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QUARTERLY REPORT
OCTOBER, NOVEMBER, AND DECEMBER 1953

Metallurgy Division

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For The Atomic Energy Commission

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December 31, 1953

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R E P O R T R E V I S I O N

The indicated material in the following Quarterly Progress Reports of the ANL Metallurgy Division are to be marked:

"Delete - see ANL-5329"

ANL-4923 (81) - Item 4: X-ray Spectrometer Studies of the Preferred Orientation in Rolled Uranium Rods (last four paragraphs only, starting "In order to test").

ANL-4966 (32) - Item 3: (last two paragraphs only).

ANL-5234 (44) - Item 3a: Preferred Orientation in Uranium Rods Rolled at Various Temperatures.

Supersedes Report Revision dated 3-18-57

Hayward D. Young

6-17-57

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QUARTERLY REPORT
OCTOBER, NOVEMBER, AND DECEMBER 1953
METALLURGY DIVISION

ABSTRACT

I. Water Cooled Reactors - Activity 4105

Extruded zirconium tubing, clad with copper, has been reduced up to 70 % by cold drawing. Rotary pierced tubing has also been cold drawn to a reduction of nearly 60 %. The surface ripples on the pierced tube were pretty well ironed out after the second draw. The major remaining problem in the commercial production of zirconium tubing is that of annealing after cold working. A reasonably inert atmosphere must be used, otherwise no softening occurs and such atmospheres are difficult and expensive to obtain and maintain on a large scale.

Uranium-niobium alloys containing 3 and 6 w/o niobium have been successfully clad with Zircaloy II by the picture frame roll bonding technique. A total of 32 plates were made from which 12 will be selected for irradiation in the MTR hot water loop. Clad to core bond strengths ranging from 30,000 to 60,000 pounds per square inch have been obtained. Edge and end bonds, corrosion resistant to 260°C water, have been obtained. Quenching from the gamma region (about 850°C) is necessary to develop maximum corrosion resistance in the core alloy; adequate quenching of these thin plates can be obtained by pressing between water cooled copper chill plates. Thirty of the plates were submitted to the Reactor Engineering Division for static and dynamic corrosion testing in 260°C water; only four of the plates showed defects in the edge or end closures.

Considerable development work on the resistance roll bonding method of producing zirconium clad uranium ribbon was carried out. A strip of uranium is enclosed with the zirconium edge strips and cover plates and the outer edges inert arc welded. The assembly is then passed through a strip welding machine to bond the cover plates to the core and to the edge strips. Bonding of the zirconium cover plates to the uranium core is quite good, but bonding between cover plate and the edge strips is incomplete. Presumably, too much of the welding current passes through the core and through the already existing edge weld and not enough heat is developed at the zirconium cover plate-edge strip interface to effect bonding.

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II. Liquid Metal Cooled Reactors - Activity 4110 and 4711

A new fuel charge for the EBR has been prepared and shipped to Arco. The fuel slugs were centrifugally cast U^{235} -2 w/o Zr alloy and were prepared without difficulty. The fuel blanket slugs were natural uranium-2 w/o zirconium alloy and were prepared by rolling cast billets into rod, followed by swaging, straightening, machining and heat treating for stabilization. Specimens from each rod were tested for stability by thermal cycling. An unexpected difficulty arose in that not all rods were equally stable. A sufficient amount of material was made to allow loading of the fuel rods with slugs showing good stability. In general it appears that metal high in nitrogen (i.e., 200 ppm) or in which nitrogen segregation is severe was less stable. A detailed study of variables in the response of this material to the stabilizing heat treatment is under way.

A technique for the fabrication of fuel plates for the fast exponential experiments has been developed. Fully enriched uranium is mechanically diluted with natural uranium in the following manner. An enriched uranium plate is enclosed by natural uranium edge strips and cover plates, the assembly clamped between copper chill blocks and the exposed outer edges of the natural uranium joined by inert arc welding. With proper argon gas shielding the welds are clean, sound, and smooth. Very little contamination of the surroundings occurred.

III. Reactor Development Metallurgy Activity 4530/4540

A study of melting practice for uranium-zirconium alloys has shown that cored biscuit alloys can be successfully melted in MgO washed graphite crucibles. Loss of zirconium and pickup of carbon and nitrogen are relatively small. An occasional biscuit was very gassy and frothed badly in the crucible; such biscuits appear to be very high in magnesium content. In a few cases the boiling was so severe that the molten metal was thrown from the crucible and cemented the stopper rod to the crucible cover in such a way that the heat could not be cast.

Four commercially available titanium base alloys and two experimental zirconium base alloys have been tested for tensile strength at 650°C. Zirconium alloys containing 4 w/o aluminum had tensile strengths in the range of 40,000 - 50,000 pounds per square inch at this temperature and were comparable to Type 347 stainless steel. Only one of the titanium alloys showed promise; an alloy containing 3% Al + 5% Cr has a tensile strength of 30,000 pounds per square inch.

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IV. Basic Metallurgy Activity 5411-01

The thermocouples used in the thermal analysis of the transformation temperatures and melting point of high purity uranium have been recalibrated and a few additional runs made. The average values (17 runs on 5 different samples) for these critical temperatures are:

	<u>Heating</u>	<u>Cooling</u>
$\alpha \rightleftharpoons \beta$	665.6	656.7
$\beta \rightleftharpoons \gamma$	771.1	766.5
$\gamma \rightleftharpoons \text{Liquid}$	1129.8	1129.6

Three uranium single crystals were compressed in directions that would result in maximum contraction in each of the following twin systems: (130), (172), and (121). The direction of maximum contraction was chosen on the premise that it corresponded to the direction most favorable for the operation of a given twin system. In the case of (130) twinning, slip on the (010) planes preceded twinning, even though the crystal was relatively unfavorably oriented for slip on this plane. If one considers the onset of noticeable contraction on the stress-strain curve as being due to slip preceding twinning, a value of 0.35 kg/square millimeter is obtained for the critical resolved shear stress on the (010) slip system. Twinning on the (172) planes was also accompanied by (010) slip but only after a number of microscopically observable twins had formed. The crystal oriented for (121) twinning failed to yield twins of this system, thus contradicting the findings reported by Cahn.¹ The crystal deformed by (010) slip and by kinking involving this slip system.

A preferred orientation study has been made on uranium rods rolled to 75% reduction in area at 300°, 400°, 500°, 600°, and 640°C. The rod rolled at 300°C showed the (010) and (120) texture components with the (010) component predominating. As the rolling temperature was increased there was a gradual decrease in the amount of the (010) component and a corresponding increase in the amount of the (120) component. At the higher temperatures the (120) component shifted over to a (110) component with a minor (010) component. Upon annealing in the high alpha temperature range, the rods rolled at 300°, 400°, and 500°C developed the typical (140) and (010) texture components; the rods rolled at 600° and 640°C showed no appreciable change upon annealing.

¹R. W. Cahn, "Plastic Deformation of Alpha Uranium; Twinning and Slip," Acta Metallurgica, Vol. 1, No. 1, 49-70, January, 1953.

A preliminary study of the preferred orientation in a rod of high purity uranium rolled to 85% reduction in area at 300°C has been made. This material showed a duplex texture with (041) as the major and (352) as the minor components. The textures appear to be somewhat sharper than those of similarly treated reactor grade metal. Upon recrystallization the (041) component is apparently retained while the (352) component is broadened and shifted to something which approximates the (140) component previously reported as commonly present in recrystallized uranium rod.

Some preliminary work has also been done on the preferred orientation in beta treated uranium sheet. As expected, the sheet was nearly random in orientation although there appeared to be some detectable difference in orientation from the center to the surface of the sheet, with the surface showing a slightly higher degree of orientation.

A series of liquation experiments have been carried out on reactor grade uranium in an effort to measure the solubility of carbon in liquid uranium at temperatures slightly above the melting point. The values obtained were: 250 ppm at 1190°C, 225 ppm at 1145°C and 170 ppm at 1138°C. The experiments are being repeated on high purity uranium-carbon alloys. A series of high purity uranium-carbon alloys were annealed at temperatures ranging from 700° to 1100°C and water quenched. Metallographic examination is not yet complete but it does appear that the solubility of carbon in gamma uranium is less than 250 ppm at 900°C.

A metallographic study of high purity uranium-zirconium alloys is being carried out in an effort to check certain features of the phase diagram of importance in the heat treatment of these alloys. At 640°C only the 0.09 w/o zirconium alloy was single phase; the 0.6 w/o zirconium and higher alloys were all two phase. The solubility of zirconium in uranium at 640°C appears to lie somewhere between 0.1 and 0.6 w/o zirconium.

Specimens of U-4-1/2 w/o Zr-1-1/2 w/o Nb alloy quenched from 800°C (in the gamma phase) show a martensitic plate-like structure yielding only diffuse alpha uranium X-ray diffraction lines. Upon annealing the quenched specimens at 350°C for 3 hours, the microstructure was unchanged, the X-ray diffraction lines sharpened up somewhat but no new phases could be detected. The hardness increased from RC-47 for the quenched specimen to RC-58 for the annealed specimen, indicating age-hardening.

V. Applied Metallurgy - Activity 5461

The zone melting principle has been applied to the purification of uranium-zirconium alloys. Experiments have been carried out in alundum and in graphite boats at speeds ranging from 4/5 to 1/16"/minute. Zirconium concentrated at the leading end of the bar but only slowly and only at low rates of zone movement. The specimens contained 2 w/o zirconium

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and in the best run had been reduced to 1.8 w/o zirconium in the trailing end and increased to 2.4 w/o zirconium in the leading end of the bar. Carbon and nitrogen segregate readily toward the trailing end of the rod. Iron, nickel and chromium also segregate toward the trailing end, but more slowly. The behavior of the aluminum and silicon impurity is uncertain.

Silicon dissolves readily in liquid NaK and this solution has been used to siliconize the surface of uranium, thorium and stainless steel specimens. Adherent coatings have been produced which show improved corrosion resistance.

An uranium single crystal made by the grain coarsening technique and a pseudo single crystal made by the beta-alpha transformation method have been examined after a burnup of 0.5% in MTR. These specimens, originally short right cylinders, are now thin ribbons with growth occurring in the [010] direction, shrinkage in the [100] direction and practically no change in the [001] direction.

Beta heat treated natural uranium specimens have now been irradiated to a burnup of 1.75% in Kittel capsules in MTR. These samples now contain about 1% plutonium. The specimens were still in one piece although very rough. At these high burnups the instantaneous growth rates are considerably less than at low burnups. As an example, the initial rate of growth was 20% per 1% BU; at 0.8% burnup this rate has dropped to about 10% per 1% BU.

Additional specimens of uranium-2 w/o zirconium alloys in the as cast condition have been examined after burnups of 0.9 and 3.4%. The specimen irradiated to a burnup of 0.9% is still smooth and straight and has grown in length at a rate of only 3% per 1% BU. The 3.4% BU specimen is smooth and has increased in length about 6% per 1% BU, but shows considerable swelling over the center half of its length. The central metal temperature of this specimen is estimated to have been 900°C and presumably fission gases have diffused to internal defects and have formed bubbles of free gas.

A specimen of U²³⁵ wire (0.050" diameter) which had been jacketed in stainless steel at Los Alamos was examined after 1.24% average burnup in an MTR reflector stringer. The wire had received 82% cold reduction in area with no subsequent beta treatment and should have grown to some 30-40 times its original length had it been free to grow. The actual longitudinal growth was less than 2% in the 5-3/4" length. The restraining steel jacket had a wall thickness of 6 mils and had been swaged tightly to the uranium. The longitudinal restraint was apparently sufficient to prevent appreciable growth even though the end welds were cracked.

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VI. Aqueous Corrosion - Activity 5411-03

An unexpected difficulty has arisen in the use of the eddy-current metal thickness gauge. Simple aging of 2S aluminum without corrosive attack at temperatures of 250° and 300°C results in an apparent increase in thickness. The most rapid changes occur within the first 40 hours of aging and are of the order of 100 microinches. Any process occurring in the aluminum which increases the electrical conductivity would explain this effect. Specimens which are to be corrosion tested at these elevated temperatures must be preaged and uncorroded blank specimens should be aged at the same temperature and for the same length of time as the corrosion specimens. Preliminary tests on a new gauge designed and constructed by the Remote Control Division indicate that thickness measurement to better than 0.1 microinch should be possible.

Corrosion tests on wet-ground aluminum specimens in distilled water at 50° and 70°C for one day indicate that, regardless of the actual rate of corrosion of the metal, approximately one-tenth of the corrosion product is lost to the solution.

At pH 3.5 both sodium silicate and potassium dichromate seem to offer some inhibition in the aqueous corrosion of 2S aluminum at 250°C. It is not easy to be certain that it is true because in the absence of the potential inhibitors the testing equipment corrodes too rapidly to allow adequate tests of the aluminum corrosion. With the inhibitors present at 50 ppm, protection does not seem to be adequate to prevent ultimate intergranular corrosion of the aluminum. At higher temperature this type of attack is accentuated.

Anodizing zirconium in alkaline solution at lower current densities than previously used seems to provide data which correlate better with the corrosion resistance of different samples in water at elevated temperatures.

