber shown in Figure 6. In this equipment the billets with seal pins removed are subject to three evacuation and air-flushing cycles to reduce the argon entrapped in the billets to a very low level; this is necessary to prevent blister formation in the rolled fuel plate. Before welding the pressure of the chamber is reduced to a low level (0.1 micron) after which seal pins, pressed into the electrodes, are inserted into the mating purge opening in the billet ends. The seal pins are then welded to the billet end plug under vacuum. The welding cycle is performed in three steps. First, the billet end plug in the vicinity of the purge opening and the seal pin are heated 10 seconds with a current flow of 1000 amps; second, the power level is then raised to approximately 1350 amps which melts the seal pin just above the end plug establishing the arc; and third, the arc is permitted to persist for a predetermined 2 seconds which consumes a portion of the electrode and deposits weld metal in the circular groove surrounding the purge opening. Weld failure rate is very low. The billet now is completely sealed. Clean surfaces are presented for bonding; and the bonding interfaces are protected from contamination by outgassing of the steel can.

Rolling billet preparation is completed by fitting the cladding billet into the steel cans and the weld closure of the steel can (Figure 7). Welding of the steel is accomplished in two steps. First, with the can halves pressed together, the joints are sealed by a deposit of Oxweld No. 32, CMS filler rod in the root of the "V" by the Heliarc process; and second, the "V" is completely filled by conventional arc welding with Lincoln Jetweld No. 2 rod. The Heliarc welding is done to prevent flux from entering the can during the arc welding.

d. Roll Bonding and Heat Treatment

Bonding of the uranium alloy core to all Zircaloy-II components and the bonding among the Zircaloy-II components are accomplished by heat, reduction, and pressure in the equipment shown in Figure 8. The billets, in groups of three, are preheated in an electric resistance furnace shown in the lower right side of Figure 8. This preheating cycle to $850^{\circ}\text{C} \pm 10^{\circ}\text{C}$ is completed in two hours. The billets, one at a time, are then rolled from right to left and entered three abreast in the furnace shown at left in Figure 8. Subsequent rolling is done in a cycle of two passes per reheat, with

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Figure 5. Fixture for Positioning and Holding Cladding Billets for Evacuation and Vacuum Welding of Seal Pins.

Electrodes with seal pins attached shown at top of billets. Top cover, through which electrode extension tubes protrude, forms a vacuum seal with chamber shown in Figure 6.

ANL Negative No. 106-2258

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Figure 6. Chamber with Auxiliary Equipment Used for Evacuation
and Vacuum Welding of Seal Pins.

ANL Negative No. 106-2261

Figure 7. EBWR Billet Jacket Assembly and Dimensions.

BILLET JACKET ASSEMBLY

① BILLET JACKET
Two REQD

BILLET JACKET DIMENSIONS (INCHES)

	THIN BILLET (0.210 PLATE)	THICK BILLET (0.273 PLATE)
<u>A</u>	0.550 ± 0.005 -0.000	0.728 ± 0.005 -0.000
<u>B</u>	3.687 ± 0.005 -0.000	3.705 ± 0.005 -0.000
<u>C</u>	3.680 ± 0.005 -0.000	3.698 ± 0.005 -0.000
<u>D</u>	1.100 ± 0.005 -0.000	1.455 ± 0.005 -0.000

JACKET PLUGS
Two REQD

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Figure 8. General View of 17" x 24" Mill, Furnaces and Auxiliary Equipment Used for Rolling EBWR Fuel Plates.

the exception of the last pass, first pass from left to right, and second pass from right to left. The reheating period is 20 minutes in the furnace at $850^{\circ}\text{C} \pm 10^{\circ}\text{C}$. The final rolling is a single pass from left to right. Rolling is done at 125 feet/minute. The rolling schedule used for the bonding of the fuel is presented in Table III. Movement of plates from furnace to mill and back to furnace is accomplished by the power-driven roller tables shown.

TABLE III
EBWR Billet Rolling Schedule

Pass No.	Roll Gage (in.)	Reduction (in.) (%)	Material Gage (in.)	Remarks
1	2.300	0.060 2.5		Reheat
2	2.070	0.230 10.0		
3	1.895	0.175 8.5		Reheat
4	1.700	0.195 10.3		
5	1.500	0.200 11.8		Reheat
6	1.300	0.200 13.3		
7	1.120	0.180 13.8		Reheat
8	0.960	0.160 14.3		
9	0.830	0.130 13.5		Reheat
10	0.690	0.140 16.8		
11	0.570	0.120 17.4		Reheat
12	0.475	0.095 16.7	0.480-0.483	

Immediately following rolling the plates are placed three at a time between platens of the press shown in Figure 9 for flattening while hot, and are held under pressure until cooled well below color temperature.

Upon cooling, the plates are dimensioned and some of the excess steel is trimmed. Enough steel, however, is allowed to remain on the fuel plate to serve as protection during the isothermal heat treatment. The heat treatment which follows, consists of a solution treatment at $820^{\circ}\text{C} \pm 10^{\circ}\text{C}$, followed immediately by an isothermal quench and 24-hour hold in lead at $640^{\circ}\text{C} \pm 10^{\circ}\text{C}$. Air-cooling of a stack of seven plates separated by asbestos sheets follows the removal from the lead.

