

UNCLASSIFIED

ANL-5153(Del.)

Photostat Price \$ 10.80

Microfilm Price \$ 3.90

Available from the  
Office of Technical Services  
Department of Commerce  
Washington 25, D. C.

ARGONNE NATIONAL LABORATORY  
P. O. Box 299  
Lemont, Illinois

QUARTERLY REPORT

JULY, AUGUST, AND SEPTEMBER 1953

METALLURGY DIVISION

Frank G. Foote, Director  
James F. Schumar, Associate Director

September 30, 1953

Previous Quarterly Reports:

- ANL-5097 April, May, June, 1953
- ANL-5036 January, February, March, 1953
- ANL-4966 October, November, December, 1952

Classification changed to Unclassified with deletions  
by authority of Charles E. Lester, Jr. (2/12/57)  
by Nash Kinan date 8/17/05  
and D. Williamson date 8/17/05

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission to the extent that such employee or contractor prepares, handles or distributes, or provides access to, any information pursuant to his employment or contract with the Commission.

Operated by The University of Chicago  
under

Contract W-31-109-eng-38

UNCLASSIFIED

242 001

4440



## **DISCLAIMER**

**This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.**

## **DISCLAIMER**

**Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.**

u 17

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT . . . . .	5
<b>I. WATER COOLED REACTORS</b> [REDACTED]	
1. Manufacture of Zirconium Tubing	
a. Extrusion . . . . .	9
b. Resistance Welding . . . . .	9
c. Piercing . . . . .	11
2. Roll Cladding of Uranium Alloys with Zircaloy II	
a. Fabrication of Uranium-Niobium Core Alloys . . . . .	13
b. Fabrication of Zircaloy II Sheet . . . . .	13
c. Roll Bonding Zircaloy II to Itself . . . . .	14
d. Cladding of Uranium Alloys with Zircaloy II . . . . .	14
<b>II. LIQUID METAL COOLED REACTORS</b> [REDACTED]	
1. Centrifugal Casting of EBR Fuel Slugs . . . . .	18
2. Uranium-Zirconium Alloy Rod for EBR Fuel Blanket Slugs . . . . .	18
3. Effect of Mechanical Restraints Upon Uranium Growth During Thermal Cycling . . . . .	20
a. Zirconium Jacketed Assemblies . . . . .	20
b. Stainless Steel Jacketed Assemblies . . . . .	21
<b>III. REACTOR DEVELOPMENT METALLURGY</b> [REDACTED]	
1. Fabrication of Enriched Uranium Reactor Fuses . . . . .	22
<b>IV. BASIC METALLURGY</b> [REDACTED]	
1. Preparation of Uranium Single Crystals for Study of Elastic Constants . . . . .	23
2. Thermal Cycling of Uranium Single Crystals . . . . .	25
3. Thermal Expansion Coefficients of Uranium Single Crystals . . . . .	28
4. Deformation of Uranium Single Crystals . . . . .	32
5. Preferred Orientation in Hot Pressed Uranium . . . . .	41
6. Diffusion in the System Copper-Uranium . . . . .	42

DECLASSIFIED

242 002

TABLE OF CONTENTS

		<u>Page</u>
V.	APPLIED METALLURGY [REDACTED]	
	1. Casting of High Purity Uranium Billets . . . . .	45
	2. Casting of Uranium Rich Alloys . . . . .	45
	3. Crucibles for Uranium Melting . . . . .	47
	4. Effect of Irradiation Upon Normal Uranium. . . . .	47
	5. Effect of Irradiation Upon Partially Enriched Uranium- Zirconium Alloys . . . . .	47
VI.	AQUEOUS CORROSION [REDACTED]	
	1. Metal Thickness Gauge . . . . .	53
	2. Corrosion of Aluminum in Dilute Aqueous Solutions . . .	53
	3. Aqueous Corrosion of Aluminum at Elevated Temperature . . . . .	53
	4. Mechanism of Aqueous Corrosion of Zirconium . . . . .	54
	5. Aqueous Corrosion of Uranium Alloys at Elevated Temperatures . . . . .	54
	6. Corrosion of Zircaloy Clad Uranium-Niobium Sandwich Specimens . . . . .	57
	7. Microstructural Features of an Uranium-3 Percent Niobium Alloy . . . . .	58

DECLASSIFIED

242 003

QUARTERLY REPORT

JULY, AUGUST, AND SEPTEMBER, 1953

METALLURGY DIVISION

ABSTRACT

## Liquid Metal Cooled Reactors

Fabrication of a complete  $U^{235}$  -2% Zr EBR fuel slug charge by centrifugal casting is in progress; approximately three quarters of the charge has been cast.

Fifteen billets of normal uranium-2 w/o zirconium alloy have been cast and rolled as stock for fuel blanket slugs in the reloading of the EBR. An isothermal heat treatment was given to these slugs for stabilizing the alloy against growth.

Further investigation of the effect of mechanical restraints on uranium growth during thermal cycling was undertaken. Zirconium jackets over uranium and uranium alloy cores, the jackets being up to 0.050" in thickness, are ineffective in restraining the growth of either unalloyed uranium or a U-2 w/o Zr alloy when cycled into the beta or gamma phase. Stainless steel jackets of 0.020", however, showed considerable restraining influence on growth during cycling into the beta phase.

## General Reactor Development

Fissionable link type reactor safety fuses, made of fully enriched uranium soldered with 95% Sn-5% Sb solder, were made and tested successfully in the CP-3' and Borax experimental reactors.

## Basic Metallurgy

Attempts are being made to prepare single crystal plates of uranium for the study of elastic constants by the contamination-inhibition-grain coarsening technique previously developed.

A single crystal of uranium was thermal cycled 10,000 times, and a sensitive method of determining length change after cycling was used for measurements. The experimental results were conclusive in affirming that no growth occurred in any dimension of the crystal during the cycling process; also, X-ray photograms showed no evidence of strain after cycling.

Thermal expansion measurements of single crystals of high purity alpha uranium were made. Specimens measured, all of whose orientation was close to the [010] direction, show a negative expansion with increasing temperature. Crystals will be isolated and tested for coefficient of expansion in the other two principal crystal axes; when these data are obtained a least square analysis can be applied to calculate the expansion coefficient along each of the three principal axes.

Single crystals of alpha uranium were subjected to compressive loading to study the deformation mechanisms. One crystal was compressed in the [010] direction at 600°C, and the other was compressed at room temperature in the [100] direction.



Compression of a uranium single-crystal in the [010] direction at 600°C resulted in (130) twinning, in much the same way as the process occurs at room temperature upon compression in this direction. This result is significant in that it had been assumed that uranium deforms at the higher temperatures by slip, with twinning confined to deformation at low temperatures. Compression of a single crystal in the [100] direction at room temperature resulted in kinking, with [001] the axis of rotation.

X-ray intensity measurements were made for various reflections from cross and longitudinal sections of a hot pressed uranium slug. Results obtained show that the material is nearly randomly orientated.

Diffusion experiments, using copper-uranium couples, were conducted; only one new phase forms as a result of diffusion. The concentration range of the upper phase,  $UCu_5$ , has not been determined.

### Applied Metallurgy

Three high purity uranium billets were made from electrolytic crystals; the largest billet weighed 7 kg. Production of large billets of high purity uranium has been demonstrated and is limited only by the amount of electrolytic crystals available.

Uranium rich alloys, binaries and ternaries with zirconium and niobium, were made for corrosion studies. Water-cooled copper molds were used to minimize segregation. The segregation of zirconium with carbon in the U-2 w/o Zr alloy was established.

A program for the prevention of crucible failures under the high melting temperatures necessary for preparation of uranium-zirconium or uranium-niobium alloys is underway.