The corrosion rate of reactor grade uranium in boiling water has been shown to be consistently reduced as the temperature of prior vacuum annealing is increased.

The uranium alloy which is currently believed to offer the best possibilities as fuel element material for certain high temperature water cooled reactors has been shown to suffer partial destruction of its corrosion resistant properties after annealing for as little as 4 hours at 375°C.

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I. WATER COOLED REACTORS - [ACTIVITY 4105]

1. Cold Drawing of Extruded Zirconium Tubing (E. A. Wright, R. E. Macherey)

The surfaces of the zirconium tubes that were extruded from copper jacketed billets were uniformly covered with a layer of copper (see ANL-5153 for extrusion data). These tubes were pointed and given several draws with the copper serving as a drawing lubricant. This copper was very effective until it started to loosen on the surface and strip at the drawing die. This left bare zirconium in contact with the draw die and resulted in scratches on the surface of the tubes. It became necessary to remove the copper before further drawing could be continued. If additional base tubes are produced in this manner, it would be advisable to remove the copper from the surface of the tubes before any drawing is started.

A trial draw equivalent to 30% reduction of the cross sectional area of the extruded base tube was made. Total reductions equivalent to 70% were made between anneals. This showed that the zirconium was quite ductile and could withstand severe cold working without breaking. The limiting factor at present seems to be the lubricant available for the drawing operation. In order to reduce the chance for breakage of the tubes during drawing, smaller reductions were made on the majority of the tubing. The following list is the draw schedules used on some of the zirconium tubes:

<u>Operation</u>	<u>O.D. (In.)</u>	<u>Wall (In.)</u>	<u>% Reduction</u>
I. Extruded tube size	2.000 x 0.125		
Draw	1.875 x 0.115		14
Draw	1.750 x 0.095		22-1/2
Draw	1.687 x 0.085		13
Total reduction 42%. Tube is quite hard. Copper coat is fairly well intact.			
II. Extruded tube size	2.000 x 0.220		
Draw	1.875 x 0.180		22
Draw	1.812 x 0.160		13
Draw	1.750 x 0.140		15
Draw	1.687 x 0.130		10
Total reduction 48-1/2%. Tube is very hard. Copper coat intact.			
III. Extruded tube size	2.125 x 0.188		
Draw	2.000 x 0.156		21
Draw	1.937 x 0.145		10
Draw	1.875 x 0.130		12-1/2

Total reduction 38%. Tube is very hard. Copper coat in fair condition.

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These tubes were all quite hard, 84/88 Rockwell B. They were individually placed into a 2-1/4" diameter steel tube and the assembly was evacuated to -29" Hg and filled with helium. The assembly was then annealed at 760°C for 30 minutes. A few of the tubes were softened to a hardness of 60/65 Rockwell B while the hardness of others remained unchanged. The copper was removed from all tubes by nitric acid stripping. The annealing was repeated in an argon atmosphere at temperatures as high as 930°C (1700°F) for 30 minutes without any decrease in hardness. Microscopic examination of the metal showed a recrystallized structure. The hardness is probably due to oxygen from the initial annealing bomb or from the helium used as an atmosphere.

Table I gives some of the lubricants tried in drawing zirconium tubes and a summary of the results of these tests.

2. Cold Drawing of Pierced Zirconium Tubing (E. A. Wright, R. E. Macherey)

The base tube that was formed by piercing during September, 1953, was reduced by cold drawing as follows:

<u>Operation</u>	<u>O.D. (In.)</u>	<u>Wall (In.)</u>	<u>% Reduction</u>
Pierced tube size	3.125 x 0.350		
Draw	2.875 x 0.293		22
Draw	2.750 x 0.255		16

This tube had very rough spiral marks on the outside diameter due to working by the rolls during piercing. The first draw showed some chatter. The spiral marks were ironed out until they were not very obvious after the second draw. The tube was quite hard after the second draw and was annealed at 760°C (1400°F) for 25 minutes in a gas fired furnace with the products of combustion serving as the furnace atmosphere. Hardness after anneal was 60/63 Rockwell B. The annealed tube was further reduced as follows:

<u>Operation</u>	<u>O.D. (In.)</u>	<u>Wall (In.)</u>	<u>% Reduction</u>
Annealed	2.750 x 0.255		
Draw	2.622 x 0.218		17
Draw	2.500 x 0.200		12-1/2
Draw	2.357 x 0.179		14
Draw	2.250 x 0.160		15
Draw	2.125 x 0.140		17

Total reduction 56%. Tube is very hard. Spiral marks are not very apparent.

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TABLE I

Drawing Lubricants

Name of Lubricant	Composition	Remarks
Whitfield G. Richards	Commercial	This lubricant is a thick, putty-like substance that was applied to the tubes by hand. The lubricant was not suitable as it would not adhere to the zirconium during drawing and resulted in zirconium pickup on the tools. The tubes were badly scratched by this metal pickup.
Copper Coat from Extrusion of Copper Jacketed Billet	Copper	This copper coat was very satisfactory for several draws in cases where the coat was firmly attached to the zirconium and was continuous over the surfaces of the tube. After a few draws the copper coat began to flake off and caused bare zirconium to be exposed. This practice also resulted in nonuniform thickness of the zirconium tube wall due to variations in the thickness of the copper coat. The copper was removed by pickling in HNO_3 . This method is generally not satisfactory and it is not recommended for production practice. Regular copper oil lubricants were used to lubricate the copper coat during drawing.
Copper Brazing Paste	Copper powder with oil	This lubricant was applied by hand. It consisted of a heavy mixture of very fine copper particles in an oil and is quite difficult and messy to apply. The material would not stick to the zirconium during drawing and resulted in contact of the zirconium with the tools. Metal pickup on the pin and die resulted in severe scratching of the surface of the tube. This lubricant was not satisfactory.
Battelle Memorial Institute Lubricant	50 cc of lacquer thinned 3:1 with lacquer thinner. 30 gms Molykote, 10 gms lead-zinc oxides.	This lubricant was satisfactory in service. It would not be desirable for production, however, for the following reasons: 1. It is flammable; this would be hazardous in use; 2. It is difficult to apply and remove; 3. It contains a sulfur compound which could attack annealing facilities at high temperatures; 4. It requires constant agitation to keep the solids in suspension; and 5. The ingredients are quite expensive. In the absence of a more desirable lubricant this one will continue to be used.

3. Resistance Welding of Roll Formed Zirconium Tubing (E. A. Wright, R. E. Macherey)

The 3/4" O.D. x 0.058" wall zirconium tubing, roll formed and welded from 2.365" wide x 0.058" thick strip as reported in ANL-5153, has been evaluated. In general, it showed that the process was a feasible method for making zirconium tubing and was worthy of additional effort and development. It is believed that by annealing the strip to a hardness of 48/52 Rockwell B, forming a tube with an inside diameter large enough to accommodate an internal scarfing tool, and by shielding the weld area with purified argon, a good welded tube could be made. All of these conditions are possible and can easily be met.

A summary of the tubes formed in the initial trial is given in Table II.

4. Cladding of Uranium-Niobium Alloys with Zircaloy II (R. E. Macherey, C. Bean)

The program on roll cladding uranium-niobium alloys containing 3 w/o and 6 w/o niobium with Zircaloy II, first reported in ANL Quarterly Report ANL-5153, has been completed.

From this investigation, it was found that plates with the following dimensional tolerances could be rolled:

Width	± 0.015 " in width range from 1-1/2" to 3"
Thickness	± 0.001 " in thickness range from 0.062" to 0.250"
Straightness	Less than 1/8" camber in 2 feet
Cladding Thickness	$\pm 10\%$ on 0.010" to 0.020" thick cladding

Plates can be made with core to clad bond strengths of from 30,000 to 60,000 psi; and reductions in excess of 90% in thickness, although not necessary for bonding, can be made for economical productions of long plates.

Edge bonds which are corrosion resistant to 260°C water have been obtained; and end seals made by shielded arc welding of inserts to the cladding have been made which are also corrosion resistant to water at this same temperature.

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TABLE II
Detailed Information on Welding of Zirconium Tubing

Setup No.	A.C. Volts	Speed (fpm)	60-Cycle Amps	P.F. Lag	Heat Tap	Heat Used	Remarks
1	178	34	180	0.65	3	42	The weld between the zirconium and nickel broke in all cases on leading and trailing strips. 100-X examination showed a pronounced overlap on the I.D. that extended approximately one-sixth of the way through the wall of the tube. The bond line was visible with an intermittent string of oxide. Small pits were burned into the wall of the tube by the electrode.
2	178	34	100	0.65	3	42	This strip forms harder than 1015 steel and has more spring-back after leaving the forming rolls. The zirconium tube wall was burned through at several points along the path of the electrodes. This caused alloying between the copper electrode wheel and the zirconium and made the electrode rough. This condition increased the size of the pits in the tube along each side of the weld seam.
3	178	50	80	0.65	4	42	This setting was too hot and the zirconium was burned through in several spots. The edgers were damaging the edge of the strip because too much metal was being removed. The edgers were readjusted and the heat was changed.
4	160	50	110	0.65	3	42	More pressure was given at the side rolls. A good weld was obtained that held for a 20% expansion test without failing. Electrode pit marks were evident along the weld seam; however, they were practically removed by the scarfing tool. 100-X examination showed a very faint diagonal weld seam that was invisible much of the way through the wall. It was visible at each end of the seam but vanished toward the center. A wedge was formed by the flash on the inside of the tube and the overlap extended through about one-sixth of the way through the wall.
5	160	50	120	0.65	3	42	Less upset pressure was used. Electrode pits were still present along both sides of the weld. This tube failed to expand 20% without splitting. 100-X examination showed a definite but intermittent seam. At some spots the seam is very definite; at others it disappears. Wedge, not as pronounced as in case #4 above, extends one-tenth of way into tube wall.
6	160	50	120	0.65	3	42	Removed edger to give wider strip into weld area. Sample split on expansion of 20%.
7	160	55	90	0.65	3	36	Sample split on expansion test. Showed stitches in weld; evidently more heat or higher frequency required for weld. Pits caused by electrodes not as bad as those at higher heats. Protrusion on I.D. of seam with no serious crack or overlap in inner wall. Very pronounced weld seam on inside which diminishes toward the outside.
8	160	55	100	0.68	3	42	Sample split on expansion test. Split showed clean metal along the seam. 100-X examination showed the presence of the flash on the I.D. in the form of a protrusion. The weld seam starts off on the inside and outside rather pronounced, but fades out toward the center of the tube wall.
9	160	40	120	0.68	3	50	Sample withstood 10% expansion but split when expanded to 20%. The split showed clean metal and the evidence of a fairly uniform weld. 100-X examination showed the presence of the protrusion on the I.D. again. The overlap along the side of the protrusion extended about one-tenth of the thickness of the wall. A series of oxide nodules were present about the first one-third of the weld seam from the inside and the outside; however, they completely disappeared toward the center.

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Clad plates have been quenched from solution temperature of 850°C by pressing between water cooled copper dies to maintain flatness. The niobium core alloy had the same corrosion resistance as cores which were water quenched from the solution temperature.

A series of clad plates were prepared which are intended for irradiation tests of uranium-niobium alloy core material in the MTR water loop at 260°C. Six clad plates with 3 w/o niobium cores and six clad plates with 6 w/o niobium cores are required for the test.

A total of 32 plates from 18 billets was made for the selection of the above number of plates. The specified dimensions of the plates are as follows:

Over-all length	7-1/4" $\pm$ 1/16"
Over-all width	1.875" +0.000" -0.030"
Over-all thickness	0.125" +0.000" -0.005"
Core thickness	0.095" +0.000" -0.005"
End clad	0.080" minimum
Side clad	3/16" $\pm$ 1/16"
Clad thickness	0.010" minimum

Fourteen of these plates were rolled to thickness and width tolerance, adjusted to within length tolerance by cutting. The core was etched out and the exposed core sealed by welding a Zircaloy insert to the cladding using shielded arc technique.

Following heat treatment of the plates for development of corrosion resistance in the core (850°C solution treatment and water quench) the plates were prepared for corrosion testing by vapor blasting clean and pickling.

Eighteen plates were rolled with the cladding oversize, 30 mils on thickness and 1/16" on the width, so that 15 mils of cladding on each face and 1/32" of cladding on edges could be removed by machining for obtaining corrosion resistant surfaces. Machining on these plates was done after end sealing and heat treatment.

Acceptance tests performed on the finished plates consisted of the following:

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- a. Inspection of autoradiographs for clad uniformity.
- b. Static corrosion testing in 260°C water.
- c. Dynamic corrosion testing in 260°C water at approximately 20 feet/second.
- d. Eddy-Current clad thickness measurement.
- e. Supersonic bond test.

Plates survived static and dynamic corrosion testing ranging from 499 hours static - 0 hours dynamic to 291 hours static - 168 hours dynamic. Of the thirty plates tested, one plate swelled but did not rupture after 264 hours static corrosion testing at 260°C; two plates showed a white streak along one edge, one of which was salvaged by machining off the corroded area; the end weld on one plate corroded white; and the edge bond on one plate split part way through but did not enter the core.