Figure 9. 50 Ton Hydraulic Straightening Press Used to Hot Flatten Rolled EBWR Fuel Plates.

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The steel can is now removed from the fuel plate by shearing along a line approximately 1/16" away from the sides of the fuel plate and peeling the steel from the plate faces. Fuel plates are next dimensioned in length, width, and thickness.

e. Final Machining, Cleaning and Inspection of Fuel Plates

Location of the ends of the core with respect to the ends of the Zircaloy-II cladding is necessary in the machining of plates to length so that the end clad will be equal at both ends of the plate (core centered lengthwise in the plate). The core location is determined by radiographing both ends of the plate.

A stress relieving operation is performed following end radiography. This stress relief consists of heating groups of plates in air in an electric furnace operating at 400° C for 8 hours followed by a furnace cool.

Machining of plates to width by straddle milling and to length by milling completes the fabrication. Dimensional inspection, total radiograph for verification of minimum side and end clad thickness readies the plates for final cleaning.

The fuel plates are then wet abrasive blasted with 400 mesh Al_2O_3 at a speed which removes approximately 0.001" from the plate thickness. This operation removes all stains so that the action of the acid pickle which follows will be uniform.

Acid pickling of the plates completes the manufacturing procedure. The plates are suspended horizontally in an acid bath containing by volume 35% concentrated HNO_3 , 5% concentrated HF, and 60% water. The acid bath is operated in the temperature range 36° to 40° C. The plate is moved in the bath to prevent pitting type of attack. From 3 to 4 mils of cladding are removed from the plate thickness in the pickling operation. Three separate tap water rinses and two distilled water rinses (final rinse, boiling distilled water) follow the pickling operation.

The finished plates are dimensioned, inspected visually for gross defects, and wrapped for transfer for corrosion testing.

f. Status of Manufacture

At the end of this quarter 568 cladding billet cores, acceptable with respect to chemical composition and physical soundness, had been cast. The above number represents 78% of the total number of cores cast.

The homogeneity of the heats has steadily increased during the production of castings. The soundness of the castings made has also increased.

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Approximately 75% of the Zircaloy-II stock required for billet components has been rolled. About 55% of the cladding components required have been completely finished.

The anticipated number of 495 cladding billets required for the thin (0.210") natural and enriched plates have been completed (assembled, welded, sealed, and jacketed in steel). A total of 310 cladding billets has been rolled to fuel plates; and of this number, 142 plates have been completely finished, with the remaining 168 in the finishing processes.

Complete data have not as yet been compiled for the calculation of plate survival value; however, one plate of the first group of 18 that were corrosion tested in 290° C (550° F) water failed almost immediately. This plate apparently failed because of defects in the Zircaloy-II cover plate.

2. Measurement of Clad Thickness of EBWR Fuel Plates (W. J. McGonnagle, W. N. Beck)

The phototube and anthracene scintillator crystals used in the clad thickness measuring equipment are sensitive to temperature fluctuations. The stability of the equipment has been improved by placing the phototubes and crystals in an insulated box. Water from a constant temperature bath is circulated around the phototube and crystals. Temperature regulation is of the order of 0.1° F. The operating temperature of the water bath is a few degrees above room temperature to provide maximum stability.

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

During the past quarter 622 core castings were inspected by the ultrasonic (5 Mc) through-transmission technique.

Approximately 87% of the castings were considered acceptable for fabrication of EBWR fuel elements. The remainder indicated the presence of porosity, blowholes or pipe.

The linear scanning speed has been increased from 1.8" per minute to 6.4" per minute. The pulse repetition rate of the ultrasonic generator has been increased from 60 to 180 per record. The sensitivity of the equipment was improved so that a defect 1/32" in diameter or larger can be detected and recorded.

4. Examination of EBWR Ceramic Prototype Fuel Elements Irradiated in CP-5 (F. L. Brown, S. H. Paine)

Examinations of ThO₂-10 w/o UO₂ (enriched) fuel pellets irradiated in a water loop in the CP-5 reactor by the Reactor Engineering Division have continued. An Al-1 w/o Ni protection tube containing four pellets,

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irradiated at 450° - 515° F (230° - 270° C) to a calculated depletion of 3.23% of the uranium atoms, was examined before and after removal of the protection tube. In contrast to a previous test, the tube was only slightly distorted. However, it was heavily scaled with corrosion product and rust, as shown in Figure 10. Upon removal of the tube the pellets were found to be fragmented in characteristic manner. The lead bonding material entered the fractures in some places, as shown in Figure 11.

5. Borax-IV Fuel Fabrication (J. H. Handwerk)

A series of fired ThO_2 pellets was made for the Reactor Engineering Division for measurements of the danger coefficient to determine the resonance escape probability. Also, 343 tubes of pressed but unfired $3/4$ " pellets, containing 109.2 kgs of ThO_2 , were fabricated for use in experiments to determine the Fermi age of ThO_2 and water mixtures.

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Figure 10. Surface of Al-1% Ni Protection Tube After Irradiation.

Macro 19183

6-X

View of random area illustrating heavy scale formed in reactor autoclave.

Figure 11. Portion of Ceramic Pellet from Prototype Element.

Macro 19198

6-X

Fractured portion of a pellet with lead globules in cracks.