Irradiations of natural uranium in MTR have continued, with total atom burnups as high as 0.88% being studied. Other specimens still in the reactor have burnups well above 1%.

A group of uranium-zirconium alloys containing 1 w/o and 2 w/o Zr and 10% enriched with  $U^{235}$ , were irradiated in MTR stringers. The most satisfactory resistance to irradiation changes was exhibited by the uranium-2 w/o zirconium alloy in the as cast condition, although it grew at a greater rate than previous thermal cycling tests had indicated.

### Aqueous Corrosion

The metal thickness gauge, developed to provide reliable readings of metal thickness in corrosion specimens, has been improved, and corrosion curves are being measured with it.

Several varieties of tests are being run in an effort to explain characteristics of the curve of corrosion of aluminum versus exposure time; these curves show an initial rapid rate of reaction, followed by a linear rate of corrosion. Work being done has for an objective the evaluation of factors which influence this rapid initial corrosion.

Tests are continuing to determine the maximum permissible operating temperature, corrosion wise, for aluminum in aqueous solution. The addition of sulfuric acid to pH 3.5 provides genuine beneficial effect on the metal by reducing its corrosion rate; at 200°C, samples from this test were in excellent condition after several weeks of exposure.

The mechanisms of aqueous corrosion of zirconium appear to be somewhat dependent upon the orientations of the zirconium crystal lattice being investigated.

Low niobium alloys of uranium show maximum resistance to corrosion in distilled water at elevated temperature when quenched from the gamma phase. Their corrosion resistance is considerably reduced by aging subsequent to the gamma quenching. An uranium alloy containing 1-1/2 w/o Nb and 5% Zr appears to possess more desirable properties for high temperature reactor use than any other so far studied.

Samples of an uranium-3 w/o niobium alloy were examined metallographically after three different heat treatments: (1) quenched from 1100°C; (2) quenched and annealed for 84 hours at 350°C; and (3) quenched and annealed for 24 hours at 500°C. Results obtained indicated a precipitation hardening phenomenon occurring at the 350°C anneal, with the anneal at 500°C resulting in an overaging of the alloy, rendering it much less resistant to corrosion than the as quenched alloy.

DECLASSIFIED

242 007

## I. WATER COOLED REACTORS

### 1. Manufacture of Zirconium Tubing (E. A. Wright and R. E. Macherey)

a. Extrusion - Nine copper jacketed zirconium billets have been extruded into tubing at the Detroit plant of the Wolverine Tube Division. All billets were 4-5/8" O.D. with a 1-3/4" longitudinal center hole. Four of the billets were made from arc melted crystal bar and five were made from Bureau of Mines arc melted sponge zirconium. All material was forged in air at 900°C to 4-7/8" O.D., then machined to size. The arc melted crystal bar casting was 6" in diameter, and the arc melted sponge casting was 9" in diameter.

The billets were completely jacketed with copper, and all joints in the copper jacket were closed by welding. Three of the billets with 1/8" jackets were extruded at 750°C into a tube 2" in diameter with 0.125" wall. One billet with a 1/16" jacket was partially extruded (about 2 feet) before the press stalled due to insufficient lubrication of the zirconium by the copper. The remaining five billets were extruded at 750°C into tubing 2-1/8" in diameter with 0.188" wall.

The copper jacket served to protect the zirconium during the heating and extrusion cycle and served as a lubricant during extrusion. The extruded tube was jacketed with copper with very few bare spots of zirconium exposed. This jacket was left on the tube for the heavy breakdown draws before removing with H<sub>2</sub>SO<sub>4</sub>. No evidence of alloying between the copper and zirconium was noted. The copper jacket on the base tube was loosely held and could be stripped easily by mechanical means. An analysis of the zirconium will be made to check for any copper pickup.

These tubes were reduced by cold drawing. Reductions in cross section ranged from 15% to 30% without trouble. A summary of the extrusion data is given in Table I.

b. Resistance Welding - Several attempts were made to resistance weld zirconium strip into tubing. The strips were 2.365" wide x 0.058" thick and in lengths ranging from 6 to 120 ft. The tube size formed and welded was 3/4" in diameter x 0.058" wall. A Yoder resistance welding tube mill was used with Wolverine modified forming rolls. Inasmuch as this was a feasibility experiment, the added cost of adding an inert atmosphere shield to the welding machine was not considered justifiable.

The zirconium used in this experiment was originally cast into a 6" diameter billet by arc melting Grade II crystal bars. The billet was then forged in air to a slab 2" x 6" at 925°C. The slab was hot rolled in air to 1/2" at 815°C. The strip was then finished by cold rolling approximately



50% between anneals to final size. The strip was slit to the proper width and annealed in an argon atmosphere for 3 hours at 790°C. The resulting hardness of the strip was 60/65 Rockwell B.

In order to save as much zirconium strip as possible, a length of steel strip was welded to the front and rear of the zirconium to serve as guides for the tube forming machine. A nickel section was placed between the steel and zirconium strip to serve as a common bond. In every case the nickel to zirconium weld broke in the forming rolls. Unless a better bond between zirconium and steel can be developed, all future runs will be made without using the steel guide strips.

The zirconium strip formed quite readily in the forming rolls. It was evident, however, that the formed tube had more spring back than ordinary low carbon steel strips of the same dimensions. To eliminate this undesirable condition it would be desirable that the hardness of the strip be in the range of 50/55 Rockwell B. The zirconium strip upset and lost more metal at the weld seam than steel strip of the same dimensions.

The best of the resulting welds appear to be quite good. Expanding the tube until a split occurred showed that uniform welds were being made. Welds were made that withstood 20% expansion without splitting. A more detailed analysis of the weld will be made before further runs are made. The most objectionable mechanical defects were small pits on both sides of, and parallel to, the weld seam. These appear to have been caused by the electrodes coming in contact with the tube. It is believed that with more experience these pits can be eliminated.

This method of making zirconium tubing has many advantages over extrusion. After the welding procedure is perfected the fabrication cost of producing zirconium tubing will be a very minor part of the total cost of the tubing at present zirconium metal prices. The tubing can be formed with a much greater ratio of finished tubes to original quantity of metal. The welded tube will be more concentric than extruded and drawn tubes.

A compilation of detailed data collected during the above described experiment is given in Table II.

c. Piercing - A 3" O.D. x 36" long zirconium billet was pierced into a base tube at the Detroit plant of the Wolverine Tube Division. The billet was made from a 6" diameter casting of arc melted crystal bar forged to 3-1/8" diameter in air at 950°C. The billet was then machined to size.

This method of making seamless base tube is by the rotary piercing process. The billet was heated to 900°C in a gas fired furnace with an excess of CO and CO<sub>2</sub> present. The heated billet was forced into the two convex helical rolls. The piercing rolls are mounted side by side with their axes inclined at opposite angles. These rolls form a conical converging