All of the plates rolled to final thickness and width had uniform and acceptable clad thicknesses. The plates which were machined to thickness and width, however, had variation in clad thickness which was severe enough to cause rejection in some cases. Wide variation in clad thickness was found both by autoradiographing and eddy-current testing by J. A. DeShong, Jr.

Supersonic testing for bond continuity by Warren McGonnagle showed two plates to have breaks in the clad to core bond.

5. Resistance Roll Cladding of Uranium with Zirconium (D. E. Walker, R. A. Noland)

Considerable development work was performed during this quarter on resistance roll bonding to produce zirconium clad uranium ribbon fuel elements. The samples used were 3-7/8" long x 3/4" wide x 0.101" thick. Figure 1 shows a transverse cross section of the type of sample used.

Using 9" diameter x 1-1/2" wide soft copper wheels, bonding has been accomplished in one pass between the clad and core but not completely across the sample between the clad and frame adjacent to the side of the core. Differences in resistivity between uranium and zirconium, and the presence of the fusion weld at the sample edges, appear to be the reason complete bonding at the side does not occur. With a resistivity of 45 micro ohm-cm for zirconium and 30 micro ohm-cm for uranium, shunting occurs across the clad through the core and at the edges due to the lowered contact resistance effected by the presence of the fusion weld.

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Figure 1

CROSS SECTION OF RESISTANCE ROLL BONDING SAMPLE

Clad ——— 17 Mil Zirconium Sheet
 Frame ——— 67 Mil Thick Zirconium
 Core ——— 67 Mil Thick Uranium

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Curving of the samples around one of the wheels resulted in improper bonding since insufficient heat was produced on the concave side. This condition was relieved by the use of a jig attached to the welding machine that controlled the position of the sample as it was being bonded.

The use of simulated samples of Monel clad nickel silver and low carbon steel clad nickel silver was discontinued since the results obtained could not be directly applied to zirconium clad uranium. The effect of other properties such as specific heat, plasticity, and the tendency for diffusion to occur were more important than resistivity in obtaining a simulated sample.

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II. LIQUID METAL COOLED REACTORS - ACTIVITY 4110 AND 4711

1. Fabrication and Heat Treatment of EBR Fuel Blanket Slugs (R. E. Macherey)

The fabrication and heat treatment of uranium-zirconium alloy rod for EBR fuel blanket slugs described in the Quarterly Report ANL-5153 has been completed.

Rolling, swaging, and straightening of this nominal 2 w/o zirconium alloy proceeded without any difficulty. The isothermal heat treatment (one hour at 800°C followed by quench and held one hour in lead at 500°C) also proceeded smoothly without difficulty. Thermal cycling of samples from finished rods, however, produced growth in some cases which caused rejection for use as fuel blanket slugs.

It will be recalled that in the Quarterly Report cited above, K values of 48 samples from heat treated rod ranged from -14 to +11. These samples all came from rod rolled from one Mallinckrodt billet 7299, which analyzed 2.30%, 2.27 w/o zirconium, and 15 ppm, 9 ppm nitrogen, top and bottom, respectively. Material having K values within the above range was considered satisfactory for EBR fuel blanket slugs.

Heat treated rod rolled from another Mallinckrodt casting 7034, however, exhibited high growth after thermal cycling. The average K value of 45 samples cut at regular intervals along length of rod rolled from this casting was 45.8 with a low K value of 21 and a high of 61.

Zirconium and nitrogen contents of this casting were 2.81 w/o top, 2.56 w/o bottom, and 47 ppm top, 28 ppm bottom, respectively.

Thermal cycling results on samples rolled from ANL casting were erratic. Thermal cycling of samples from rod rolled from seven castings developed growth in K values ranging from -14 to 71. Nitrogen in these castings ran as high as 210 ppm.

Remelting of rod, which gave high growth, lowered the nitrogen content and eliminated zirconium segregation. The growth values of rolled and heat treated rod from these remelted castings varied from -13 to +19.

A summary of growth values and chemical analyses of rod from castings discussed above is contained in Table III. Castings with numbers prefixed by "H" were made at ANL from biscuit uranium and crystal bar zirconium. All other castings were made by Mallinckrodt from coreduced biscuit. Rods from each casting were numbered and/or lettered consecutively from top to bottom of the castings.

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TABLE III
Thermal Cycling Data and Chemical Analysis

Billet No.	Rod No.	Heat Treat Batch No.	Cycling Sample No.	K Value	Chemical Sample Position	Zr (%)	N (ppm)	C (ppm)	Remarks	Billet No.	Rod No.	Heat Treat Batch No.	Cycling Sample No.	K Value	Chemical Sample Position	Zr (%)	N (ppm)	C (ppm)	Remarks
7034	T1A	H-34	122	21	Top	2.81	47	---		H-220	TA	H-13	49	19	Top	2.40	---	36	
	T1B	H-34	123	44							TB	H-13	50	12	Bottom	2.07	---	4	
	T1C	H-34	124	28							TC	H-13	51	10					
	T1D	H-34	125	43							TD	H-13	52	73	Top	2.10	---	15	
7034	T2A	H-35	126	53						H-221	TA	H-14	53	33	Top	2.09	---	10	
	T2B	H-35	127	41							TB	H-14	54	61	Bottom	2.09	---	10	
	T2C	H-35	128	50							TC	H-14	55	41					
	T2D	H-35	129	51							TD	H-14	55	41					
7034	T3A	H-36	130	56						H-222	TA	H-15	56	38	Top	2.23	---	21	
	T3B	H-36	131	52							TB	H-15	57	59	Bottom	2.04	---	4	
	T3C	H-36	132	48							TC	H-15	58	58					
	T3D	H-36	133	54							TD	H-15	58	58					
7034	T4A	H-37	134	45						H-223	TA	H-16	59	26	Top	2.30	73	26	
	T4B	H-37	135	46							TB	H-16	60	-14	Bottom	1.92	5	5	
	T4C	H-37	136	56							TC	H-16	61	2					
	T4D	H-37	137	46							TD	H-16	61	2					
7034	T5A	H-38	138	51						H-224	TA	H-17	62	48	Top	2.19	147	18	
	T5B	H-38	139	54							TB	H-17	63	68					
	T5C	H-38	140	57							TC	H-17	64	71	Bottom	2.08	38	4	
	T5D	H-38	141	60							TD	H-17	65	31					
7034	T6A	H-39	142	61						H-225	TA	H-18	66	29	Top	2.35	115	23	
	T6B	H-39	143	---							TB	H-18	67	-5	Bottom	2.13	4	10	
	T6C	H-39	144	---							TC	H-18	68	25					
	T6D	H-39	145	---							TD	H-18	68	25					
7034	T7A	H-40	146	53						H-226	TA	H-19	69	---	Top	2.13	74	13	
	T7B	H-40	147	52							TB	H-19	70	43					
	T7C	H-40	148	47							TC	H-19	71	64	Bottom	2.07	29	5	
	T7D	H-40	149	42							TD	H-19	72	33					
7034	T8A	H-41	150	51						H-227	TA	H-20	73	17	Top	2.26	140	13	
	T8B	H-41	151	47							TB	H-20	74	-7	Bottom	2.08	< 5	3	
	T8C	H-41	152	48							TC	H-20	75	34					
	T8D	H-41	153	45							TD	H-20	75	34					
7034	T9A	H-42	154	43						H-228	TA	H-21	76	57	Top	2.21	133	20	
	T9B	H-42	155	42							TB	H-21	77	19					
	T9C	H-42	156	51							TC	H-21	78	35	Bottom	2.09	30	6	
	T9D	H-42	157	45							TD	H-21	79	48					
7034	T10A	H-43	158	45						H-229	TA	H-22	80	73	Top	2.25	210	18	
	T10B	H-43	159	42							TB	H-22	81	---	Bottom	2.09	---	2	
	T10C	H-43	160	46							TC	H-22	82	-2					
	T10D	H-43	161	48							TD	H-22	83	2					
7034	T11A	H-44	162	49						H-265	TA	H-46	170	1	Top	2.01	17	20	Remelt of H-221 and H-222
	T11B	H-44	163	40							TB	H-46	171	-2	Bottom	1.99	<10	11	
	T11C	H-44	164	47							TC	H-46	172	2					
	T11D	H-44	165	47							TD	H-46	172	2					
7034	T12A	H-45	166	35						H-266	TA	H-47	173	7	Top	2.03	23	11	Remelt of H-222 and H-223
	T12B	H-45	167	22							TB	H-47	174	-13	Bottom	2.01	15	15	
	T12C	H-45	168	38							TC	H-47	175	-5					
	T12D	H-45	169	21							TD	H-47	175	-5					
7034	T12A	H-45	166	35						H-267	TA	H-48	176	11	Top	2.03	18	12	Remelt of H-223 and H-224
	T12B	H-45	167	22							TB	H-48	177	-2	Bottom	2.03	21	9	
	T12C	H-45	168	38							TC	H-48	178	4					
	T12D	H-45	169	21							TD	H-48	178	4					
7034	T12A	H-45	166	35						H-268	TA	H-49	179	19	Top	2.05	17	6	Remelt of H-225 and H-226
	T12B	H-45	167	22							TB	H-49	180	-1	Bottom	2.05	36	6	
	T12C	H-45	168	38							TC	H-49	181	14					
	T12D	H-45	169	21							TD	H-49	181	14					

Some general observations can be made upon these data. The carbon content of all alloys analyzed was low, 2 to 36 ppm. The zirconium content of alloys with low growth rate was very uniform from top to bottom, 0.03% maximum difference. The nitrogen content of alloys with low growth rate was low, < 10 to 36 ppm. The segregation of zirconium in alloys with grew at a high rate was much greater than in those exhibiting low growth, 0.43% vs 0.03% segregation, respectively. Finally, the nitrogen level of alloys with high growth rates was very high, 210 ppm maximum; and the segregation of nitrogen was great, 147 ppm top, < 5 ppm bottom in the severest case.

JK 2. Fabrication of Fuel Plates for Fast Exponential Experiment (C. C. Stone, R. A. Noland)

A technique suggested by one of the authors to permit mechanical dilution of fully enriched U^{235} with natural uranium has been successfully accomplished. The enriched material, in the form of a flat plate, is fully enclosed by an unbonded welded natural uranium box of the picture frame manner. The fuel plate assembly is made up of:

1. An enriched core plate.
2. Four narrow strips of natural uranium to act as the picture frame.
3. Two cover plates.

After hand assembling, the unit is placed in an appropriate copper jig and inert arc welded (argon arc) around the natural uranium outer edges. Accurate control of the movement of the tungsten shielded electrode was accomplished with a suitable machine carriage attached to a rigid track and table. Adequate shielding of the work from oxidation was extremely vital, this factor being probably the single most important variable requiring control. Straight polarity direct current is supplied by a rectifier type welding machine.

Welds appeared to be clean, sound, straight and smooth in the as welded condition. A few samples run to determine the weight changes produced by welding indicated that under properly controlled conditions, weight changes varied from no change to a few tenths milligram per inch of weld. *JK*

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III. REACTOR DEVELOPMENT METALLURGY - ACTIVITY 4530/4540

1. Melting and Casting of Uranium-Zirconium Alloys from Co-reduced Mallinckrodt Biscuit (J. E. Baird, R. E. Macherey)

Seven co-reduced biscuits containing from 0.1% to 5.0% zirconium were melted in vacuum. Six biscuits were melted in graphite crucibles that had a spray coated MgO wash. Five of these biscuits were cast into 3" diameter tapered nose graphite molds which had also been spray coated with MgO wash. The sixth biscuit, #437, could not be cast after melting. The seventh biscuit, #436, was melted in a Magnorite crucible and poured into a 2" x 4" rectangular graphite mold.

Sampling of the biscuits disclosed a highly segregated layer containing magnesium, carbon, and zirconium on biscuits 436 and 411. The top 1/2" of each biscuit was discarded and not melted.

The biscuit analyses for zirconium, carbon, nitrogen, and magnesium contents appear in Table IV.

The original nitrogen analyses made in March and April, 1953, were in error. On resampling five of the biscuits it was found that the skulls had been disposed of, and it was decided to take only one sample for nitrogen analysis. All of the sixth biscuit, #441, was intact, so there are three analyses for that biscuit. The seventh biscuit, #437, was melted before it was sampled and the analysis furnished by Mallinckrodt was used. All other analyses are by Argonne.

The two biscuits, #436 and #437, which contained from 4.0% to 5.84% zirconium, had numerous rounded smooth holes throughout. The other biscuits which contained from 0.10% to 1.23% zirconium were reasonably sound. Biscuits #436 and #437 melted with a frothy, spitting, boiling action that loaded the crucible cover, stopper rod and sight glasses with drops of molten metal. Three melts were made with biscuit #437, but no ingots could be cast. Each time the metal became molten, it boiled up out of the crucible and froze the stopper rod to the crucible cover and the crucible. Biscuit #436 also boiled and frothed, but it was possible to pull the stopper rod before it froze at the top of the crucible. The other biscuits melted with only a normal amount of boiling, and with no frothing or spitting. The summary of melts appears in Table V. The ingot analysis and the per cent loss of zirconium content appear in Table VI.