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II. FAST POWER BREEDER REACTOR PROGRAM - ACTIVITY 4104

1. Examination of Irradiated EBR-II Prototype Fuel Element (F. L. Brown, S. H. Paine)

A composite fuel slug of U-2 w/o Zr, irradiated in CP-5 reactor to an estimated maximum burnup of 0.77% of total atoms, was examined for the Reactor Engineering Division. The original length of the slug was approximately 14-1/4" and was assembled from short castings by butt welding. Assembly subsequently was welded into a stainless steel protection tube. After removal of the protection tube the slug was in five pieces, some fractures ascribed to handling mishaps and other fractures of unknown origin. The individual sections retained excellent dimensional stability; the surfaces were finely textured. Circumferential tool marks were still visible in some places, as shown in Figure 12.

2. Effect of Alpha Annealing on the Irradiation Growth Rates of Wrought Uranium-Zirconium Alloys (J. H. Kittel, S. H. Paine)

Irradiation results obtained on uranium-zirconium alloys prepared by KAPL showed an unexpected shortening of specimens subjected to irradiation (ANL-5257). The specimens which showed this effect had all been annealed for 48 hours at 575° C after initial alpha rolling. Previous results on unannealed specimens of similar alloys had not shown negative growth under irradiation. It appeared, therefore, that the long anneal may have been responsible for the shortening observed on the KAPL material.

In order to determine the influence, if any, of various alpha annealing treatments on alpha rolled uranium-zirconium alloys, irradiation specimens were made up of the materials shown in Table IV. Specimens from each bar were annealed for times ranging from 0 to 96 hours at temperatures of 500°, 575°, and 625° C. They were then placed in NaK capsules and irradiated to burnups ranging from 0.031 to 0.045 total atom per cent at temperatures ranging from 125° to 160° C.

Shrinkage rates of the specimens under irradiation are shown in Figures 13 through 18. All specimens were observed to shorten, whether they were annealed prior to irradiation or not. Although in many cases the effect of annealing time and temperature appeared to be only random, some general trends are apparent. For example, the rates of shortening were usually markedly increased by a 2-hour anneal, whereas the longer annealing times often tended to reduce the shrinkage rates. It was also observed that the higher annealing temperatures generally tended to produce higher shrinkage rates.

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Figure 12. EBR-II Prototype Fuel Slug After 0.77% Total Atom Burnup.

Macro 18460

4-X

Note circumferential tool marks still visible on surface of the fuel.

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Figure 13. Effect of Annealing on the Irradiation Shrinkage Rate of Bar 3B1.

Figure 14. Effect of Annealing on the Irradiation Shrinkage Rate of Bar 4B4.

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Figure 15. Effect of Annealing on the Irradiation Shrinkage Rate of Bar L-40B-1.

Figure 16. Effect of Annealing on the Irradiation Shrinkage Rate of Bar L-42B-1.

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Figure 17. Effect of Annealing on the Irradiation Shrinkage Rate of Bar L-52B-1.

Figure 18. Effect of Annealing on the Irradiation Shrinkage Rate of Bar L-53B-1.

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TABLE IV

Uranium-Zirconium Alloy Bars Used for Irradiation Specimens

Bar No.	Zr, w/o	Description
3B1	1	Cast by KAPL, rolled at 565° C by Battelle.
4B4	2	Cast by KAPL, rolled at 565° C by Battelle.
L-40B-1	1	Made at ANL, rolled at 600° C.
L-42B-1	2	Made at ANL, rolled at 600° C.
L-52B-1	1	Made at ANL by coreduction, rolled at 600° C.
L-53B-1	2	Made at ANL by coreduction, rolled at 600° C.

3. Plutonium Fuel Elements for EBR-I (L. R. Kelman)

The plutonium fuel elements for EBR-I were produced at Rocky Flats and delivered to H. V. Lichtenberger at Arco, Idaho. Rocky Flats submitted a report (CD55-1936) in which they described methods used as well as the problems they encountered in casting, canning, and inspecting these fuel elements.

Aluminum-stabilized plutonium slugs were cast (by a double cast cascade method), machined to 0.345" diameter by 3.75" long, and jacketed by drawing on a 0.020" wall aluminum can and motor arc welding the aluminum cap. A total of 433 standard slug assemblies, 22 experimental slug assemblies, and 17 specimens for property measurements were prepared.

In general, the specifications that had been mutually agreed upon by ANL and Rocky Flats were satisfactorily met. Some of the slugs had aluminum contents exceeding the 1.24 w/o upper limit, but test results to date do not show any deleterious effects attributable to this. The canned fuel elements were required to pass freely through a 0.402" diameter full length gauge, which they all did. However, there was sufficient weld overhang in some cases to cause concern about possible galling on removal from the close-fitting stainless steel fuel tubes after irradiation. This is easily remedied by die forming the weld to reduce overhang since the weld is extremely ductile and easy to work.

A plutonium specimen containing 1.4 w/o aluminum was found to have a linear expansion coefficient of $15 \times 10^{-6}/^{\circ}\text{C}$ in the range of 20° to 500° C. Thermal cycling tests are now in progress; after metallographic and thermal conductivity studies are completed, a final program report will be prepared.

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4. Plutonium Elements for ZPR-III (L. R. Kelman)

Three potential fabricators of plutonium for ZPR-III have been approached - Rocky Flats, Hanford, and Los Alamos. All three have indicated an interest in making the plutonium elements. Though Los Alamos was the least anxious to take on a production job, they are by far the best qualified.