DEPOSITED

242 010

Table II

## DETAILED INFORMATION ON WELDING OF ZIRCONIUM TUBING

Set-up No.	AC, Volts	Speed FPM	60-Cycle Amps	Power Factor Lag	Heat Tap	Heat Req'd. (arbitrary scale)	Remarks
1	178	34	180	0.65	3	42	Weld broke between zirconium and nickel. Microscopic examination revealed a wedge-shaped unwelded portion on the inside of the tube, extending over approximately 1/4 the wall thickness.
2	178	34	100	0.65	3	42	This strip forms with greater difficulty than 1015 steel and has more spring-back after leaving forming rolls. The zirconium tube wall burned through at several points along the path of the electrode. This caused alloying between the electrode wheel and the zirconium and resulted in quite severe pitting along the weld seam.
3	178	50	80	0.65	4	42	The 120-ft length strip was inserted, and the zirconium-to-nickel weld broke on the leader. This setting was too hot, and the zirconium was burned through in several spots. The cutter was damaging the edge of the strip because too much metal was being removed. The cutter was readjusted to remove less metal.
4	160	50	110	0.65	3	42	More pressure was given at the electrode. In this case, a good weld was obtained and held for normal condenser tube expansion. Electrode marks were evident along the weld seam. Metallographic examination showed a lap weld at the seam. This was caused by too much pressure on the sizing rolls at the electrode.
5	160	50	120	0.65	3	42	Less upset pressure. Lowered scarfing tool to make contact and scarf off weld metal. Electrode marks still present alongside weld seam. Need a softer strip or a wider seam guide ahead of the electrodes.
6	160	50	120	0.65	3	42	A short strip - the weld broke on leader between nickel and zirconium. Removed edge trimming tool to give more pressure. The trailing strip broke between zirconium and nickel and jammed the machine.
7	160	55	90	0.65	3	36	Sample split on expansion test. Showed stitches in weld; evidently more heat required.
8	160	55	100	0.68	3	42	Sample split on expansion test - showed fairly good bond along seam.
9	160	40	120	0.68	3	50	Sample withstood 10% expansion but split at 20% expansion. An examination of the split seam showed clean metal and evidence of a good weld. The remainder of the 120-ft length strip was run at this setting.

242 011



surface and later a conical diverging surface. Both rolls rotate in the same sense which forces the billet forward in a spiral motion. The metal at the center of the billet opens up to form a hollow as the billet passes the point of the rolls where the change in form from conical converging to conical diverging occurs. A mandrel and piercing pin are mounted on a reciprocating carriage. The piercing pin is positioned at the point of metal breakage and serves to open the hollow and iron it out into a good surface to form the inside of the tube. The surfaces, internal and external, are further ironed out by the mandrel and flat external rolls as the tube is pierced.

While the tube from this mill looked good, further examinations must be made before determining its worth. The zirconium billet was pierced on the same setup as is used for piercing copper base tube and with equal ease.

## 2. Roll Cladding of Uranium Alloys with Zircaloy II (C. H. Bean, R. E. Macherey)

a. Fabrication of Uranium-Niobium Core Alloys - Bars of uranium-niobium alloy to be used for roll cladding experiments were fabricated by forging and rolling castings of 3 w/o and 6 w/o niobium. A total of twelve 1-5/8" diameter x 6" to 8" long chill castings were used. Eight of these castings were the 3% alloy and four were the 6% alloy.

The castings were heated to 850°C in a helium atmosphere, held at temperature for 1/2 hour, and forged to rectangular bars 1-3/4" wide x 0.900" thick. The metal could be worked at temperatures as low as 700°C without cracking or tearing.

Forged bars were hot rolled at 850°C with reductions of 6 to 7% per pass. The rolled bars were flattened after the final pass and water quenched to prevent excessive oxide formation on the surface. Bars were rolled to within 1/16" to 1/8" of the required machined dimensions.

b. Fabrication of Zircaloy II Sheet - Zircaloy II sheet was fabricated from Allegheny Ludlum cast ingot No. 1X082 which was forged to a 2" thick slab at 980°C.

The forged slab was scalped to remove surface defects and contamination. Approximately 1/16" of metal was removed from the surface. The scalped slab was hot rolled to 3/4" plate at 840°C and again scalped to remove surface contamination. This plate was finished by hot rolling, cleaning, and cold finishing to sizes ranging from 0.037" to 0.195" in thickness.

All sheet was cleaned by sandblasting and pickling in a 10% HNO<sub>3</sub>-2% HF solution prior to cold finishing. Sheet was clean and bright with no evidence of cracks, checks, or tears after cold finishing.

DECLASSIFIED

242 012

c. Roll Bonding Zircaloy II to Itself - A number of test billets were prepared to study the effects of rolling temperature and reduction on the bonding of Zircaloy II to itself. Temperatures from 740°C to 870°C and total reductions of 80 to 90% in thickness were investigated. These temperatures and reductions were selected as they appeared to be most desirable for roll bonding of Zircaloy II to uranium-niobium alloys.

Cold rolled Zircaloy II sheet, 0.100" thick, was sheared to size, bright dipped in hot concentrated nitric acid containing a trace of hydrofluoric acid, and edge welded to form a sealed plate for roll bonding. These plates were rolled in Ti-namel steel cans, duplicating, as nearly as possible, procedures used for roll cladding.

Metallographic and physical examination of all roll bonded strips showed that metallurgical bonds were formed at all temperatures and reductions which were investigated.

Further tests will be made on roll bonding Zircaloy II to itself by varying methods of material preparation, and by rolling without a protective Ti-namel steel can.

d. Cladding of Uranium Alloys with Zircaloy II - The fabrication of plate type fuel elements of uranium-niobium alloys roll clad with Zircaloy II was effected using techniques developed for roll cladding unalloyed uranium with zirconium.

Uranium-niobium alloys of 3 w/o and 6 w/o niobium were used for core materials because of their water corrosion resistance and dimensional stability as heat treated. Zircaloy II was selected as a cladding material because of its water corrosion resistance. It was found that the rolling characteristics of Zircaloy II closely matched those of the alloy core material at temperatures between 740°C and 840°C.

Clad plates were rolled with 0.100" to 0.125" of core material clad with 0.010" to 0.020" of Zircaloy II. Modifications in billet design and variations in core size and cladding thickness have made it possible to produce plates with the dimensional tolerances specified for MTR Loop Test Plates.

Cladding billets were assembled by jacketing a machined uranium alloy core in rolled and sheared strips of Zircaloy II. The core material was sandblasted prior to assembly, and the Zircaloy II was prepared by an acid bright dip, machining, or vapor blasting. The jacketed core was sealed by inert gas shielded arc welding between pressurized water cooled plates to minimize contamination at the interface and enclosed in a Ti-namel steel can for rolling.

242 013

DECLASSIFIED



Rolling temperatures from 740°C to 840°C with total reductions of 50% to 90% were investigated. Reductions of 50% resulted in incomplete bonding of the core to clad, but complete metallurgical bonds were effected by 80% to 90% reduction at all temperatures investigated. The thickness of the diffusion layer which formed at the bond interface was found to be directly proportional to the rolling temperature and was usually more brittle than either the core or clad. A rolling temperature of 770°C was found to produce the most favorable bond interface.

All plates rolled in a Ti-namel steel can had excellent dimensional tolerances, good core end geometry, and were free from camber. One plate which was finished by hot rolling without a protective steel can had an appreciable width variation. The cladding thickness on all plates was uniform within  $\pm 10\%$ , with an average deviation of 0.60 to 0.65 mil for cladding thicknesses of 10 to 20 mils.

One group of plates was clad with Zircaloy II which had been fabricated by hot rolling to a total of 92-1/2% reduction in thickness at 980°C without sufficient cleaning to remove surface contamination. Little or no bond was present between the Zircaloy II and Zircaloy II at the edge or end of any of these plates. Subsequent plates fabricated with Zircaloy II which were forged at 980°C, scalped, hot rolled at 840°C, cleaned, pickled, and cold finished, resulted in complete bonds between the Zircaloy II parts.

Clad plates were heat treated by heating in lead at 800° - 850°C for 1/2 hour and quenching either in water or between water-cooled copper plates to prevent warping. Heat treating reduced the hardness of both the core and clad and improved the ductility of the plates as noted on bend tests and cold finishing operations. Table III gives hardness values of uranium-3 w/o niobium alloy core material at different stages of fabrication and heat treatment.

Attempts to cold finish hot rolled plates were unsuccessful. Reductions of 5% caused severe cracking and rupture of both the core and clad. Clad plates which had been heat treated could be readily cold worked to 20% to 30% reduction in thickness without edge cracking or other defects.