The percentage loss of zirconium content was calculated from the average analysis of the biscuit and the average analysis of the ingot. The average analysis of the biscuit was obtained by averaging only the bottom sample and 1/2" from the top sample. The average analysis of the ingot

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was the average of the bottom sample and the 2-1/2" from the top sample. The top ingot samples were not used because of the segregation, and because the top few inches contained shrinkage pipe and are discarded before rolling.

TABLE IV
Biscuit Analysis

Biscuit	Sample Location	Zr (%)	C (ppm)	N (ppm)	Mg (ppm)
430	Skull	0.22	48	25, 28	20
	1/2" from top	0.095	47		15
	Bottom	0.11	31		15
431	Skull	0.22	29	<10	15
	1/2" from top	0.21	19		15
	Bottom	0.22	20		20
432	Skull	0.42	26	12, 18	20
	1/2" from top	0.46	21		20
	Bottom	0.45	19		20
433	Skull	0.58	20, 22	13	20
	1/2" from top	0.64	20		20
	Bottom	0.64	15		20
436	Skull	5.5, 5.4	525	560, 580	2000
	1/2" from top	5.0	130		1500
	Bottom	4.0	28		70
*437	Skull				
	1/2" from top	5.84			
	Bottom	4.21			
441	Skull	1.95	390	31, 44	>1000
	1/2" from top	1.23	43	<10	15
	Bottom	1.22	53, 60	27	20

*437 analysis by Mallinckrodt; all other analyses by Argonne.

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TABLE V

Melt Data

Ingot No.	Biscuit No.	Charged Weight (kg)	Cast Weight (kg)	Cross Section	Length (in.)	Crucible	Mold	Temperature		Melt Time	Furnace Vacuum (μ)
								Max. °C	Pouring, °C		
895	436	19.03	11.90	2" x 4"	5-1/2	Magnorite	Graphite	Sight-glass splattered with molten metal		2 hr-15 min	300
L-1	430	26.07	25.10	3" diam	14	Graphite	Graphite	1310	1310	1 hr-50 min	3
L-2	441	20.81	20.02	3" diam	12	Graphite	Graphite	1300	1300	1 hr-55 min	2
L-3	431	22.03	20.51	3" diam	12	Graphite	Graphite	1400	1300	1 hr-10 min	1
L-6	432	23.32	22.78	3" diam	13	Graphite	Graphite	1225	1225	0 hr-50 min	10
L-7	433	18.28	17.20	3" diam	10	Graphite	Graphite	1250	1250	1 hr-35 min	2
	437	13.93		Metal boiled out of crucible - no casting							

TABLE VI
Ingot Analysis

Ingot No.	Location	% Zr	C (ppm)	N (ppm)	Biscuit No.	% Loss of Zirconium Content
895	1" from top	4.34, 4.49	53, 51	318, 327	436	12.2
	Bottom	3.65, 3.68	16, 17	48, 50		
L-1	Top center	0.075	175, 150	17	430	28.5
	Top outside	0.078	210, 185	13		
	2-1/2" from top at center	0.070	185	13		
	2-1/2" from top at outside	0.076	230, 215	11		
	Bottom	0.073	120, 150	13		
L-2	Top center	1.35	40, 40	99	441	2.0
	Top outside	1.21	13	19		
	2-1/2" from top at center	1.20	7	17		
	2-1/2" from top at outside	1.18	8	11		
	Bottom	1.21	12, 13	17		
L-3	Top center	0.366	530	44	431	27.0
	Top outside	0.171	315	122		
	2-1/2" from top at center	0.149	300	<10		
	2-1/2" from top at outside	0.168	295	11		
	Bottom	0.156	315	11		
L-6	Top center	0.45	125, 125	32	432	3.3
	Top outside	0.44	31, 33	30		
	2-1/2" from top at center	0.45	46, 41	38		
	2-1/2" from top at outside	0.47	14, 14	38		
	Bottom	0.42	28, 31	24		
L-7	Top center	0.57	139, 106	38	433	11.0
	Top outside	0.57	145, 152	<10		
	2-1/2" from top at center	0.58	20, 23	<10		
	2-1/2" from top at outside	0.57	26, 25	19		
	Bottom	0.57	40, 41	15		

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2. High Temperature Strength Zirconium and Titanium Base Alloys (K. F. Smith, H. H. Chiswik)

Four commercially available titanium base alloys and two experimental zirconium base alloys had been tested for tensile strength at 650°C. These alloys were selected as "promising" on the basis of fragmentary extrapolated data available in the literature. For comparison purposes, an annealed stainless steel specimen was also tested. The experimental Zr-4% Al and Zr-7% Ti alloys were made at Armour Research Foundation. The alloys were rolled to 3/8" diameter at 980°C for the Zr-4% Al alloy and 900°C for the Zr-7% Ti alloy.

A schematic drawing of the apparatus designed and constructed for the tests is shown in Figure 2. The design is conventional except for the extensometer. A tube furnace is employed to heat a small specimen, with provision for an argon atmosphere, and a controlling thermocouple wired about the center of the specimen length. The whole unit is suspended from the upper crosshead of a Baldwin-Southwark tensile machine. The reduced section of the specimen was 2-3/4" x 1/8" in diameter.

To measure strains for calculation of the yield point a special type extensometer was made. Clamps attached to the reduced section of the specimen operated a tube-and-push-rod assembly extending out one end of the furnace. When the specimen elongated, the clamps pulled apart, and as the rods pulled out of the tubes, four electric strain gages on metal cantilevers were actuated, providing a measure of the extension. Calibration was effected by pulling a steel rod of known elastic modulus and by use of thickness spacers. Temperature correction was accomplished by observing the zero shift with a fused quartz rod under zero stress, used in place of a specimen. Temperature variation along the gage length of the specimen was observed to be within $\pm 3^\circ\text{C}$, when a split tube three section furnace was employed as the heating element.

All testing to date has been done at temperatures near 650°C. The effect of rate of loading was not fully appreciated at first and the crosshead speed was set at 0.017" per minute, which is quite slow. At very slow speeds and elevated temperatures the creep rate of the specimen becomes appreciable, distorting the true tensile values. Later, the crosshead speed was set at 0.050" per minute for comparison with data published in steel trade literature.

Tensile data taken to date are shown in Table VII. The effect of loading rate is apparent from the two Zr-4% Al entries. Zirconium-4% aluminum appears to compare very well with Type 347 stainless steel in ultimate strength, exceeding it materially in yield strength. The stainless steel used in this comparison was fully annealed, except for a cold worked skin from machining after the anneal. The zirconium alloys had

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Figure 2. Schematic of Hot Tensile Apparatus

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no heat treatment subsequent to rolling. The Zr-4% Al alloy was machinable with a good resulting chip after a hardened case was penetrated. The case undoubtedly was caused by unsheathed rolling at 980°C and is probably due to nitrogen contamination. Springback encountered in machining this alloy is probably inescapable in any material of low modulus and high yield strength. The Zr-7% Ti alloy is shown to be an intermediate strength material with a good ductility reserve, which should be ideal as a base for ternary alloy development.

TABLE VII

Tensile Strength of Alloys

Alloy	Commercial Designation	Testing Temp (°C)	Crosshead Speed (in/min.)	Ultimate Strength (psi)	0.2% Yield Strength (psi)
Ti-3% Al-5% Cr	MST-3% Al-5% Cr	650	0.017	29,500	17,000
Ti-4% Al-4% Mn	RC-130B	655	0.017	7,650	5,500
Ti-2.7% Cr-1.3% Fe	Ti-150A	635	0.017	9,600	9,000
Ti-7% Mn	RC-130A	647	0.017	6,760	---
Zr-4% Al	Experimental	650	0.017	38,200	35,000
Zr-4% Al	Experimental	650	0.050	49,300	---*
Zr-7% Ti	Experimental	650	0.017	22,100	20,000
347	Annealed Stainless Steel	645	0.050	50,900	23,500

*Extensometer trouble on this run.

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IV. BASIC METALLURGY - ACTIVITY 5411-011. Thermal Analysis of High Purity Uranium (J. E. Baumrucker, H. H. Chiswik)

Transformation and melting point temperatures have been determined by thermal analysis for three more high purity uranium ingots (see ANL-5036, Quarterly Report for March 31, 1953) and the thermocouple used in all the runs was calibrated against an NBS standard thermocouple (G 12141a). The calibration of the thermocouple is shown in Table VIII.

TABLE VIII

Calibration of Recording Thermocouple

Standard G 12141a Millivolts ⁽¹⁾	Thermocouple Temperature (°C)(2)	Recording Thermocouple Millivolts ⁽¹⁾	Temperature (°C)(2)	Error (°C)
5.2575	603.8	5.2605	604.2	-0.4
6.2635	701.1	6.2635	701.1	0.0
7.3120	799.4	7.3120	799.4	0.0
8.4430	901.2	8.4405	901.0	+0.2
9.6535	1006.7	9.6500	1006.5	+0.2
10.8465	1111.0	10.8450	1110.9	+0.1
11.2840	1148.3	11.2820	1148.1	+0.2
12.0270	1210.7	12.0235	1210.4	+0.3

(1) The Millivolts - Temperature relations are those given in NBS Circular 508, "Reference Tables for Thermocouples," May 7, 1951.

(2) Temperatures are in degrees centigrade (Celsius) according to the International Temperature Scale adopted in 1948.

Specimens, as in the previous runs, were in the form of tapering cylinders conforming with the interior contour of the urania crucibles. Dimensions were approximately 2" long x 7/8" top diameter, with a 1/4" hole through the core to receive the urania protection tube for the recording thermocouple. Before testing each new specimen, a preliminary run was made with only the urania crucible, cover, and protection tube components in the furnace. This run served to outgas the ceramic components as well as to give results on their heating characteristics. Rates of heating and cooling (see Table IX) were controlled by a separate recorder through a differential thermocouple arrangement. The chemical analysis of the

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TABLE IX

Thermal Arrest Duration Versus Approaching Rate of Temperature Change ($^{\circ}\text{C}/\text{Minute}$)

Specimen	Weight (Grams)	$\alpha - \beta$		$\beta - \alpha$		$\beta - \gamma$		$\gamma - \beta$		$\beta - \alpha$		$\beta - \alpha$	
		Time (Min)	Heating Rate ($^{\circ}\text{C}/\text{Min}$)	Time (Min)	Cooling Rate ($^{\circ}\text{C}/\text{Min}$)	Time (Min)	Heating Rate ($^{\circ}\text{C}/\text{Min}$)	Time (Min)	Cooling Rate ($^{\circ}\text{C}/\text{Min}$)	Time (Min)	Heating Rate ($^{\circ}\text{C}/\text{Min}$)	Time (Min)	Cooling Rate ($^{\circ}\text{C}/\text{Min}$)
370	309.484	38	1.25	50	0.97	79	1.0	36	1.95				
		42	1.1	--	--	127	0.54	35	1.5				
		27	1.59	57	0.83	57	1.34	43	1.58	31	2.78	67	1.18
		--	--	34	1.35	26	2.43	35	2.27	35	3.02	72	1.35
		18	2.03	45	1.12	35	1.83	45	1.72				
417	314.013	40	1.09	38	1.18	105	0.73	32	2.04	27	3.16	63	1.18
		33	1.21	40	1.10	69	0.87	40	1.81	31	3.46	95	1.13
		28	1.45	35	1.26	57	1.12	37	1.85				
		22	1.49	40	1.15	35	1.62	38	1.94				
		23	1.42	39	1.19	36	1.59	33	1.94	30	3.25	74	1.25
427	321.247	21	2.0	59	0.72	51	1.34	45	1.71	35	2.02	51	1.89
		22	1.48	60	0.7	--	--	38	1.87				
		24	1.62	38	1.24	59	1.31	35	2.03	42	2.78	52	2.60
		6	6.08	--	--	9	7.05	--	--	20	4.93		

ingots is shown in Table X. In addition, carbon and nitrogen analyses were received for ingot #369 previously reported, and were as follows: Carbon - top 17 ppm, bottom 15 ppm; nitrogen - top 14 ppm, bottom less than 10 ppm.

TABLE X

Chemical Analyses of Specimens As Received (in ppm)

	Al	Cr	Cu	Fe	Mg	Mn	Na	Si	C	N
Specimen #370										
Top	5	<1	1	3	0.5	1	<2	10	17	
Core	5	<1	2	2	0.5	1	<2	10	22	
Specimen #417										
Bottom	5	1	1	3	0.5	0.5	<2	<10	35-55	<10
Top	5	1	2	10	0.5	2	<2	10	48-55	28-32
Core	5	1	1	3	0.5	0.5	<2	10	---	---
Specimen #427										
Bottom	10	1	2	5	0.5	0.5	<2	10	---	---
Top	10	1	1	2	0.5	0.5	<2	10	25	
Core	10	1	1	10	0.5	0.5	<2	10	---	

< = Less than. (---) = No test.