Several alloys containing plutonium have been considered for these elements. They include: (1) uranium-25 w/o plutonium alloy, (2) higher plutonium-uranium alloy, (3) unalloyed plutonium, (4) fully stabilized plutonium, and (5) partially stabilized plutonium.

The information the plutonium loading is intended to yield appears now to be obtainable from a much smaller amount of plutonium than was originally intended. A 5 to 10 kg plutonium loading may suffice (instead of 175 kg), in which case the U-25 w/o Pu alloy with a third element added to improve the properties will be used to make the elements in the ANL plutonium facilities. If, however, the full 175 kg plutonium loading is still desired in ZPR-III, Los Alamos will be approached about fabricating the elements from fully stabilized plutonium alloy. They are not set up at present for, nor are they enthusiastic about working with, the uranium-plutonium alloys.

5. Expansion Coefficients of Some Plutonium Alloys (R. J. Dunworth, L. R. Kelman)

Some preliminary studies were made to determine expansion coefficients of the following alloys: (1) Pu-1.4 w/o Al, (2) U-20 w/o Pu-10.8 w/o fission elements, * and (3) U-20 w/o Pu-5 w/o Mo. One alloy of each analysis was tested in the as cast condition. The specimens were 1/2" long and 1/8" diameter. The specimens were heated from 20° to 530° C at a rate of 4° C per minute. The mean expansion coefficients were calculated for the range 20° to 500° C, and are shown in Table V.

TABLE V

Expansion Coefficients of Some Plutonium
Alloys from 20° to 500° C

Alloy	Expansion Coefficient $\times 10^{-6}/^{\circ}\text{C}$	No. of Runs
Pu-1.4 w/o Al	15.0 ± 0.5	2
U-20 w/o Pu-10.8 w/o Fission Elements	15.2 ± 0.6	4
U-20 w/o Pu-5 w/o Mo	20.0	1

Succeeding runs of these specimens resulted in somewhat higher expansion coefficients. A study of the influence of homogenization is now in progress, and somewhat higher coefficients are anticipated than those shown in the table.

*4.3 w/o Ru, 2.8 w/o Mo, 2.5 w/o Pd, 0.7 w/o Rh, and 0.5 w/o Zr; total = 10.8 w/o - nominal concentrations.

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III. GENERAL REACTOR DEVELOPMENT - ACTIVITIES 4530 AND 4540

1. Examination of Aluminum-Nickel Alloy Plates from Corrosion Test in the ANL-MTR Water Loop (F. L. Brown, S. H. Paine)

Twenty-four Al-1 w/o Ni alloy corrosion test plates were examined after irradiation in the ANL-MTR high temperature water loop. Half of the total number of plates were in a portion of the loop protected from the neutron flux. Water was circulated at 485° - 500° F (250° - 260° C) for periods up to 540 hours. The in-pile plates received exposures of up to 5×10^{19} nvt fast and 5×10^{20} nvt thermal flux. Specimens were removed in pairs so that exposure times were duplicated for plates in and out of the neutron flux.

For short exposures, corrosion of all plates was quite uniform, and surfaces had a finely pebbled texture, as illustrated by Figure 19. In-pile plates exposed for the longer periods, however, tended to develop a coarser "pock-marked" texture as illustrated by Figure 20.

2. High Temperature Aqueous Corrosion of Aluminum Alloys (W. E. Ruther, G. Dragel)

During the past quarter, corrosion rates were determined at 290° C (~30 days) for two alloys which had appeared slightly better in short tests than the reference alloy (1 w/o Ni in commercially pure aluminum). Also, solutions of possible reducing agents were tried, since experience with commercially pure aluminum at 200° C (ANL-5500) had indicated that oxidizing agents were undesirable. Spectrophotometer tests indicated that one of the possible reducing agents, H_2SO_3 , was completely destroyed while slowly passing through the autoclave; the other, H_3PO_2 , maintained its output concentration at about 70% of the input. Results of the corrosion tests are given in Table VI.

As indicated in column 3, only the H_3PO_2 acid significantly reduced the corrosion rate. The corrosion samples had a thin adherent coating with a slight sheen after 33 days' exposure. A few microscopic pits were noted on the samples with more than 30 days' exposure. A test with the same acid at pH 4.5 is now under way to see if the desirable effects can be retained while eliminating the pitting.

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Figure 19. Al-1 w/o Ni Plate After 200 Hours' Exposure in MTR Flux.

Macro 18978

34-X

Figure 20. Al-1 w/o Ni Plate After 540 Hours' Exposure in MTR Flux.

Macro 18987

34-X

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TABLE VI

Corrosion of Aluminum Alloys at 290° C

Alloy	Condition	Rate of Metal Loss After Initial Period (mdd)	Estimated Intercept (mg/cm ²)
1100 Al + 0.9 w/o Ni ⁽¹⁾	Distilled H ₂ O	3.3	0.9
Al + 1 w/o Ni + 0.3 w/o Fe + 0.15 w/o Mn; (Alloy A-192)	Distilled H ₂ O	3.5	1.5
Al + 1 w/o Ni + 0.2 w/o Ti (Alloy A-193)	Distilled H ₂ O	2.4 ⁽²⁾	2.0
1100 Al + 0.5 w/o Ni ⁽¹⁾	H ₂ SO ₄ - pH 3.5	2.0	0.4
1100 Al + 0.9 w/o Ni	H ₃ PO ₂ - pH 3.4	0.5	0.3
1100 Al + 0.9 w/o Ni	H ₂ SO ₃ - pH 3.5	2.8	0.2

(1) Values previously reported; all rates in mg/dm²-day; "1100 Al" is new designation for "2S Al."