Heat treatment had a marked effect on bond tensile strength as noted in Table IV.

Accelerated corrosion tests at 300°C in water on sections of plate quenched between pressurized water-cooled copper plates showed that the corrosion resistance of the core material was comparable to other samples prepared by water quenching. This test revealed corrosion of the clad to core interface which was more severe than corrosion of the core material itself. This was particularly evident on plates rolled at 800°C and 840°C which had wide diffusion layers at the interface. This selective corrosion was not noted at the interface of a clad plate which was prepared with a high purity niobium foil barrier between the core and clad.

DECLASSIFIED

252 014

Table III

## HARDNESS MEASUREMENTS OF URANIUM-3 w/o NIOBIUM ALLOY

Fabrication	Hardness	
	DPH	Rockwell C
As cast	475	47
As hot rolled 45 % reduction at 850°C	512	50
As roll clad 80% reduction at 770°C	620	57
As roll clad 80% reduction at 840°C	762	63
Heated 1/2 hour at 800°C, and water quenched	319	32
Heat treated and aged 84 hours at 350°C	430	44
Heat treated and aged 24 hours at 500°C	473	47

Table IV

BOND STRENGTH MEASUREMENTS OF URANIUM-3 w/o NIOBIUM  
CLAD WITH ZIRCALOY II

Plate No.	Roll Bonding Temperature (°C)	Heat Treatment	U.T.S. (psi)
7	770	None	43,200
8	800	None	44,200
9	740	None	44,000
10*	770	None	45,000
7	770	1/2 hour at 850°C. Water quench	28,800
8	800	1/2 hour at 850°C. Water quench	28,200
9	740	1/2 hour at 850°C. Water quench	24,700

\*Billet rolled with 0.005" thick high purity niobium foil barrier between the core and cladding.

242 015

DECLASSIFIED

Clad plates, with ends as rolled and as closed by welding, were corrosion tested in 260°C water for periods up to 6 days. One plate, which did not have a Zircaloy II to Zircaloy II bond as rolled, failed after 72 hours. The Zircaloy II cladding on this plate was known to have defects which might result in failures. All other clad plates have shown no failures at the bond, although some white corrosion product was noted on the surface of the Zircaloy II after corrosion testing. Attempts are being made to determine the cause of this corrosion and to find ways of eliminating it.

242 016

DECLASSIFIED

## II. LIQUID METAL COOLED REACTORS

### 1. Centrifugal Casting of EBR Fuel Slugs (Frank L. Yaggee)

Work on the fabrication of a complete  $U^{235}$ -2 w/o Zr EBR fuel slug charge is currently in progress. The  $U^{235}$ -2% Zr alloy fuel slugs are centrifugally cast to the proper diameter in copper molds, then notched, broken, and faced to length.

Approximately three-quarters of the EBR fuel slug charge has been cast to date. Of these a sufficient number are ready for loading into the fuel rods to comprise one-half of the total EBR charge.

### 2. Uranium-Zirconium Alloy Rod for EBR Fuel Blanket Slugs (R. E. Macherey)

For a reloading of the EBR fuel rods, approximately 250 ft of natural uranium-2 w/o zirconium alloy rod, 0.40" diameter, are required for fuel blanket slugs. The rod is to be rolled, isothermally heat treated, evaluated by thermal cycling, machined into upper and lower fuel blanket slugs, and jacketed in stainless steel.

For this loading, 15 billets of nominal uranium-2 w/o zirconium alloy have been cast. Two of the billets were cast at Mallinckrodt from co-reduced uranium-zirconium biscuit. These billets were 3" in diameter and weighed approximately 76 kg. The remaining 13 castings were made at ANL using biscuit uranium and crystal bar zirconium. These castings were 1-3/4" and 2" in diameter, weighing approximately 7 kg. Partial chemical analyses of the billets are given in Table V.

All billets were rolled to 0.420" diameter at 600°C. Salt bath heating ( $Li_2CO_3/K_2CO_3$ ) was used for both preheating and soaking to maintain temperature during rolling. The 3" diameter Mallinckrodt billets were first rolled to 1-1/2" diameter in open square and hand round passes. The 1-3/4" and 2" diameter ANL billets were rolled to 1-1/2" diameter in a hand round pass. Intermediate rolling of all bars from 1-1/2" to 3/4" diameter was done in oval and guide round passes at 600°C. The final rolling operation on the rods was hand round rolling from 3/4" diameter to approximately 0.42" diameter at 600°C from salt.

After rolling, the salt was removed with warm water in preparation for swaging. For swaging the rods were heated to 300°C in oil and swaged to approximately 0.40" diameter.

To stabilize the alloy against growth as evaluated by thermal cycling, isothermal heat treatment has been prescribed. This heat treatment consists of a one hour solution treatment at 800°C followed by an isothermal quench at

DECLASSIFIED

242 017

500°C. For protection of the alloy rods during solution treatment, heating was done in an alundum-lined, steel tube filled with argon gas. The isothermal quenching medium was lead at 500°C.

Table V

## CHEMICAL ANALYSES FOR U-Zr CASTINGS

Billet No.	Zr (w/o)		N (ppm)		C (ppm)	
	Top	Bottom	Top	Bottom	Top	Bottom
6919	2.30	2.27	15	9		
7299	2.19	2.45	10	10		
H-220	2.21, 2.20	2.04, 2.07			36, 36	3, 5
H-221	2.10	2.09			14, 16	9, 11
H-222	2.23	2.04			22, 20	4, 3
H-223	2.30	1.92			25, 27	5, 4
H-224	2.19	2.08			17, 18	4, 5
H-225	2.35	2.13			23, 23	12, <10
H-226	2.13	2.07			14, 12	5, 5
H-227	2.27	2.08			14, 12	4, 2
H-228	2.21	2.09			17, 22	7, 6
H-230	2.25	2.09	210, 210		21, 16	2, 2
H-232	2.06	1.96	61, 69		16, 12	3, 3
H-233	2.19	2.03	170, 165		10, 15	4, 4
H-235	2.07	2.01	81, 86, 91, 92		11, 11	8, 9

The rods were heat treated in batches of three or four in lengths of about 3 ft. Before the rods were loaded into the bomb, the bomb was heated to 800°C  $\pm$  5°C in a muffle furnace and flushed with argon. After loading, the bomb was evacuated and filled with argon four times, leaving a positive pressure of from 2 to 4 pounds after the last flush. Following the solution treatment of one hour, the rods were removed one at a time and quenched horizontally in the lead bath held at 500°C  $\pm$  5°C. The rods were allowed to remain in the lead for one hour after which they were removed and air cooled.

242 018

DECLASSIFIED

One sample was cut from each rod for thermal cycling. These slugs were ground to 0.374" diameter x 1.025" long. The slugs were cycled in groups of 12 in the Woosher by S. T. Zegler. The samples were cycled 100 times between 50°C and 550°C in a 5-5-15-5 cycle. The average K value for 48 samples thus far tested varied from -14 to +11.

### 3. Effect of Mechanical Restraints Upon Uranium Growth During Thermal Cycling (S. T. Zegler and H. H. Chiswik)

#### a. Zirconium Jacketed Assemblies

Cycling into the Gamma Phase - The two types of "solid" and "wire" zirconium-jacketed uranium assemblies described in the last Quarterly Report (ANL-5097) were given another 100 cycles into the gamma range (100°-800°C; total 200 cycles). The assemblies continued to elongate and deform with no apparent correlation between the magnitude of the length changes and the zirconium jacket wall thicknesses (thickness varying from 0.010 to 0.050"). All assemblies showed pronounced warping except for the "wire" type assembly in the heaviest jacket (0.050"). However, no ruptures were noted even after 200 cycles, as was thought would be the case on the basis of the observations made after 100 cycles. The magnitudes of the length and diameter changes after 200 cycles are shown in Table VI.