Elements listed are those for which analyses were above the limits of detection. The following elements were below the limits of spectrographic detection: Ag, As, B, Be, Bi, Ca, Co, K, Li, Mo, Ni, P, Pb, Sb, Sn, Ti, Zn.

The results are summarized in Table XI. The values given had been corrected for the calibrations indicated above. Corrected values are also included for the previously run ingots #327 and #369.

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TABLE XI

Thermal Arrest Points⁽¹⁾
(Degrees Centigrade)

Specimen ⁽²⁾	$\alpha - \beta$	$\beta - \alpha$	$\beta - \gamma$	$\gamma - \beta$	M.P. Heating	F.P. Cooling
327	666.7	--	773.7	771.8	--	--
	667.0	--	773.7	--	1130.2	--
	--	656.4	773.0	765.7	1131.0	1131.1
	--	655.7	--	768.6	1130.5	1131.0
369	666.0	--	771.2	767.7	--	--
	666.4	656.5	771.6	762.2	1130.8	1130.9
	666.3	656.5	771.1	766.1	1130.8	1130.8
370	664.7	657.1	770.4	767.1	--	--
	665.0	--	770.3	767.8	--	--
	666.0	658.2	771.2	767.4	1129.7	1129.4
	--	657.0	771.6	766.0	1129.1	1128.5
	665.8	657.3	771.1	767.1	--	--
417	663.9	655.8	769.5	765.8	1128.5	1128.0
	663.9	655.7	769.3	765.1	1128.3	1128.0
	664.1	654.8	769.2	765.0	--	--
	664.2	655.2	769.4	763.1	--	--
	663.9	655.1	769.3	764.6	1127.7	1127.7
427 ⁽³⁾	667.6	659.5	772.4	768.4	1130.4	1130.8
	666.9	658.8	--	767.6	--	--
	667.1	658.3	771.5	767.3	1130.2	1129.7
Average of All Runs	665.6	656.7	771.1	766.5	1129.8	1129.6

(1) Values are corrected for thermocouple calibration. Mv. versus temperature values used are those in NBS Circular 508, "Reference Tables for Thermocouples," May 7, 1951. Temperatures are according to International Temperature Scale adopted in 1948.

(2) Each row represents one cycle of heating and/or cooling the specimen.

(3) This specimen was run with an NBS standard thermocouple (# G 12141b).

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Figure 3. Composite Photomicrograph of the Two Metallographic Faces of Crystal I Showing the Traces Observed After the Third Compression.

Macro #14960

Polarized Light

Approximately 31-X

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TABLE XII

Traces Observed on Crystals I, J, and K

Face	Trace	Angular Measurement with Respect to Common Edge*	Identity
<u>Crystal I After Third Compression</u>			
A	a	81°C	($\bar{1}72$)
A	c	68°C	($\bar{1}30$)
A	e	44°CC	(130)
A	g	79°CC	(010)
B	b	73°C	($\bar{1}72$)
B	d	80°C	($\bar{1}30$)
B	f	64°CC	(130)
B	h	85°CC	(010)
<u>Crystal J After Third Compression</u>			
A	a	70°CC	(130)
A	b	89.5°C	($\bar{1}30$)
A	c	87°CC	(130)
B	d	41°CC	($\bar{1}72$)
B	e	88°CC	(130)
A	f	59°CC	($\bar{1}72$)
A	g	76.5°CC	(0 $\bar{1}0$)
B	h	65.5°CC	(0 $\bar{1}0$)
B	i**	44°CC	($\bar{1}30$)
<u>Crystal K After Second Compression</u>			
A	a	34.5°CC	($\bar{1}30$)
B	b	17°CC	($\bar{1}30$)
A	c	44.5°C	($\bar{1}30$)
B	d	47°C	(130)
A	e	13.5°C	($\bar{1}72$)
B	f	6.5°C	($\bar{1}72$)
A	y	13.5°CC	($\bar{1}72$)
A	h	79°CC	($\bar{1}12$)
B	i	34.5°C	($\bar{1}72$)
A	j	18.5°C	(0 $\bar{1}0$)
B	k	14.5°C	(010)
B	l	65.5°CC	kink

*C indicates that the angle is measured clockwise from the common edge; CC = counterclockwise from the common edge.

**This trace appeared after the fourth compression.

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Figure 4. Load-Contraction Curves for Crystal I.

Macro #14997

1/2-X

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The crystal was then given a second compression which resulted in further twinning as evidenced by the sudden load drops accompanied by audible clicks. Metallographic examination after this second compression gave no indication of appreciable change other than the presence of some more twins. A third compression resulted in slip traces appearing on face A (trace "g"). These traces, together with traces "h" on face B, were shown by two-surface analysis to be caused by (010) plane slip. In addition, traces "f" on face B were formed which could be coupled over the common edge to traces "e" on face A. Two-surface analysis showed these traces to be caused by (130) plane twins.

No new deformation traces resulted from the fourth compression. In general, the (130) twins increased, as did the (010) plane slip.

As had been hoped, this crystal showed considerable (130) plane twinning (the specimen was so oriented that the (130) plane twinning should occur in preference to the ($\bar{1}30$) plane twinning). This twinning, however, was preceded by (010) plane slip, even though the crystal was relatively unfavorably oriented for slip on this system, the slip plane and slip direction being oriented at an angle of 74 degrees from the compression direction. If one considers the onset of noticeable (load = 18 pounds) contraction in the stress-strain curve as being due to slip preceding twinning, a value of 0.35 kg per mm² is obtained for the critical resolved shear stress on the (010) slip system. This value however, should be considered approximate only, since the mechanical features of the tensile testing equipment were not sufficiently accurate to yield a straight line portion on the stress-strain curve, and the sensitivity of the strain gage is probably too low to pick up the very small contractions resulting from the early stages of slip. In fact, the curvature of the stress-strain curve might be indicative of the onset of fine slip at the very early stages of compression, at loads considerably below 18 pounds.

Crystal J

The orientation of crystal J was chosen analogously to that of crystal I; that is, the crystal was compressed so that the formation of irrational {172} type twins would result in maximum contraction. The corresponding direction was 75.5° from [100], 24.5° from [010], and 71.5° from [001]. A Laue photogram taken after preparation of the crystal showed the actual compression direction to be three degrees from the desired direction. The metallographic faces for two-surface analysis were inclined at 128°.

Prior to deformation the crystal exhibited four incidental twin trace directions near the compression faces (probably as a result of preparation of the crystal by grinding). These are traces "a," "b," and "c" on face A and "e" on face B (see Figure 5 and Table XII). Two-surface analysis showed traces "a" and "e" to be caused by ($\bar{1}30$) plane twins. One-surface

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Figure 5. Composite Photomicrograph of the Two Metallographic Faces of Crystal J Showing the Traces Observed After the Third Compression. The irregular shaped marking on the upper half of face A is a superficial scratch resulting from handling the crystal, and its presence should not have appreciably affected the deformation mechanisms occurring during the deformation.

Macro #14958 Polarized Light Approximately 31-X

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analysis indicated that traces "b" and "c" could have been caused by (130) plane twins. With the exception of these traces, the crystal was free from imperfections and strains as indicated by lack of asterism on X-ray Laue diagrams. The crystal was subjected to a series of four compressions in the Tinius-Olsen tensile machine. On the first compression the crystal was removed from the compression fixture after the first indication that twinning had occurred. Metallographic examination revealed the formation of one twin on the lower half of face B (twin A in Figure 6). This twin, designated as trace "d" in Figure 5, was analyzed by one-surface analysis to be an irrational $(1\bar{7}2)$ type twin. The second compression resulted in formation of additional traces of "d" on face B and their continuation over the common edge to traces "f" on face A (see Figure 5). Two-surface analysis of these traces identified them as irrational $(1\bar{7}2)$ plane twins.

A third compression increased the number of these $(1\bar{7}2)$ twins and gave the first metallographic evidence of slip having occurred in the crystal. Two-surface analysis of these slip traces ("g" on face A and "h" on face B) showed them to be (010) . The fourth and final compression brought about the formation of additional $(1\bar{7}2)$ twins, more (010) slip and the formation of $(1\bar{3}0)$ twins. The latter occurred as traces parallel to traces "b" on face A and traces "i" nearly parallel to traces "d" on face B. These could be easily followed over the common edge and are clearly shown to be $(1\bar{3}0)$ plane twins by two-surface analysis.

This crystal is the first one that we have studied which resulted in the formation of the irrational $\{172\}$ type twin in a manner suitable for two-surface analysis. It was possible to take an X-ray Laue back-reflection photogram from face B after the third compression that included the orientation of both the parent and twinned metal. The stereographic solution indicates the pole of the mirror plane to coincide with the $[312]$ direction, which is in accord with the findings of Cahn.²

The series of microphotographs shown in Figure 6 illustrate the progressive growth of the (172) twins as a result of gradually increasing deformations. Twin A, formed on the first compression, has progressed only a little more than halfway across the face. After the second compression this twin has traversed the face entirely. Similarly, twins B and C have only partially traversed the face after the second compression, but grew on the third compression to cross the face completely.

Crystal K

Crystal K was compressed in a direction 32 degrees from the $[100]$, 81 degrees from the $[010]$, and 60 degrees from the $[001]$ which should result, upon compression, in the formation of $\{121\}$ type twins in the maximum

²R. W. Cahn, "Plastic Deformation of Alpha Uranium; Twinning and Slip," *Acta Metallurgica*, Vol. 1, No. 1, 49-70, January 1953.

Figure 6. Composite Photomicrograph Showing the Lower Portion of Face B, Crystal J, in Three Stages of Compression. It is possible to follow the twin traces designated by the letters A, B and C in the various stages of compression and to note that they continue to traverse the crystal as a result of continued compression.

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Polarized Light

Approximately 31-X

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contraction of the crystal. Subsequent Laue photograms indicated the actual direction of compression to be 4 degrees from this desired direction. Two faces inclined at 132 degrees were polished metallographically for two-surface analysis.

Prior to deformation the crystal exhibited nine minor trace directions near the compression faces and near the outer edges, none of which could be followed over the common edge for solving by two-surface analysis. Traces "a," "c," "e," "g" and "h" were found on face A and traces "b," "d," "f" and "i" appeared on face B. The angular location of these with respect to the common edge is given in Table XII together with their identities on the basis of the locus of poles method. All of the identities are reasonably certain except that of trace "h." The locus of poles for this trace did not pass as close to the $(\bar{1}\bar{1}2)$ pole as did the loci of the other traces through their respective poles. The trace itself was quite short, which necessarily would lead to difficulty in measuring accurately its angular relation with respect to the common edge. In spite of the relatively large number of traces observed near the outer surfaces, Laue spots from the crystal did not exhibit asterism.

The crystal was subjected to two compression tests. The load-contraction curves are given in Figure 7. During the first compression the crystal deformed fairly elastically until a load of 46.5 pounds was reached. At this load appreciable plastic deformation began. Loading was continued until a fair amount of plastic deformation had occurred and the specimen removed for microscopic examination. No new twin traces were found on the metallographic faces of the crystal; however, both faces gave evidence of slip traces (trace "j" on face A and trace "k" on face B). A two-surface analysis of these traces showed them to be (010) slip. The load-contraction curve of the second compression indicated increased deformation by slipping and was terminated after a sudden falling of the load from 51 to 47.5 pounds. Metallographic observations indicated this sudden drop of load to be caused by kinking involving the (010) slip plane and the [100] slip direction. This kink band appeared only on face B of the crystal (trace "l"). It could be observed macroscopically on the three nonmetallographic faces which had been ground perpendicular to the compression faces, and on the top compression face. The band on the top compression face was almost parallel to the edge between this face and face A, and appeared extremely close to this edge. Since the band did not appear on face A it was impossible to obtain a two-surface analysis of the pole of the plane bisecting the angle between the slip planes in the parent crystal and those in the kinked material. X-ray photograms on face B from an area which included the parent and kinked material showed the typical rotation of the lattice around the [001] direction. This may be considered sufficient evidence of the identity of this band as "kinking." No additional compressions were made, for it was believed that deformation would continue to proceed by (010) slip and kinking. Thus, the crystal failed to yield the $\{121\}$ type twins reported by Cahn,³ even though compressed in a favorable direction.

³R. W. Cahn, op. cit.

Figure 7. Load-Contraction Curves for Crystal K.

Macro #14999

1-X

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If one considers the beginning of marked contraction on the stress-strain curve as coinciding with the initiation of slip (at 46.5 pounds, Figure 7), the calculated critical resolved shear stress for (010) slip is 0.92 kg per mm², which is more than twice the value found for crystal I. The discrepancy is probably further evidence that the initiation of substantial contraction is probably associated with macroslip rather than indicative of the initiation of the early stages of slip. To check this point, it would be necessary to examine the faces at high magnifications at successive stages of compression prior to the onset of macrodeformation.