(2) Estimated from weight gains; normal stripping technique did not remove oxide.

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

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

The main effort on this program during the past quarter has been directed to the development of proper techniques to grind and polish flat and parallel crystallographic faces suitable for high frequency ultrasonic measurements. Some of the techniques tried were as follows. The single crystals, having diameters in the order of 0.20 to 0.21", are mounted in a room temperature setting plastic which is surrounded by a 1" diameter steel ring whose end faces are parallel within 0.0001". The crystal is oriented so that the desired crystallographic plane is parallel to the end faces of the steel ring. The technique for attaining this orientation is as follows: the unmounted crystal is rotated on a goniometer so that the desired crystallographic plane is parallel to a flat reference plane, as determined by Laue X-ray back-reflection photograms; the steel ring is then placed over the crystal so that its end faces are parallel to the reference plane and the liquid plastic is poured into the assembly and allowed to harden without disturbing the crystal orientation. One face of the mount is then ground and polished by metallographic techniques to prepare a flat plane on the crystal which is parallel to the opposite reference face of the steel ring. The opposite face is then prepared in the same manner, using the polished face as a reference plane. The grinding is continued to produce specimens approximately 1/8" thick. After both surfaces have been mechanically polished the worked surfaces are removed by electropolishing.

The grinding and polishing must be maintained normal to the central axis of the specimen mount. For this purpose, attempts have been made to use an ordinary metallographic grinding lap fitted with a special specimen holder. Although the axis of the mount is maintained vertical as the specimen traverses the rotating lap, some difficulty has been encountered in maintaining flatness of the lap. Attempts have been made to overcome this difficulty by changing the alignment of the specimen holder to compensate for changes in the lap surface. This procedure, however, was unsatisfactory in a number of respects, and other techniques for automatic grinding and polishing are being investigated.

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

Refining of the Highly Depleted Uranium: Calculations have been made which show that the use of uranium highly depleted in U^{235} is a necessary requirement for self-diffusion studies of alpha uranium, in view of the expected small value of the diffusion coefficient. The available highly depleted material is highly contaminated (approximately 5400 ppm impurities by weight), and must be purified before it can be used in the present studies.

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The apparatus for the production of UCl_3 has been modified to include some new safety features. Mock-up UCl_3 manufacture runs have been successfully completed and one batch of highly depleted UCl_3 has been made. A dummy material of the same chemical composition as the highly depleted uranium has been prepared, and electrolyses using this material for anodes are being started to test the feasibility of purifying such highly contaminated material by this method.

Analysis of Diffusion Layers: The following analysis procedure has been adopted for analyzing the total uranium content of a removed diffusion layer. The uranium is removed from the grinding paper by dissolution in 40% HNO_3 followed by several H_2O washes. The resulting solution is filtered and the volume is reduced by evaporation. An aliquot of this solution is mixed with a solution saturated in $\text{Al}(\text{NO}_3)_3$, the uranium is extracted with ethyl acetate and back extracted with water,¹ leaving the interfering ions (dissolved from the grinding paper) in the $\text{Al}(\text{NO}_3)_3$ saturated solution. The extractant is analyzed for uranium by the thiocyanate method.² To test the reproducibility of this procedure, five duplicate samples have been analyzed; a standard deviation of 1.3% was obtained, which is quite satisfactory.

Machining of Diffusion Layers: The grinding machine being built at the Institute for the Study of Metals, University of Chicago, and which we hope to use for preliminary tests, is not yet finished. In the meantime, we are experimenting with producing flat surfaces by hand grinding and measuring the thickness of the removed layers by means of an optical flat.

3. The Delta Phase in the Uranium-Zirconium System (M. H. Mueller)

As suggested in the last quarterly report, there may be phases in other binary alloy systems, such as the omega phase found in many titanium binary alloys, which may be isostructural with the delta phase found in the uranium-zirconium system. It is apparent that there are a number of similarities between these two phases. Although the remarks in regard to this comparison will be made more specifically between the uranium-zirconium binary and the titanium-vanadium binary, there is good evidence that there are a large number of intermetallics of this type. Similarities in such alloys would not be too surprising since these alloys might be considered as involving the elements titanium, zirconium, and possibly hafnium in the IV A Group of elements, all of which have a hexagonal low temperature form and a body centered cubic high temperature form.

¹Robert P. Larsen, ANL, CEN, Private Communication.

²Carl E. Crouthamel and Carl E. Johnson, "Spectrophotometric Determination of Uranium by Thiocyanate Method in Acetone Medium," Anal. Chem. 24, 1780, (November 1952).

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Both the delta and omega phases have been previously described as hard brittle phases.

In both binary systems there is a high temperature body centered cubic phase which may be described as a solid solution phase of the body centered cubic high temperature form of titanium or zirconium. This high temperature BCC phase may be retained by rapidly quenching alloys of the proper composition. The formation of the delta or omega phases may be brought about by a relatively low temperature anneal of these quenched alloys. Both phases appear to be formed by a tripling in three directions of the small BCC lattice, which is probably the result of an ordering of the atoms in the various sites.