Table VI

DIMENSIONAL CHANGES IN JACKETED URANIUM UPON THERMAL CYCLING

Material and Assembly Type <sup>(1)</sup>	Gamma Cycling (100°-800°C) 200 times		Beta Phase Cycling (100°-730°C) 200 times	
	% Δ L	% Δ D	% Δ L	% Δ D
U, Zr jacket, "solid"	6.44 to 8.28 <sup>(2)</sup>	3.2 to 12.0	2.21 to 6.03	-0.7 to 13.7
U, Zr jacket, "wire"	2.16 to 5.83	-1.6 to 15.9	2.25 to 3.43	-1.2 to 7.5
2 w/o Zr-U alloy, Zr jacket, "solid"	3.73 to 8.87	-0.3 to 4.4		
U, Stainless jacket, "solid"			-0.24	0.7 to 1

(1) Type of assembly refers to either "solid" or "wire" as described in the last Quarterly Report (ANL-5097).

(2) Ranges indicate growth value for jacket wall thickness of from 0.010" to 0.050" for zirconium, and of 0.020" for stainless steel.

242 019  
 REPRODUCED

Uranium-Zirconium Alloys - Solid type assemblies containing uranium-2 w/o zirconium alloy were cycled 200 times into the gamma range. No improvement over the behavior of equivalent unalloyed uranium assemblies could be noted (see Table VI).

Cycling into the Beta Phase - Cycling of unalloyed uranium assemblies (both "solid" and "wire" types) into the beta phase (100°-730°C) also resulted in considerable deformations in length and cross section, not much different from those noted on gamma cycling. Warp was evident in all assemblies and was most pronounced in those of thinner wall.

b. Stainless Steel Jacketed Assemblies

Cycling into the Beta Phase - Two "solid" type unalloyed uranium assemblies jacketed in Type 347 stainless steel of 0.020" wall thickness were cycled 200 times from 100° to 730°C. The resultant length and cross section changes were considerably less than those of the corresponding zirconium jacketed assemblies(see Table VI).

Discussion

The results of all the cycling tests indicate clearly that zirconium jackets up to 0.050" in thickness are ineffective in restraining the growth of either unalloyed uranium or a 2 w/o Zr-U alloy when cycled into the beta and/or gamma phases. Stainless steel jackets of 0.020", however, do exert a considerable restraining influence.

RECORDED

242 020

### III. REACTOR DEVELOPMENT METALLURGY

#### I. Fabrication of Enriched Uranium Reactor Fuses (Frank L. Yaggee)

Two enriched uranium (93.24%  $U^{235}$ ) reactor fuses have been fabricated and transferred to J. T. Weills of the Reactor Engineering Division for in-pile tests.

The fabrication of the fuse components and their assembly under vacuum was done in accordance with the techniques developed by R. A. Noland and D. E. Walker, insofar as these techniques lend themselves to the procedures for handling and working enriched uranium. In assembling these fuses a new technique was used for applying the Sn-Sb solder which made it unnecessary to pretin the mating fuse surfaces. The solder was applied as a foil, 5/8" by 5/8" by 0.002", appropriately placed between the silver-coated surfaces of the enriched uranium fuse components, and the entire assembly placed in a soldering fixture. Soldering was accomplished by heating the fuse-fixture assembly in vacuum.

The first enriched fuse was transferred to J. T. Weills after a normal uranium fuse, fabricated and soldered in an identical manner, had been proof tested by stressing at 1200 psi for 24 hours. The second fuse was proof tested at a stress of 1115 psi for 15-3/4 hours.



#### IV. BASIC METALLURGY

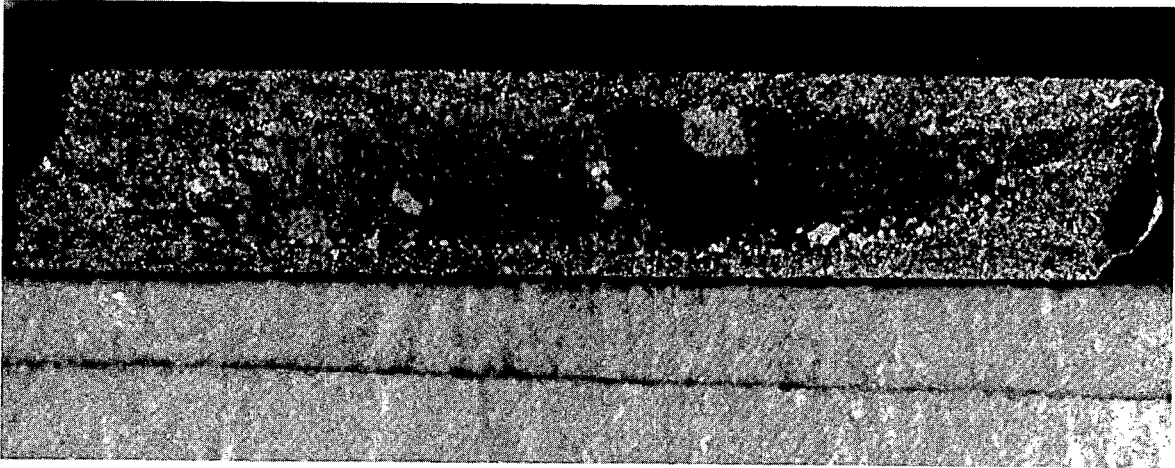
##### 1. Preparation of Uranium Single Crystals for Study of Elastic Constants (E. S. Fisher)

Introduction - Although single crystals of 3 to 4 mm diameter can be readily prepared by a process which involves controlled contamination and diffusion in evacuated Vycor capsules, this process has been found less efficient for preparing larger diameter crystals. This difference in efficiencies is related to the proportionally larger sizes of the rods during heat treatment prior to fabrication. Although a number of single crystals of 5 mm diameter have been made from rods which were approximately 14 mm in diameter during heat treatment, the effect of the heat treatment has not been consistent. Similarly inconsistent results have been found in the processing of 14 mm square bars for plate crystals. Such discrepancies apparently result from the effect of various factors on the contamination process, as indicated by the differently appearing reaction products obtained from consecutive and similar heat treatments. These results indicate the need for a less complex process for introducing the contaminant concentration gradient. The process of depositing SiO<sub>2</sub> by vacuum coating and subsequent diffusion of coating appears to be a feasible method, and the apparatus for this method is now being assembled.

Preparation of plate crystals - Three bars, each approximately 14 mm square x 2.5" long, were cut from a 15" long bar prepared by forging and rolling a high purity uranium ingot. The bars were given different periods of contamination treatments at 1000°C in evacuated Vycor or quartz tubing, to which silicon pebbles were added. After different diffusion periods they were similarly rolled by step-reduction to 3.5 mm thick plates. A treatment consisting of 24 hour contamination and 24 hour diffusion produced fairly satisfactory dispersion of inhibitor as indicated by the grain size distribution after 650°C coarsening, (Figure 1). As shown in Figure 1, the cross sections consisted of 3 to 4 large, coarse grains surrounded by layers of fine grains. (The grain at the left of the specimen was approximately 8 mm wide and grew the full length of the 8 mm long specimen.) However, an experiment made to produce a more optimum dispersion, by shorter contamination and longer diffusion periods (16 hours and 50 hours, respectively), was unsuccessful. This bar had a silvery appearing film after quenching from the contamination operation, in contrast to the brown film on the 24 hour treated specimen, and one face showed evidence of having been partially melted during the heating period. Specimens from the 3.5 mm thick plate produced from this specimen showed heavy inhibition to grain growth over half the width during the final anneal, whereas the remainder of the specimen consisted of a number of coarse grains, and no evidence of an inhibitor gradient.