3. Preferred Orientation in Uranium (M. H. Mueller, H. W. Knott)

a. Uranium Rods Rolled at Various Temperatures

A number of physical and mechanical properties have been reported previously in ANL-5097 by R. M. Mayfield for a number of uranium rods rolled at 300°, 400°, 500°, 600° and 640°C. All rods were given a 75% final reduction with both hand round and oval pass roll designs. A preferred orientation study has also been completed on these same rods using the reflection technique. The pole charts obtained from these rods indicated that the rods rolled at the lower temperatures showed an approximate (010) and (120) texture component with the (010) predominating. There was a gradual decrease of the (010) component with temperature and a corresponding increase of the (120) component. At the higher temperatures the (120) component has shifted to a (110) with a minor (010) component. A study of the texture in these same rods after annealing in the high alpha range showed that the rods rolled at 300°, 400°, and 500°C developed the typical approximate (140) and (010) components after annealing, whereas the rods rolled at 600° and 640°C showed no appreciable change. There appeared to be little difference in orientation results between the hand round rolled and the oval rolled rods.

b. High Purity Uranium Rod, 300°C Rolled and Recrystallized

A relatively small piece of high purity uranium rod, 3/8" in diameter, which had been previously rolled to an 85% final reduction at 300°C, was used for an orientation study. Pole charts were constructed from the intensity data obtained from twenty-one different reflections as a function of ϕ . After analyzing these curves, together with the $I \sin \phi$ corrected curves, the texture developed in this particular rod as rolled could be described as a duplex (041) and (352) texture with (041) being the major component. However, further work on other high purity rods is necessary in order to determine if these components are typical of this type of material. It was also noted that the textures seemed to be somewhat sharper than observed previously with project grade uranium rolled to the same final reduction.

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Inverse pole figures were constructed according to the method given by Harris⁴ from the transverse section of the as rolled and also the recrystallized high purity rod. The inverse pole figure from the as rolled material confirmed the previously mentioned (041) and (352) components. The (041) is apparently retained after recrystallization but the (352) has shifted and broadened somewhat so that there now appears to be a high intensity area bounded by the (130), (131) and (150) in terms of an (001) standard projection. It is interesting to note that this area includes the (140) which is one of the texture components previously reported for recrystallized uranium rod.

c. Beta Treated Uranium Sheet

Some preliminary work has been done on preferred orientation found in uranium sheet after beta treating at 740°C and water quenching. This 1/8" thick sheet had been previously rolled to an 87% final reduction at 300°C. The intensity data obtained from a number of different reflections were plotted in terms of an inverse pole figure according to the method of Harris.⁵ Although the sheet appeared to be nearly random after beta treating, there appeared to be some detectable difference in orientation from the center to the outside of the sheet. Further work is necessary to determine the depth of this outer slightly oriented layer.

4. The Constitution of the Uranium-Carbon Alloys (B. Blumenthal, B. G. Allen)

The work on the constitution of the high purity uranium-carbon alloys at low carbon concentration progressed toward:

1. The determination of the liquidus temperatures at low carbon concentrations;
2. The determination of the solubility limits of carbon in gamma uranium.

a. The Liquidus Curve

Previous determinations of the liquidus temperatures by Snow (CT-954 and CT-1102), Carter (CT-609), and by Mallet, Gerds, and Nelson (J. Electrochem. Soc., 99, 197-204 (1952)) began at a temperature of 1350°C and a concentration of 1000 ppm of carbon. Their data represent saturation concentrations of carbon in uranium for a given temperature or temperature range. The data by these authors agree fairly well for temperatures of 1350° to 1600°C and concentrations of 1000 to 5000 ppm of carbon.

⁴G. B. Harris, "Quantitative Measurement of Preferred Orientation in Rolled Uranium Bars," Philosophical Mag. Series 7, 43, 113 (1952).

⁵G. B. Harris, op. cit.

It was first felt that the saturation method would be applicable to alloys of less than 1000 ppm carbon. However, melting experience with uranium in graphite crucibles repeatedly showed that it is difficult to restrict the carbon pickup to saturation concentrations. The carbides form rather rapidly even at a relatively low temperature. It therefore appeared more attractive to approach the problem from the opposite side and liquate alloys of higher carbon concentration at a constant temperature in a resistance furnace and analyze for the carbon retained in the metal. One might object that subsequent concentration changes during solidification will cause the concentrations at the liquidus temperatures to appear lower than the equilibrium concentrations at the liquation temperatures. However, the rate at which the carbides rise to the top is rather small at the temperatures and concentrations concerned, and experience with many liquations in previous years has shown that even directional solidification should not affect the result very much. Regarding the time factor, it is probably sufficient to liquate for five hours, though it may be advisable to extend the time to perhaps twelve hours to attain true equilibrium.

The feasibility of the approach was demonstrated by a series of liquations which were carried out for the purpose of removing carbon from reactor grade uranium. The melts were made in urania crucibles in our resistance furnace. The data are listed in Table XIII and plotted in Figure 8. The individual ingots have a remarkably uniform composition. The solubility of carbon in liquid reactor grade uranium at its freezing point is about 170 ppm. Similar experiments will now be made with high purity uranium.

TABLE XIII

Carbon Content of Liquated Reactor Grade Uranium

No.	Melting Conditions	Sample Location	Carbon Content (ppm)	Average Carbon Content (ppm)
B-96	Liquated at 1190°C for 24 hours. Directional solidification.	Upper center Lower center	260 240	250
B-473	Liquated at 1145° to 1155°C for 6 hours, 20 minutes. Stationary solidification.	Top Bottom	235,240 190,225	223
B-474	Liquated at 1138°C for 24 hours. Stationary solidification.	Top Bottom	166,174 173,181	172

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b. The Solubility of Carbon in Gamma Uranium

The classical metallographic method of determining solubility limits in the solid state consists of heat treating a series of alloys of increasing solute concentration at various constant elevated temperatures, subsequent water quenching, and observing metallographically at room temperature whether or not these alloys are homogeneous, assuming that the quench will cause no structural changes that will obscure the high temperature equilibrium conditions.

A triple melting procedure was devised to obtain high purity uranium-carbon alloys of uniform concentration. The alloys were prepared by saturating the melt with carbon in a high purity graphite crucible at 1400°C in our vacuum resistance furnace, remelting the ingots in a urania crucible, and after cropping, remelting a second time in an inverted position at 1200°, 1300°, and 1400°C, respectively. Holding time at the third stage was one hour which, at the time of the experiment, was thought to be long enough to obtain uniform carbon distribution, particularly since the ingots were remelted a second time. The alloys were solidified by quickly lowering them from the hot zone into the cold end of the furnace tube. The ingots were scalped, annealed for six hours at 1000°C for further homogenization, and water quenched. They were then sectioned and analyzed at both ends, at the top T and the bottom B. Only one ingot was of satisfactorily uniform composition, and that was one which, at the intermediate remelting, was diluted with high purity crystals. The analytical results and the schedule of ingot preparation are shown in Table XIV. Spectrochemical analyses indicated no appreciable contamination of the high purity uranium. Only in one case a pickup of 20 ppm iron, and in another case one of 300 ppm chromium were reported, the reality of which is doubtful. Analyses showed a slight nitrogen contamination of 5 to 10 ppm over and above the nitrogen content of the high purity metal, but it is felt that this can be brought under control by longer holding times, a condition which should also improve the uniformity of the higher carbon ingots.

Sections of these ingots of 8 to 12 grams of weight were electrolytically cleaned, individually wrapped in tantalum foil, and sealed two at a time in Vycor or quartz tubes at a pressure of 1×10^{-5} mm mercury or better. The tubes with the specimens were suspended in a vertical tube annealing furnace and annealed at 700°, 800°, 900°, 1000°, or 1100°C for periods ranging from three days for the lowest temperature to one hour for the highest one. The temperature was controlled within $\pm 4^\circ\text{C}$. The alloys were water quenched by dropping the tubes into a bucket of water and breaking them instantaneously by means of an automatic device.

Only one of the sets, the one that was annealed at 900°C for 24 hours, has been metallographically examined to date. The series shows increasing amounts of the primary carbide phase with increasing liquation temperature (see Figures 9-a, -b, -c). Correlation with the analytical

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TABLE XIV

Effect of Melting Conditions on Carbon Content
of High Purity Uranium

No.	Melting Sequence	Crucible	Sample Location	Carbon Content (ppm)	Average Carbon Content (ppm)
B-459	1/2 hour at 1350°C + 2 hours at 1200°C	Graphite	T B	135,160 610	---
	Diluted with new crystals, 1/2 hour at 1400°C	Urania	---	---	---
	Remelted 1/2 hour at 1400°C	Urania	T B	240,243 248,258	240 260
B-468	1 hour at 1400°C	Graphite	---	---	---
	Remelted 1 hour at 1300°C	Urania	---	---	---
	Remelted 1 hour at 1200°C	Urania	T B	471,472 403,416	470 410
B-471	1 hour at 1400°C	Graphite	---	---	---
	Remelted 1 hour at 1300°C	Urania	---	---	---
	Remelted 1 hour at 1200°C	Urania	T B	454,487 472,419	470 450
B-465	1 hour at 1400°C	Graphite	---	---	---
	Remelted 1 hour at 1400°C	Urania	---	---	---
	Remelted 1 hour at 1300°C	Urania	T B	510,515 313,385	515 350
B-461	1 hour at 1400°C	Graphite	---	---	---
	Remelted 1 hour at 1400°C	Urania	---	---	---
	Remelted 1 hour at 1400°C	Urania	T B	513,563 408,433	540 420

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Figure 9. Uranium-Carbon Alloys, Annealed 24 Hours at 900°C, Water Quenched.
(All specimens hand polished only)

9-a. 470 ppm Carbon.

Micro #15039

100-X

B-468T - Last melting at 1200°C.

9-b. 515 ppm Carbon.

Micro #15038

100-X

B-465T - Last melting at 1300°C.

9-c. 550 ppm Carbon.

Micro #15037

100-X

B-461T - Last melting at 1400°C.

9-d. 250 ppm Carbon.

Micro #15036

100-X

B-459 - Last melting at 1400°C.

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results is uncertain. Substantially less of the primary phase is present in the specimens containing 250 ppm carbon (Figure 9-d). The contours of the primary phase are rounded because of the heat treatment in the gamma range.

As etched, all of the specimens show precipitate both at the alpha grain boundaries and inside the alpha crystals. The quantity of the precipitate is slightly less in the 250 ppm carbon alloy (Figure 10-a) than in the other ones (Figure 10-b). An estimate is difficult to make as the lamellae or strings of precipitated particles frequently follow the substructure of the alpha grains and are abundant when they are sectioned parallel to their largest dimension, but seem to be almost absent when they are sectioned perpendicular to this direction. Figure 10-b shows two adjacent grains of alloy B-468T with 470 ppm carbon, one with much precipitate, the other one almost void.

The experiments show that at 900°C the solubility of carbon in gamma uranium is less than 250 ppm.

5. Uranium-Zirconium Alloys (S. T. Zegler, H. H. Chiswik)

Solubility of Zirconium in Alpha Uranium. A series of uranium-zirconium alloys containing from 0.09 w/o Zr to 2.5 w/o Zr were rolled at 550°C or 600°C and heat treated for one week at 1000°C, furnace cooled to 640°C, held for 90 hours, and water quenched. Metallographic examination indicated a single phase structure in only the 0.09 w/o Zr-U alloy (H171). All the specimens contained angular inclusions in small quantities, as shown in Figure 11; in some instances, the inclusions appeared as discontinuous stringers. The alloys containing 0.6 w/o (H-174), 1.0 w/o (H-163), 1.7 w/o (H-160) and 2.5 w/o (H-165) zirconium were all two-phase alpha uranium and a spheroidal particle phase in the form of a fine precipitate. The microstructures of the two-phase alloys are typified in the photomicrographs of the 0.6 w/o Zr-U and the 2.5 w/o Zr-U alloys in Figures 12 and 13. The amount of precipitate phase increased with increasing zirconium content. From Figure 13-a it can be readily seen that there is no difficulty in distinguishing the spheroidal particles of the second phase from the inclusions.

The alpha grain size of the lowest alloy in the series, as viewed under polarized light was very coarse and a somewhat progressive decrease in size was observed with increased zirconium content up to about 1 w/o Zr, indicating a restricting influence of zirconium upon alpha grain size. Beyond 1 w/o Zr, no clear-cut alpha grain structure could be resolved under polarized light, presumably due to presence of large quantities of precipitated second phase.

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Figure 10. Uranium-Carbon Alloys, Annealed 24 Hours
at 900°C, Water Quenched.

(Electrolytically etched in oxalic acid)

10-a. 250 ppm Carbon.

Micro #15040

250-X

B-459 - Some precipitate.

10-b. 470 ppm Carbon.

Micro #15047

250-X

B-468T - Precipitate in adjacent grains.

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Figure 11. U-0.09 w/o Zr Alloy Showing Angular Inclusions in a Matrix of Alpha Uranium.

Micro #14946 Bright Field 500-X
 H_3PO_4

Figure 12. U-0.6 w/o Zr Alloy Showing Distribution and Spheroidal Character of Second Phase in Matrix of Alpha Uranium. Longitudinal Section.

12-a.

Micro #14944 Bright Field 500-X
 H_3PO_4

12-b.