In the case of the omega phase found in the Ti-15 w/o V alloy, the lattice parameter of the tripled cell is approximately 1% larger than three times the parameter of the small body centered cubic cell. However, in the delta phase found in the uranium-zirconium alloys studied to date, there is a shrinkage of something less than 0.4% which varies with composition. This difference in the relative change of parameter when forming the tripled cell may account for the fact that it seems to be easier to form a single delta phase alloy in the uranium-zirconium system than a single omega phase alloy in the titanium-vanadium system.

The X-ray diffraction powder patterns of the delta and omega phases appear to be similar in regard to relative position of lines and intensities. To date there has been no displacement of line positions in the omega patterns from that expected for the large cell as had been previously observed³ in some room temperature patterns of the delta phase.

It was also found that it is possible to partially transform the small body centered cubic high temperature phases to the larger or ordered cell by the proper heat treatment. This was indicated by the presence of very diffuse lines on the powder patterns from both types of alloys. The relative positions of the first few diffuse lines which appeared in both the uranium-zirconium and titanium-vanadium systems were the same.

It is also interesting to note that for some time the omega phases in the titanium alloys have been considered unstable phases which decompose with time at relatively low temperatures. In the case of the titanium-vanadium binary system, the omega decomposes to alpha titanium plus the beta phase, which is the solid solution body centered cubic phase of vanadium. The question of the stability of the delta phase found in the uranium-zirconium system has been under discussion for some time. In view of the possible similarity between the omega and delta phases, a further study of the possible correlation of the stability of these alloys should be of interest.

³Mueller, M. H., "The Delta Phase Found in the Uranium-Zirconium Alloys," *Acta Crystallographica* 8, 849-50, (December 1955).

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4. Transformation Kinetics of the Uranium-Niobium Alloys (A. E. Dwight)

The Time-Temperature-Transformation curve for an alloy of U-4.9 w/o Nb has been determined over the range 600° to 650° C. The line representing time for initiation of transformation as determined by metallographic examination is shown in Figure 21. The curve was developed for conditions of interrupted quenching by transferring specimens from a furnace at 800° C to a furnace at the transformation temperature for various times, followed by water quenching.

5. Uranium Corner of the Uranium-Niobium-Zirconium System (A. E. Dwight, L. T. Lloyd, R. S. Lindberg)

The uranium-niobium-zirconium phase diagram has been determined up to 11 w/o Nb and 40 w/o Zr and a topical report is being written. The work on the uranium-niobium binary system up to 11 w/o Nb, supplemented by data reported by the Ames Laboratory for higher niobium contents, indicates a two phase $\gamma_1 + \gamma_3$ region above 634° C, extending from 8 to 45 w/o Nb. X-ray diffraction patterns show the coexistence of two gammas after quenching from 640° C, in an alloy of 10.5 w/o Nb. The course of this monotectoid reaction originating at 634° C has been traced into the ternary system by metallographic and X-ray diffraction methods. The monotectoid moves with decreasing temperature and increasing zirconium toward a critical point, which is beyond the maximum niobium content of our present experimental alloys. At the critical point, the uranium-rich gamma phase (γ_1) and the niobium-rich gamma phase (γ_3) merge into a single gamma phase ($\gamma_{1,3}$).

Similarly, there is a monotectoid reaction in the uranium-zirconium binary system reported by D. Summers-Smith⁴ as lying at 6.3 w/o Zr and 693° C. The present investigations revealed no evidence of two gammas in a ternary alloy U-20 w/o Zr-4 w/o Nb, or in an alloy of U-8 w/o Zr-1 w/o Nb. It is concluded that the monotectoid which originates at 6.3 w/o Zr and 693° C moves with decreasing temperatures and increasing niobium toward a second critical point.

The dotted lines in Figure 22 show the course of the two monotectoid valleys as a projection upon the 630° C isothermal section. The other lines of Figure 22 are phase boundaries as they exist at 630° C. In Figure 23 is shown a vertical section with 5 w/o Zr constant. This section is included to demonstrate the phase changes which occur in the 5 w/o Zr-1.5 w/o Nb alloy. The phase diagram was determined by metallographic, X-ray

⁴D. Summers-Smith, "The Constitution of Uranium-Zirconium Alloys," J. Inst. of Metals, 83, 277-282 (1954-55).

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Figure 21. TTT Curve for Isothermal Transformation of Uranium-4.9 w/o Niobium Alloy.

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Figure 22. Isothermal Section at 630°C of the Uranium Corner of the Uranium-Niobium-Zirconium Phase Diagram.

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Figure 23. Vertical Section of the Uranium-Niobium-Zirconium Phase Diagram with Constant 5 w/o Zr.

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diffraction, and electrical resistivity investigations. In Figure 23 a dashed line is shown separating the $\alpha + \gamma_{1,2}$ from the $\alpha + \epsilon$ fields on the assumption that ϵ^* is an ordered form of $\gamma_{1,2}$.