An attempt was made to identify the composition of the silvery layer by X-ray diffraction. Some of the high intensity peaks correspond to the spacing values of UO<sub>2</sub> and silicon; however, a number of peaks could not be identified.

Figure 1. Grain Size Distribution in Uranium Plate #422-2.



Macro #14532

6-X

This gradient in grain size from surface to center was produced during coarsening at 650°C. This specimen was cut from 3.5 mm plate which had been rolled from 14 mm square bar which had received a 24 hour contamination heating followed by 24 hour diffusion treatment.

RECEIVED

242 023

It appears that the observed inconsistency of the contamination versus heating time relationship may have been due to differences in the degree of contact between the uranium bars and the quartz walls, either because of the position of the bars in the capsules or because of differences in thickness or composition of intermediate layers. In all cases the uranium bars or rods were placed in the capsules so that only the edges were in physical contact with quartz. However, tilting of the capsules during insertion in the furnace or thermal expansion of the uranium during heating may cause a change in the geometry. It is planned to investigate the effect of using spacers to prevent physical contact on the ability to control contamination. Contamination of square bars by evaporation coating with SiO followed by diffusion heating is also planned.

Contamination in vacuum coating unit - In the previous Quarterly Report (ANL-5097) it was mentioned that some 9 mm diameter rods have been coated with SiO in a small vacuum coating unit. The rod which appeared to have the thickest film was wrapped in tantalum sheet, sealed in an evacuated Vycor capsule, heated for 30 hours at 1000°C, and water quenched. After step-reduction swaging to 4 mm diameter, specimens were cut and annealed at 650°C for 24 hours. Although no heavy surface skins of fine grains were found, which would indicate heavy contamination, the grains produced by coarsening were very large; in fact, a single crystal of the specimen diameter was found in one specimen. These results indicated that a concentration gradient of inhibitor had been established which decreased the number of grains which coarsened during annealing. Further evidence that some contamination had occurred was indicated by chemical analysis. Specimens of this rod were reported to contain 20 ppm of silicon, whereas the uncontaminated rods of the same high purity ingot contained less than 10 ppm.

Further tests are planned in an improved coating unit. If successful, this method would be particularly helpful in the processing for large size single crystals.

## 2. Thermal Cycling of Uranium Single Crystals (H. H. Chiswick and L. T. Lloyd)

In ANL-4825 (Quarterly Report for March 31, 1952) it was reported that the growth changes of single crystals,  $3/16$ " long x  $1/8$ " in diameter, after 200 cycles in the Woosher were within  $\pm 0.0005$ " of the original dimensions, and that these changes were only slightly greater than the limits of accuracy of the measuring method used, namely, a cathetometer measuring the distance between two fine scratches inscribed on the surface of polish. Thus, it remained uncertain whether the observed changes were real or resulted from experimental errors of measurement (or perhaps from slight oxidation on the surfaces). If real, the dimensional changes would be significant, even if small, since a length change of only  $0.0005$ " would be equivalent to a K value of 13, which is in the range of beta treated materials.

REF ID: A51111

212 024

To resolve this difficulty two experimental courses are open, either increasing the length of the specimen, or increasing the total number of cycles, both of which would tend to decrease the relative experimental errors. Lacking crystals of appreciably greater length, the second choice was selected, and a crystal was cycled in the Woosher 10,000 times between 50°-550°C. In addition, a more sensitive method of measuring length changes was adopted, making use of a microscope and a filar eyepiece at a magnification of about 25X (154 filar units = 1 mm), the measurements being made between cross-hairs accurately aligned parallel to sharply polished edges.

The crystal was isolated and three flat, longitudinal surfaces with common edges were polished as shown in Figure 2. Microscopic and X-ray examination of the center longitudinal surface showed it to be free of imperfections and strains (twins or streaks).

For cycling, the crystal was sealed in an evacuated Vycor tube ( $5 \times 10^{-5}$  mm Hg) which was in turn welded into a stainless steel tube to permit cycling in NaK. The cycling variables were: 1 minute in cold tank, 1 minute in hot tank, and 30 seconds transfer time (total time for 10,000 cycles was about 2 weeks).

Upon removal of the crystal from the Vycor tube after cycling, the metallographic surfaces were still bright and could be examined microscopically without repolishing, although a very thin oxide film was present, as evidenced by slight discolorations. The dimensions of the center longitudinal face were then measured and, as shown in Table VII, the differences between the initial dimensions and those after cycling are insignificant, yielding a negligible K value. The results are conclusive in affirming that, upon cycling, no growth occurred in any of the several dimensions measured.

Table VII  
FILAR MEASUREMENTS OF CRYSTAL H BEFORE AND  
AFTER 10,000 CYCLES

(1.0 mm = 154 Filar Units)

Dimension	Before Cycling (Filar Units)	After Cycling (Filar Units)
A-B**	520	518*
B-C	321	320
C-D	520	518
D-A	316	316

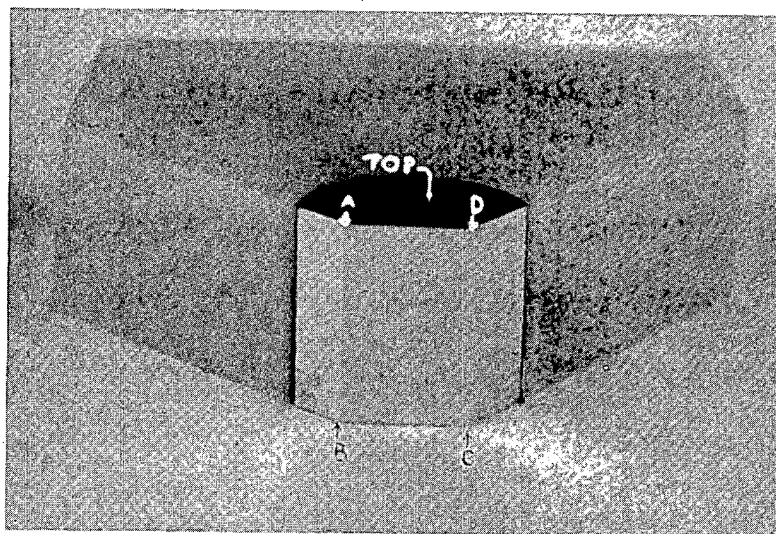
\*Average of three readings; all other readings are averages of four readings.

\*\*Refer to Figure 2.

RELASPEE

228 025

Figure 2. Uranium Single Crystal - Cycling Test Specimen.

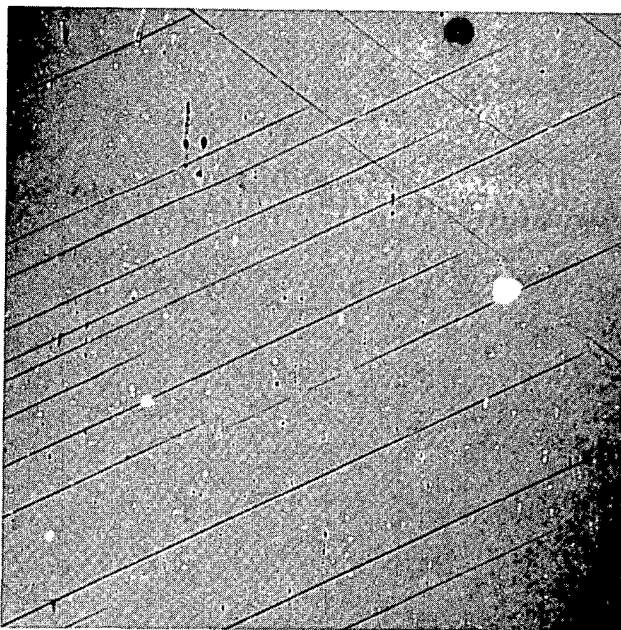


Macro #14360

8-X

Macroscopic view of crystal H before cycling showing the various edges from which dimensional measurements were made.