Micro #14945 Bright Field 2000-X
 H_3PO_4

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Figure 13. U-2.5 w/o Zr Alloy Showing Large Volume of Spheroidal Second Phase. Note also inclusion stringers in Figure 13-a.

Micro #14951 Bright Field 500-X
 H_3PO_4

Micro #14952 Bright Field 1000-X
 H_3PO_4

Figure 14. Typical Inclusions Found in All Quenched Alloys.

Micro #14762 Bright Field 500-X

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From the observations made, it is tentatively considered that the limit of zirconium solubility in alpha uranium at 640°C is less than 0.6 w/o Zr, which is considerably below the values indicated in either the B.M.I., Ames, or N.B.S. diagrams.

Microstructures of Alloys Quenched from 800° and 1000°C. Specimens from the above series of alloys, in the form of slivers 1/2" long by about 0.050" in cross section, were heat treated for two hours at 800°C and 64 hours at 1000°C and drastically quenched in 10% NaOH solution. The following microstructural features were noted:

1. Inclusions. All the specimens contained some angular primary inclusions which did not dissolve even after 64 hours at 1000°C (see Figure 14). The total content of inclusions increased slightly up to 1 w/o Zr. The inclusions tended to be larger in size in the 1000°C quenched specimens.
2. Veining. The 800°C quenched specimens began to develop a "ghost boundary" veining constituent at a zirconium content of 0.60 w/o, which increased in size with increasing zirconium content. This "veining" constituent was more pronounced in the 1000°C quenched alloys, and was present even in the 0.09 w/o alloy. A typical illustration of this structure is shown in Figure 15. That the boundaries outlined by the veining constituent are not related to the alpha uranium boundaries is clearly shown in Figure 16, a and b, illustrating the same area under bright field and polarized light, respectively. The crystallographic nature of the veins in Figure 16-b suggests that they are probably related to the gamma grain structure.
3. Grain Size. The alpha uranium grain size decreases progressively up to about 1 w/o Zr, beyond which it is no longer possible to distinguish grain boundaries clearly under polarized light.
4. Acicular Structure. In the 800°C quenched alloys an acicular structure begins to appear at about 0.71 w/o Zr (see Figure 15-a). At 1.6 w/o Zr the whole microstructure is finely acicular. In the 1000°C quenched alloys the same structure is observed, although heterogeneously, as shown in the series of photomicrographs of Figure 17. This type of microstructural heterogeneity was previously reported in ANL-5079 (Quarterly Report, 30 June 1953) and was ascribed to nitrogen content variations. Subsequent analysis of the material indicated, however, the nitrogen analysis to be uniform and below 10 ppm, which makes this interpretation untenable. The present series of alloys showed a uniform nitrogen content throughout the ingot. The cause of this microstructural heterogeneity remains obscure, except that it may be indicative of chemical heterogeneity with respect to zirconium content on a microscale.

Figure 15. Veining Constituent at Ghost Boundaries.

15-a. 0.71 w/o Zr Alloy Quenched
from 800°C.

Micro #14779 Bright Field 550-X

15-b. 0.60 w/o Zr Alloy Quenched
from 1000°C.

Micro #14808 Bright Field 500-X

Figure 16. Relationship Between Veining Boundaries and Alpha Uranium Structure. 0.21 w/o Zr Alloy Quenched from 1000°C.

16-a. Bright Field

Micro #14795

500-X

16-b. Same area in polarized light

Micro #14796

500-X

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Figure 17. Microstructures of 1.62 w/o Zr Alloy Quenched from 1000°C.

17-a. Note absence of acicular structure in some areas.

Micro #14809 Bright Field 100-X

17-b. Acicular structure and veining.

Micro #14813 Bright Field 1000-X

17-c. Tricorner boundary.

Micro #14811 Bright Field 500-X

17-d. Same area as 17-c under polarized light.

Micro #14812 Pol. Light 500-X

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6. Uranium-Zirconium-Niobium Alloys (H. H. Chiswik)

Specimens from an alloy containing 4-1/2 w/o Zr and 1-1/2 w/o Nb (nominal composition, Ingot H-203) were examined metallographically and X-ray Debye patterns and hardness measurements made after the following heat treatments: a) As quenched after 1 hour at 800°C (γ phase); b) Quenched and annealed for 3 hours at 350°C. The metallographic specimens were in the form of 1/4" cubes; for X-ray patterns, slivers about 1/2" long by 0.040" in cross section were quenched and subsequently electroetched and electropolished to a fine point.

Microstructure. The specimens contained some insoluble, angular and rosette shaped inclusions, the nature of which is uncertain. The "as quenched" specimens exhibited a typical, regularly aligned, martensitic plate-like structure resembling closely martensitic structures observed in other alloy systems (for example, In-Tl), as shown in Figure 18. This structure persisted and showed no evidences of decomposition on annealing at 350°C. The plate-like structure definitely suggests a crystallographic type of transformation directly from gamma to alpha for this alloy composition.

X-Ray Debye Patterns. The "as quenched" slivers exhibited very diffuse alpha uranium lines only, with no indications of retained gamma. Upon annealing at 350°C, the lines sharpened somewhat, although not appreciably; this is probably an indication of some relaxation of the strained martensitic lattice taking place. One sample, annealed at 500°C, yielded some additional lines of another phase, indicating the beginning of decomposition. The back-reflection lines of the alpha uranium were still broad and diffuse, however.

Hardness. The following hardness readings were obtained:

1. As Quenched	475 VPN and 47 RC
2. Annealed at 350°C	651 VPN and 58 RC

The results indicate age-hardening of the alloy.

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Figure 18. Microstructure of Quenched U-4 $\frac{1}{2}$ % Zr-1 $\frac{1}{2}$ % Nb Alloy.

Micro #14705

Polarized Light

250-X

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V. APPLIED METALLURGY - ACTIVITY 5461

1. Zone Melting of Uranium Alloys (R. J. Dunworth, R. E. Macherey)

The principles of zone melting are well described by Pfann.⁶ Only a brief description, therefore, will be given here. A bar of uranium alloy is laid horizontally in a split tube of ceramic or graphite. A short molten zone is made to traverse the length of the rod by means of a heater to melt the zone and movement either of the heater or the rod. By the processes of solute diffusion in the liquid zone and solidification at the solid-liquid interface the concentration of the solute is changed in the bar. If the process is repeated by passing the zone in the same direction, the solute is concentrated at one end of the bar. The length of the bar, the length of the molten zone, the shape of the equilibrium diagram, and the number of passes are the principal factors that determine the theoretical purification. The actual purification, in addition to these factors, depends on the solute diffusion rate and the speed of zone movement. The present program in the Metallurgy Division at Argonne is to evaluate these factors for plutonium and zirconium alloyed with uranium.

Some five zone melts have been made to test the equipment and the method. The uranium rod was 0.6" in diameter and was placed in a 15" long, 1" inside diameter, split tube. Both Al_2O_3 and graphite have been used as boats for holding the metal while melting. The RA-98⁷ grade of Al_2O_3 was satisfactory, while the RA-1164 grade broke when the uranium melted. The first four melts were made using a single turn coil and the Tocco 30 KW 10,000 cycle motor generator. The inside diameter of the coil was 1-15/16", and about 13 KW of the 30 KW available was used for melting the 0.6" diameter rod. In Table XV the data for these zone melts are listed. It may be noted that ZM-5 was melted using the Westinghouse 20 KW, 450 KC, RF Tube Oscillator, Induction Heating Generator. The generator developed about 12 KW and 3.5 KW were used for melting, using a two turn, 2" inside diameter coil made from 1/4" diameter copper tubing.

No conclusive results are demonstrated by the data in Table XV but some trends are indicated. The zirconium does not segregate unless the speed is 1/8" or 1/16" per minute with a 3/4" zone width. Similarly, chromium, copper, iron, magnesium, manganese and nickel require about this speed for appreciable segregation. To move aluminum, boron and silicon, even slower speeds seem desirable. A speed of 0.8" per minute will move nitrogen, and a speed of 0.5" per minute will move carbon. These elements may be expected to diffuse more rapidly in uranium than the metallic elements and the faster speeds are sufficient for moving carbon and nitrogen.

⁶Pfann, W. G., "Principles of Zone Melting," J. of Met., p 747, July, 1952.

⁷Manufactured by the Norton Company.

TABLE XV
Zone Melt Data

XV-A. Melting Conditions

Melt No.	Boat	Vacuum (μ)	Metal	Passes	Speed (In/Min)	Generator	Zone Width (Inches)
ZM-1	Al ₂ O ₃	0.5	H-276	16	0.8	Tocco	~3/4
ZM-2	Graphite	0.05	H-276	12	1/2	Tocco	~3/4
ZM-3	Graphite	(1)	H-276	3	1/8	Tocco	~3/4
ZM-4	Graphite	0.005	Mal. 7034	6	1/8	Tocco	~3/4
ZM-5	Graphite	0.005	ZM-2	6	1/16	West.R.F.	~3/4

(1) Ambient helium atmosphere used.

XV-B. Chemical Analyses

	Zr	C	N	Al	B	Cr	Cu	Fe	Mg	Mn	Ni	Si
Analysis of H-276	2.00	63	<10	10	<0.1	7	2	60	1	3	20	40
ZM-1A	1.97	100	<10	15	<0.1	10	1	70	1	3	20	50
E	2.07	59	26	15	<0.1	10	1	70	2	3	20	50
ZM-2A	2.32	17	<10	10	<0.1	10	1	50	1	2	20	50
E	2.02	114	108	5	0.1	10	1	70	1	3	20	40
ZM-3A	2.42	12	<10	10	<0.1	5	1	30	1	3	10	100
E	1.76	118	185	10	<0.1	15	1	100	1	7	30	30
ZM-4A	3.15	50	<10	5	0.1	2	2	30	1	<0.5	5	40
E	2.48	525	56	10	<0.1	5	5	200	150	1	15	30
ZM-5A	2.42	150	13	20	<0.1	4	1	20	1	--	10	20
E	1.88	60	10	20	<0.1	8	6	60	1	--	30	20

A = Starting end of rod.

E = Finishing end of rod.

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2. Siliconizing of Uranium (C. Marzano and R. A. Noland)

Specimens of austenitic stainless steel, uranium and thorium have been diffusion coated with silicon by immersion in heated eutectic NaK alloy containing dissolved elemental silicon metal.

The process is believed to be applicable to a number of metals and their alloys, but most of our effort has been concentrated on the coating of unalloyed natural uranium. Coatings have been produced by treating as described for one to forty-eight hours in a temperature range of 450° to 600°C with silicon concentrations of the order of 0.04 to 4 w/o. In all cases the reaction layer has been identified (X-ray diffraction) as largely the beta form of the intermetallic compounds USi_2 with some USi and a trace of UO_2 . Spalling of part of the coating has been observed on some specimens. Preliminary experiments indicate that this tendency to spall increases directly with increasing time, temperature, and silicon concentration in an interrelated fashion.

3. Effect of Irradiation Upon Natural Uranium Single Crystals (J. H. Kittel, F. Taraba, S. H. Paine)

Two additional single crystals (crystals B and C), and two pseudocrystals of alpha uranium have been examined and have been observed to develop the same crystallographic directional changes as were noted in the first irradiated crystals (crystals A and Pseudo-A) described in ANL-5097. Lengthening occurs in the [001] direction and shortening in the [100], while changes in the [001] direction, if any, are small. Figures 19 through 22 and Table XVI show the dimensional changes in the crystals, which were in the form of short cylinders before irradiation. The pseudocrystals, made by slowly transforming large beta grains into the alpha phase, show in particular a remarkably large amount of elongation. Pseudocrystals B and C were so badly distorted that dimensional changes could not be measured.

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Figure 19. Alpha Uranium Crystal "A" After 0.11% Burnup.

19-a. Looking in the [100] Direction.

Macro #14331

5-X

19-b. Looking in the [010] Direction.

Macro #14327

5-X

Figure 20. Alpha Uranium Pseudocrystal A After 0.11% Burnup.

Macro #14334

5-X

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Figure 21. Alpha Uranium Crystal "C" After 0.5% Burnup.

21-a. Looking in the [100] Direction.

Macro #14894

2-X

21-b. Looking in the [001] Direction.

Macro #14896

2-X

Figure 22. Alpha Uranium Pseudocrystal C After 0.5% Burnup.

Macro #14892

2-X

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TABLE XVI

Effect of Irradiation on the Dimensions of
Alpha Uranium Single Crystals

Crystal	Burnup, %	% Change			Average Growth Coefficient, K*		
		[100]	[010]	[001]	[100]	[010]	[001]
A	0.11	-50	30	-9	-640	240	-80
B	0.3 ¹	-58	210	0	-290	380	0
C	0.5 ¹	-77	300	0	-290	280	0
Pseudo-A	0.11	-76	57	-5	-1300	410	-55

$$*K = \frac{\ln(L/L_0)}{\text{Burnup}}$$

¹ Estimated burnup

4. Effect of Irradiation Upon Polycrystalline Natural Uranium (J. H. Kittel,
F. R. Taraba, S. H. Paine)

Irradiations of natural uranium in the MTR have continued. Specimens were examined this quarter with total atom burnups which, based on analyzed specimens, are up to 1.75%. Figures 23 and 24 show a typical specimen before and after irradiation. Although the surface of the irradiated material shows considerable roughening, the specimens appear to be sound, with no indication of over-all disintegration. It has been observed that the growth rate of the 300°C rolled, beta quenched material, upon which most of the data have been obtained, tends to decrease with increasing amounts of burnup, as is shown in Figures 25 and 26. Although the specimens begin growing at a rate of 20% per 1% burnup, this has decreased to 10% at 0.8% burnup, and at 1.75% burnup, there are indications that it has decreased to less than 6% per 1% burnup. The decrease in growth rate as burnup proceeds may be related in part, at least, to a possible stabilizing effect of plutonium which has been found to steadily build up in the specimens with reactor exposure, as shown in Figure 27.