The phase diagram now provides an explanation for the plot of electrical resistivity vs. transformation temperature which was reported in the previous quarterly report (ANL-5541). From the equilibrium isothermal sections of the phase diagrams, the percentage of gamma phase can be calculated by the law of levers because a line through the pure uranium corner and through the point representing an experimental alloy, lies on a conode. A plot of the calculated stable gamma present at the transformation temperature vs. transformation temperature is shown in Figure 24 for the ternary alloy containing 8 w/o Zr and 2 w/o Nb. This curve is quite similar in shape to the experimentally determined curve of room temperature resistivity vs. isothermal transformation temperature which was previously reported. It now appears that the high resistivity of the 8 w/o Zr + 2 w/o Nb, when quenched from above 674°C, was due to a 100% martensitic structure, which had been 100% gamma at the transformation temperature. As the percentage of alpha increased, at lower transformation temperatures, the resistivity decreased. From 640°C down, both the resistivity curve and the percentage of gamma curve became nearly vertical, indicating little change in relative quantities of the two phases at lower temperatures.

6. Corrosion Mechanism of Aluminum at Elevated Temperatures

(W. E. Ruther, J. E. Draley)

Hydrogen Analysis: One of the basic ideas of the theory of the high temperature accelerating corrosion as developed at Argonne is the penetration of the metal by the corrosion hydrogen with the subsequent formation of gas pockets (blisters). The aluminum alloys which withstand high temperatures successfully are presumed to liberate the corrosion hydrogen at the metal surface. Therefore no penetration of the metal by hydrogen should be noted.

In order to test this hypothesis, samples of 1100 aluminum and 1100 aluminum plus 0.9 w/o Ni (M388) were corroded for two days in water at 290°C. The M388 samples, when analyzed with the corrosion coating intact, produced some hydrogen (presumably from the reaction of $3\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O} + \text{H}_2\text{O} + 2\text{Al} \rightarrow 4\text{Al}_2\text{O}_3 + 3\text{H}_2$).

*Same as delta referred to in prior section. At the Ames Alloy Meeting it was decided to use the nomenclature of BMI-1000; this section of the report was written prior to the Ames meeting, hence the use of designation ϵ .

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Figure 24. Percentage of Gamma Vs. Transformation Temperature of Alloy Uranium-8 w/o Zr-2 w/o Nb (Equilibrium Conditions).

Macro 19322

The corrosion coating was removed on other samples by anodic treatment in boric acid and cathodic treatment in chromic-phosphoric acid. These samples analyzed <0.1 ppm hydrogen, indicating no penetration of the metal.

The 1100 aluminum samples showed microscopic blister attack and behaved quite differently. An analysis gave about the same amount of hydrogen as M388 after corrosion with the coating intact. However, when this coating was removed by the treatment described above, the hydrogen content was still 7.3 ppm (parent stock, uncorroded, 0.6 ppm). To further investigate the hydrogen penetration a series of samples were given the same corrosion treatment and then various amounts of metal were etched away with a dilute HNO_3 -HF mixture. The results are shown in Table VII.

TABLE VII

Hydrogen Analyses of Corroded 1100 Aluminum*

Treatment	Average Metal Etched Away (mm)	Hydrogen Content (ppm) (Whole Sample)	Estimate of Hydrogen in Increments of Etched Metal (ppm)
As Corroded	-	12.1	-
As Stripped	-	7.3	-
Etched (dilute HNO_3 + HF)	0.016	3.0	280
Etched (dilute HNO_3 + HF)	0.041	1.8	59
Etched (dilute HNO_3 + HF)	0.071	1.1	24
Etched (dilute HNO_3 + HF)	0.120	1.0	5
Etched (dilute HNO_3 + HF)	0.22	0.8	3
Blank (no corrosion)	-	0.6	-

*Corroded 2 days at 290°C in distilled water.

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The figures in column 4 are inaccurate due to the use of different samples (probably having slightly different hydrogen penetrations) for calculation. Estimates were made by subtracting the micrograms of hydrogen from one sample to the next and then dividing by the difference in etched metal. In spite of the probable inaccuracy, the trend is very evident. The hydrogen from corrosion is apparently held within a few tenths of a millimeter from the surface, producing high local hydrogen concentrations. Since the solid solubility of hydrogen in aluminum is very small, this supports the concept of gas pockets or blisters.

Aluminum Intermetallic Compounds: The presence of a strongly cathodic second phase is common to aluminum alloys which exhibit good high temperature aqueous corrosion resistance. However, all of the cathodic phases do not possess the same ability to protect. For some, the presence of other metals in the alloy greatly enhances the protective quality. A possible explanation has been previously given in terms of the dispersion of the second phase for the aluminum-nickel-iron ternary alloys. There was also the possibility that the intermetallic compound NiAl_3 , was rapidly corroded by the water, thus preventing it from remaining on the surface long enough to provide complete protection to the aluminum grains. The presence of iron would produce the FeNiAl_9 compound, which might be much more resistant. To check this point, as well as to measure their relative abilities to pass a cathodic current, the intermetallic compounds FeAl_3 , NiAl_3 , FeNiAl_9 , and CuAl_2 were prepared and corroded in 290°C distilled water.

The results are given in Table VIII. The rate of penetration is calculated on the following assumptions: (1) all the corrosion product is retained; (2) products of corrosion are FeO , NiO , CuO , and $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$. Attempts to remove the corrosion coating for a more accurate estimate were failures. Additional uncertainty arises because the samples (especially the NiAl_3) had hairline cracks due to the method of preparation. The penetration rates of the compounds do not seem large enough or different enough to explain the large differences in the corrosion behavior of some alloys containing these compounds.