Figure 3. Microstructure of Single Crystal After Cycling.



Micro #14612

Polarized Light

50-X

Microphotograph showing twin traces on crystal H after repolishing.

242 026

DECLASSIFIED

Similarly, an X-ray photogram taken from the surface of polish in the "as cycled" condition indicated no evidence of straining; the Laue spots were as sharp as before cycling. Microscopically, however, a few small twins could be seen on the surface through the oxide film. To check their magnitude and number, the surface was repolished slightly, maintaining the original orientation. Figure 3 shows a photomicrograph taken from the surface after repolishing. The twins found were very thin and their number small. It is possible, of course, that these twins did form as a result of cycling, and the dimensional changes they induced were too small to be detected by the measured length changes. It is more likely, however, that they are the result of handling of the crystal in the process of sealing up and/or repolishing. The orientation of the crystal was such that the top and bottom surfaces were inclined only  $9^\circ$  from the (010) plane, which would make the crystal susceptible to twinning on the {130} planes on compression.

### 3. Thermal Expansion Coefficients of Uranium Single Crystals (L. T. Lloyd and H. H. Chiswik)

Alpha uranium, being orthorhombic in structure, has three different coefficients of thermal expansion along the three principal crystal axes. Because of the plastic interaction between grains on heating, it is impossible to obtain accurate values of these coefficients from polycrystalline materials. A program has been initiated to measure these coefficients of expansion on high purity single crystals made by the grain coarsening technique. Thermal expansion measurements of five crystals have been made. Two parallel faces were polished perpendicular to the crystal axis, and measurements of thermal expansion were made between these faces. Metallographic examination of these faces indicated the crystals to be relatively free from imperfections (twins, included grains, etc.). Orientation determinations of the crystals were made by Laue back reflection patterns from each polished end of the crystal. The angular locations of the directions with respect to the principal axes along which thermal expansion measurements were made are tabulated in Table VIII.

After electropolishing and just before testing, the initial length of each crystal was measured to the nearest thousandth of a centimeter in a constant temperature room with a cathetometer. Four length measurements were made. The averages of these, converted to inches, are listed in Table VIII. The diameters of these crystals were approximately one-eighth of an inch.

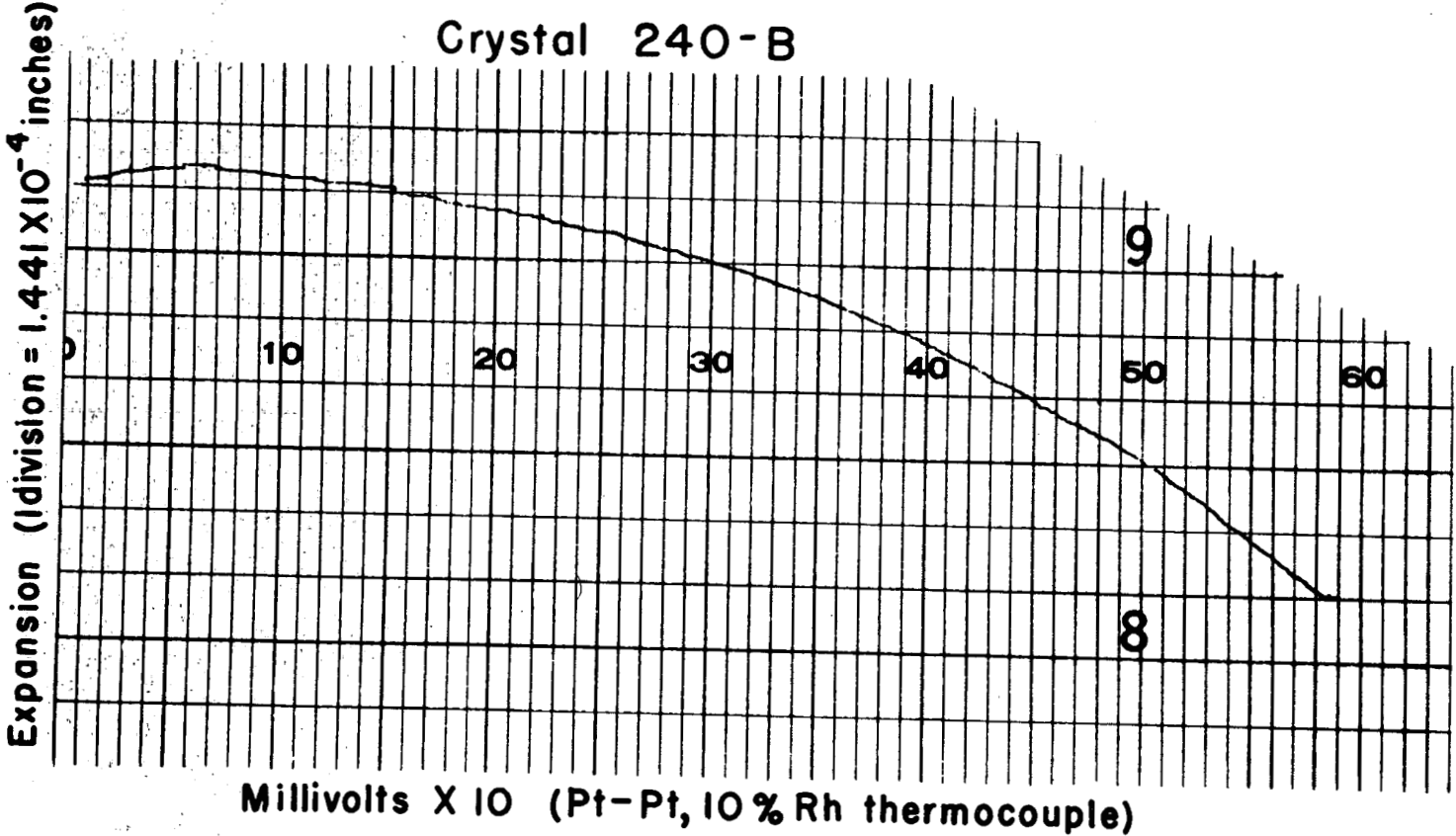
Thermal expansion data were obtained in a recording quartz differential dilatometer. The crystals were heated over a temperature range of  $21^\circ\text{C}$  to  $650^\circ\text{C}$ . The rate of heating and cooling was approximately  $5^\circ\text{C}$  per minute. A typical expansion curve as a function of thermocouple millivoltage is shown in Figure 4. Each crystal was tested several times and the data taken from a reproducible cooling curve. There was some tendency

DECLASSIFIED

252 027

29

Figure 4. Expansion Cooling Curve for Crystal 240-B.



Macro #14688

1-X

RECORDED

242

028

for the quartz dilatometer to lag behind the contraction of the sample upon heating. Metallographic observation after testing indicated that no changes in the crystal had occurred from heating and cooling and the application of load (approximately 80 grams) by the dilatometer.

Table VIII

LOCATION OF DIRECTION OF TESTING WITH RESPECT TO PRINCIPAL AXES AND INITIAL LENGTHS OF THERMAL EXPANSION CRYSTALS

Crystal	Location of Testing Direction with Respect to Principal Poles			Initial Length at 21°C (inches)
	From [100]	From [010]	From [001]	
219-2	85°	13°	78°	0.1139*
235-B	88°	8°	82°	0.0939
240-A	87.5°	12°	78°	0.1488
240-B	90°	10°	80°	0.1484
240-C	83°	13°	79°	0.1415

\*All values are averages of 4 measurements.