5. Effect of Irradiation Upon Enriched Uranium-Zirconium Alloys (J. H. Kittel,
F. R. Taraba, S. H. Paine)

Irradiations of 10% enriched 1 and 2 w/o zirconium-uranium alloys have continued. Results on the first group of six specimens which were examined after total atom burnups ranging up to 1.0% were reported in the

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Macro #14882 2-X

Figure 24. Specimen A-8, 300°C Rolled, Beta Quenched, After a Total Atom Burnup of 1.75%.

Macro #15002 2-X

Figure 23. Appearance of Typical Specimen Before Irradiation.

Figure 25 Growth of 300°C Rolled, Beta-quenched Uranium Under Irradiation

Figure 26 Growth Rate of 300°C Rolled, Beta-quenched Uranium Under Irradiation

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Figure 27 Build-up of Plutonium as Burnup Proceeds in Natural Uranium Test Specimens

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previous Quarterly Report, ANL-5153. Irradiation growth rates in that group were found to be higher than in the nine specimens examined this quarter. The latter group had total atom burnups, based on cobalt monitors, ranging up to 3.6% (31,000 MWD/T) and were irradiated at higher thermal fluxes with consequent higher metal temperatures. Calculations indicate that some of the specimens were in the gamma phase while under irradiation, and this may account in part for their better dimensional stability.

The 2 w/o zirconium alloy in the as cast condition was again found to be the best of the group. Figures 28 through 30 show the appearance of specimens of this material before irradiation and after 0.91% and 3.4% burnup. Growth rates of these current specimens were, respectively, 3 and 6% per 1% burnup, whereas the one irradiated previously elongated 18% per 1% burnup. Compared with the unalloyed specimen shown in Figure 24, the alloyed material not only shows much less growth but the original surface smoothness has remained essentially unchanged.

6. Examination of Los Alamos Rala Test Assembly (W. F. Murphy,
F. L. Brown, S. H. Paine)

A specimen of 0.050" diameter U²³⁵ wire, incorporated at Los Alamos into a special test assembly, has been examined carefully by the ANL Irradiation Group after irradiation to 1.24% average burnup in an MTR reflector stringer. Burnup value was obtained from E. H. Turk, Chemical Engineering Division, who performed a fission product analysis on the material. The wire had received 82% cold reduction in area, with no subsequent beta treatment. Temperature of the metal under irradiation probably remained well below 300°C. Under these circumstances the wire should have elongated 30 or 40 times its original length if it had been free to do so. However, the metal was found to be sound, and longitudinal growth of its containing capsule was less than 2% in 5-3/4" length.

The primary restraint was provided by 0.064" outside diameter Type 347 stainless steel tubing having a 6 mil wall thickness. This tubing was drawn down to 0.060" O.D. over the 50 mil wire after proper cleaning operations. Ends of the tubing were plugged with SS wire and sealed by welding, leaving a small gap between the core wire and end plug. The stainless steel assembly was then enclosed in an aluminum jacket drawn on and sealed in a similar fashion, and this secondary closure, in turn, was placed in a 1/2" O.D. aluminum sleeve for the purpose of increasing the heat transfer surface area.

Both stainless steel welds cracked during irradiation and the metal adjacent to the welds necked down somewhat. However, the uranium wire did not extrude out of its tubing, although the secondary jacket afforded room for this to occur. Metallography revealed an excellent metallurgical bond between the stainless steel and uranium. Only a mechanical bond existed

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Figure 28. Appearance of a Typical Uranium-Zirconium Alloy Specimen Before Irradiation.

Macro #15003

2-X

Figure 29. Specimen AA-20, 2 w/o Zr, As Cast, After a Total Atom Burnup of 0.91%.

Macro #14876

2-X

Figure 30. Specimen AA-21, 2 w/o Zr, As Cast, After a Total Atom Burnup of 3.4%.

Macro #14877

2-X

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between the aluminum and stainless steel. The evidence seems to indicate that the stainless steel capsule was completely adequate to repress growth of the uranium, except where it had been structurally affected by welding. An experimental evaluation of the secondary contribution made by the aluminum sheath is needed in order to fully understand the significance of these results.

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VI. AQUEOUS CORROSION - ACTIVITY 5411-031. Metal Thickness Gauge (W. E. Ruther)

It has been found that the apparent thickness of annealed 2S aluminum sheet changes when aged at temperatures of 250° and 300°C. The most rapid change in thickness, as measured by the gauge previously described, occurs within the first 40 hours, amounting to approximately 100 microinches. Subsequent change, although not negligible, is much smaller and apparently linear with time. The apparent thickness has always increased, even when samples which had been aged 200 hours at 300°C were placed in a 250°C oven. Any process occurring in the aluminum which could increase the electrical conductivity of the sample would explain this phenomenon. The method of annealing has some effect. Samples that have been held at 450°-500°C for 16 hours show more change than those held at 350°C for 15 minutes.

The results of these experiments indicate that the few aqueous corrosion rates measured with the thickness gauge are in error. No satisfactory method of correction is available. The modified procedure now in use simultaneously ages comparison specimens in an air furnace at the temperature of the aqueous corrosion test. Advantage is also taken of the shape of the aging curve by preaging all specimens in air for 70 hours at the test temperature. With these modifications it is hoped that accurate corrosion rates will be obtained.

Another metal thickness gauge designed and constructed by W. B. Doe of the Remote Control Division has been given some preliminary sensitivity tests. By a precision cam arrangement, rod samples of aluminum can be accurately placed within a solenoid coil with ferrite end pieces. This coil is the frequency determining inductance of a 100 kilocycle oscillator. The change in inductance brought about by changing the unknown rod sample for a standard rod is compensated by a calibrated condenser across the coil. The condenser is adjusted to return the frequency to exactly 100KC.

Preliminary calibration results indicate high sensitivity of about 20 dial divisions per microinch change in diameter. The short term stability of the unit is about 1/2 division, indicating that readings to better than 0.1 μ inch should be feasible. The range of the unit is limited to about 200 μ inch which means the specimens must be accurately prepared. Some difficulties with the temperature control system must be eliminated. The calibration will be rechecked and a corrosion test started in 50°C distilled water to attempt to pick out operating flaws in the instrument before any redesigning is attempted.

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2. Corrosion of Aluminum in Dilute Aqueous Solutions (J. E. Draley, N. Williams)

It is remarkable that tests of wet-ground aluminum surfaces in distilled water at 50° and 70°C for one day indicate that, regardless of the actual rate of corrosion of the metal, approximately one-tenth of the corrosion product is continuously lost to the solution. Apparently this is also true for much longer durations. The reason is not known, and it is perhaps indicated that a careful examination of the possible chemical reactions taking place should be made.

3. Effect of Solution Additives on Aqueous Corrosion of Aluminum at High Temperatures (W. E. Ruther, J. E. Draley)

Due to the fact that the high temperature equipment was used for tests with the thickness gauge (subsequently proved inaccurate) no new quantitative corrosion rates are available.

Tests are nearly completed at 250° and 275°C with 50 ppm potassium dichromate solution and with 20 ppm silica solution, both solutions adjusted to pH 3.5 with sulfuric acid. Qualitatively, the samples are covered with tightly adherent thin film after 14 days at 250°C in either of the two solutions. The dichromate test has produced a few strings of very tiny blisters on the specimens, but as yet no general blistering has been noted. There are no blisters on the silica samples but the corrosion does not appear uniform over the entire surface. Since the specimens are supported on artificial sapphire rods and electrically insulated from the autoclave, it is difficult to point to the cause of this nonuniformity.

At 275°C, neither one of the above solutions produces a desirable corrosion resistance. General blistering and warping of the specimens are noted, with the silica solution producing results slightly inferior to the dichromate solution. Another run at 275°C using 100 ppm silica (pH 3.5) has been started. The samples in this test have thin, tight films after 5 days exposure.

4. Corrosive Anodizing of Zirconium (R. D. Misch and F. H. Gunzel)

Anodizing has been found to be effective for evaluating corrosion resistance at low current densities. Recent work has all been done at 0.1 ma/cm² and indicates that the lowest current at which film growth begins is not sharply defined but is a function of metal quality and surface preparation. Using a 1% KOH solution as the electrolyte, the efficiency of anodic film growth has been found to vary with corrosion resistance.

Data illustrating this point are shown in Figures 31 and 32. These are curves of cell voltage vs. time for anodizing at 0.1 ma/cm^2 , 25°C . The zirconium was arc melted from Grade I (3T, 3B) and Grade III (2T, 2B, 4T, 4B, 5T, 5B) crystal bar. Each specimen was a block of approximately 20 cm^2 area. Each was stopped off with Unichrome 330 and wet polished to 400 grit emery. Different surface preparation was found to alter the shape of the curves, although their order remained the same.

The curves show the pattern of film growth since the cell voltage is proportional to film thickness. The steeper curve of 3T and 3B are evidence that ionic current (contributing to film growth) is high relative to electronic current. A flat curve is evidence that all of the current is electronic, at least after the short initial rise. It is evident that the ratio of ionic to electronic current is a sensitive function of metal composition. The lower curves for set Nos. 2, 4, and 5 is an indication that electronic conductivity is associated with low corrosion resistance. The rate controlling step in zirconium corrosion may not be ionic diffusion but electron transfer through the film. Alloying elements may be beneficial by neutralizing paths of electronic conduction.

Attention must be drawn to the fact that a voltage-time curve does not indicate the distribution of current over the surface. Impurities providing electronic conduction may be distributed uniformly or may be localized at one or two points. General corrosion resistance may be good in the latter case.

5. Corrosion Rate of Uranium Metal (W. E. Ruther, J. E. Draley)

As part of the program of investigating the corrosion properties of uranium alloys some heat treatment of reactor grade uranium has been done. Specimens of natural uranium from Los Alamos Ingot 547 (hot rolled, warm rolled, annealed) were subjected to vacuum heat treatments, suspended on tantalum wire, and their corrosion rates subsequently measured in boiling distilled water. Three samples were heat treated at one time, their surfaces cleaned by wet grinding (#400 grit finish), and then placed on test in a covered beaker of actively boiling distilled water. Fresh distilled water was passed continuously through the beaker at a low rate. One specimen was removed each day for three days. The oxide films were stripped by immersion in 25% nitric acid at room temperature, and the corrosion rate calculated from the slope of the weight loss versus time plot. The rates obtained are shown in Table XVII.

A noticeable improvement in corrosion resistance is noted as the vacuum heat treatment temperature is raised. It is particularly interesting that the reactor grade metal corroded at a lower rate than high purity metal when the former was given the heat treatment at 1000°C . A metallurgical

Figure 31

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Figure 32

examination of the specimens is planned to determine, if possible, the extent of impurity solution. The fragmentary result obtained at 1000°C will be re-checked. Samples of high purity uranium have been heat treated at 1000°C and are now on test in boiling distilled water, to determine if its rate will be changed thereby.

TABLE XVII

Effect of Vacuum¹ Heat Treating on the Corrosion
of Natural Uranium in Water at 100°C

Heat Treatment (Furnace Cooled in Each Case)	Corrosion Rate (mg/cm ² -hr)
6 hours at 600°C	5.0
5-1/2 hours at 720°C	3.3
6 hours at 800°C	3.1
1 hour at 1000°C	1.8 ²
As Received	4.9 ³

¹Approximately 1 μ pressure

²Based on only one sample corroded for 96 hours

³As reported by J. W. McWhirter, ANL-4860

6. Corrosion Resistant Uranium Alloys (W. E. Ruther, J. E. Draley)

Some additional data are available for the corrosion of Alloy H-203 (nominally 1-1/2 % niobium + 5% zirconium). This alloy was aged at 375°C for two different times. Subsequent corrosion behavior in 300°C distilled water is shown in Table XVIII. The specimens cracked cleanly apart as though a hairline fissure had been filled with corrosion product and the metal forced apart by the increased volume.

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TABLE XVIII

Corrosion Behavior of Heat Treated Uranium Alloy
H-203 in Distilled Water at 300°C

Treatment	Time-Corrosion Test (Hours)	Corrosion Rate ¹ (mg/cm ² -hr)
Sample A 4 hours at 375°C	72	0.97
	144	0.71
	216	0.74
	336	0.76 (Cracked)
Sample B 24 hours at 375°C	72	1.25
	144	1.13
	216	2.02 (Cracked)

¹Determined for each interval.

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