Electrical measurements of the cathodic polarization curves in degassed distilled water at 290°C (after one-day corrosion to establish a film) gave slopes which were not significantly different for any of the compounds (ca. 2 mv per $\mu\text{a}/\text{cm}^2$). However, the open circuit potential measured against corroded 347 stainless steel was -0.08 volt for the NiAl_3 alloy and near -0.37 volt for the others. This phase would thus be expected to be much the most efficient cathode.

These results do not offer any explanation for the need for a small amount of iron in the low aluminum-nickel alloys: the previous explanation based on distribution of the second phase is still preferred.

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TABLE VIII

Corrosion Behavior of Intermetallic Compounds in Distilled Water

Compound	Estimated Rate of Attack During Period 1-14 Days	
	Weight Gain, mg/dm ² -day	Penetration, inch/year
FeAl ₃	14	0.007
NiAl ₃	83	0.038
FeNiAl ₉	71	0.032
CuAl ₂	40	0.019

7. Mechanism of Zirconium Corrosion (R. D. Misch)

When the oxide film on zirconium is heated in vacuum the electrical conductivity of the film increases exponentially with temperature (see previous Quarterly Reports). For thicker films, the oxide is not visibly changed by this treatment, but the possibility exists that a significant fraction of the oxide dissolves during the rise in conductivity. Such a decrease in thickness may be an important aspect of the increase in conductivity. It is likely that film dissolution and conductivity changes are related, and a study of these processes should shed light on the corrosion mechanism.

The extent to which oxide films dissolve was measured by visual comparison of the interference colors of anodic films on zirconium before and after heating in vacuum. All comparisons were made under a fluorescent inspection lamp. The specimens consisted of bars machined from a slab of zirconium which had been arc melted from Grade I crystal bar and rolled to a thickness of 1/2". The bars were wet ground on 240 grit paper and etched in a mixture of HF and HNO₃* for approximately one minute, then anodized in KOH solution to produce various thicknesses of oxide. The film thickness was determined by weighing zirconium foil before and after anodizing under the same conditions as used for preparing test specimens. A conversion factor of 27 Å per volt (anodizing) was obtained.

In the vacuum bell jar, a number of specimens were studied at 450° C at times from 2 to 30 hours to determine how the dissolution varied with time. This was the lowest temperature and was closest to the range of interest in corrosion. At the other temperatures, the heating time varied from

*50 ml 70% nitric acid, 50 ml distilled water, 5 ml 40% hydrofluoric acid.

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0.5 to 15.5 hours. A vacuum of 10^{-6} mm Hg was maintained during the heating period. After cooling, the specimens were removed and compared with the standards. The oxide films on the heated specimens had decreased in thickness, and thinner films had disappeared completely. The color changes could be estimated to 3 V or about 90 Å. The change in thickness was tabulated for each strip.

In all cases, the decrease in film thickness was approximately the same for all film thicknesses. Figure 25 shows the amount of film which dissolved as a function of time when heating at 450°C. The scatter is appreciable, but the data indicate a linear dependence. The data for a range of temperatures are presented in Figure 26. The number on each point is the number of hours the specimen was held at temperature. The curve is in good agreement with the Arrhenius expression over the entire temperature range, despite different times used for the measurement. This is also indicative of a linear law of film dissolution. The activation energy is 43.5 kcal/mol.

Three features are considered to be significant in these results: (1) the colors of the films are distinct up to the point of disappearance; (2) the rate of dissolution is constant; (3) the rate of dissolution is independent of thickness. It is concluded that the disappearance of oxide represents a uniform reduction at the metal-oxide interface. Such a process requires a transfer of O^{2-} from the oxide to the metal. Simultaneously, electrons must leave the metal and enter the oxide. As a result of these processes, the metal-oxide interface moves outward.

The controlling factor may be either oxygen or electron mobility. The former process is much more likely since the electrical conductivity of the oxide becomes appreciable at times of the order of 30 minutes even at 450°C. Measurements of this type have been made on anodic films with thicknesses corresponding to 200 V. It is concluded that the energy of activation represents the process in which oxygen leaves the oxide.

Comparison with the data of Gulbransen and Andrew⁵ shows that the rate of film dissolution is negligible in comparison to film growth in oxygen, in the temperature range 200° to 425°C. After 120 minutes at 425°C in pure oxygen at 7.6 cm Hg pressure, the oxide thickness was 5,400 Å. In the same period the amount of film dissolution would be 18 Å. The energy of activation found by Gulbransen was 18,200 cal/mol. This figure represents oxygen diffusion through the oxide and is significantly less than the activation energy for film dissolution.

⁵E. A. Gulbransen and K. F. Andrew, Trans. AIME, 185, 515 (1949).

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Figure 26. Rate of Oxide Film Dissolution as a Function of Temperature.

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At the temperatures associated with corrosion testing in water, the film dissolution rate is negligible. The rate is barely significant at 450°C where conductivity changes are conveniently measured. The relationship between film dissolution and conductivity probably lies in the mobility of the oxygen in the ZrO_2 . Oxygen may be lost to the metal or vacuum and thereby produce a more conducting defect structure.

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