The results obtained for the five crystals are tabulated in Table IX in terms of inches expansion per inch of original length as a function of temperature. Specimens whose orientations are close to the [010] direction show a negative expansion with increasing temperature. The closer the direction of testing is to the [010] direction, the greater is the contraction.

No attempt has been made to analyze these data for coefficients of expansion in the three principal directions of the alpha uranium lattice. The errors in the coefficients for the [100] and [001] directions would be great because these are considerably displaced (nearly 90°) from the direction along which thermal expansion measurements were made. Crystals will be isolated and tested in directions close to these other two principal directions. When these data are available a least square analysis can be applied and good data for expansion coefficients in the principal directions obtained.

202 029

DECLASSIFIED



Table IX  
EXPANSION OF SINGLE CRYSTALS

Temp. °C	Expansion (inches per inch x 10 <sup>4</sup> )				
	219-2*	235-B*	240-A*	240-B*	240-C*
50	0.634	0.000	0.490	1.023	0.970
75	1.268	-0.764	0.966	2.032	1.960
100	1.268	-1.066	1.455	2.032	2.435
125	1.268	-1.844	1.455	2.032	2.435
150	0.634	-2.608	1.210	1.023	1.960
175	0.000	-3.069	0.966	0.504	0.980
200	-0.634	-4.611	0.490	0.000	0.000
225	-1.902	-5.375	-0.490	-1.023	-0.980
250	-3.156	-6.902	-1.455	-2.032	-2.925
275	-4.424	-8.444	-2.421	-3.559	-3.905
300	-6.326	-9.972	-3.876	-5.087	-5.850
325	-8.228	-11.514	-5.346	-6.614	-7.320
350	-10.116	-13.805	-6.802	-8.660	-9.280
375	-12.652	-16.110	-7.767	-11.196	-11.225
400	-14.554	-18.416	-9.712	-13.243	-13.661
425	-17.710	-22.249	-11.658	-16.298	-15.620
450	-20.246	-25.318	-13.589	-19.353	-18.546
475	-24.036	-29.151	-16.024	-22.912	-21.471
500	-27.826	-32.999	-18.935	-26.990	-25.390
525	-32.898	-37.596	-21.846	-31.054	-29.281
550	-37.956	-42.971	-25.246	-35.636	-33.676
575	-43.590	-49.873	-29.137	-40.218	-39.051
600	-48.706	-55.248	-33.979	-45.824	-43.936
625	-55.032	-61.387	-38.835	-52.452	-48.821
650	-58.822	-69.053	-43.216	-59.067	-54.182

\*Specimen Designation.

242 030

DECLASSIFIED

#### 4. Deformation of Uranium Single Crystals (L. T. Lloyd, H. H. Chiswik and M. D. Odie)

Two additional single crystals of alpha uranium have been isolated for studying the deformation mechanisms when subjected to compressive loading. One of these (crystal F) was compressed in the [010] direction at 600°C, and the other (crystal G) was compressed at room temperature in the [100] direction.

##### Crystal F (600°C compression) in the [010] direction

The results of room temperature compression (ANL-4860, -4966, and -5036) indicated that the major twinning plane in alpha uranium is the {130}. The high temperature compression study was designed to ascertain if this mechanism of deformation is still operative at elevated temperatures. A crystal grown by the grain coarsening techniques was isolated and two parallel compression faces ground so that they would be nearly parallel to the (010) plane. Subsequent Laue analysis indicated that the compression direction was only one degree from the [010] direction. Additional surfaces were ground on the crystal perpendicular to these compression faces, producing a crystal of regular geometrical shape. Two of these surfaces, inclined at 123° to each other, were prepared metallographically for two-surface analysis. Microscopic examination of these surfaces indicated the crystal to be free from twins and other imperfections. The orientation of face A was then determined by a Laue back reflection X-ray photogram. The photogram showed no asterism of the Laue spots, indicating the crystal to be free from strain.

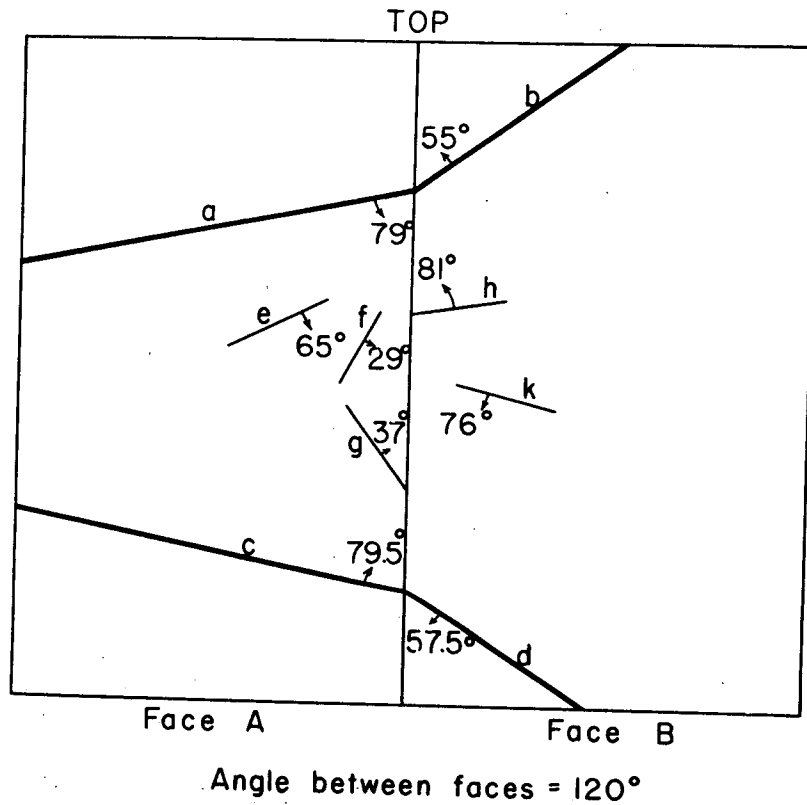
For compression, the crystal was placed in a fixture which provided for axial loading of the specimen and could be evacuated to approximately 50 microns and filled with purified argon gas. The crystal was heated by a small platinum-wound furnace (3/8" I.D. x 1" long), and temperature measurements were made by a chromel-alumel thermocouple placed at the specimen. The crystal, without load, was brought up to a temperature of 600°C in approximately 10 minutes. As the compressive load was applied an audible "click" occurred; the load was then removed, the power to the furnace shut off, and the specimen allowed to cool.

Macroscopic examination after compression showed that considerable oxidation of the crystal had occurred; there were, however, definite traces visible on both metallographic surfaces. The angles these made with the common edge were measured and recorded. The two metallographic faces were then repolished mechanically, very lightly, so that the new surfaces were as close to being parallel to the previous ones as possible. The specimen in this condition showed a total of nine different traces on the two surfaces. These are shown schematically in Figure 5, along with the letter identity assigned to each trace and the angles they made with the common edge.

DECLASSIFIED

242 031

Figure 5. Schematic Representation of Traces Observed on the Two Metallographic Faces of Crystal F After Repolishing (600°C compression).



Macro #14671

242 032

RECEIVED

Traces "a," "b," "c," and "d" were, by far, the most prominent traces observed; and, as indicated, trace "a" on face A could be followed over the common edge to trace "b" on face B, and trace "c" on face A could be followed over to trace "d" on face B. The angles that these traces made with the common edge compared favorably with those measured on the surfaces in the oxidized condition. Figure 6 shows the two-surface analysis of these traces. The pole of the plane represented by traces "a" and "b" falls close to the pole of the  $(1\bar{3}0)$  plane, and the pole of traces "c" and "d" falls close to the pole of the  $(130)$  plane.

The metallographic features of these  $(130)$  twins are shown in Figure 7. The twins are large, and their bounding edges are somewhat irregular, but in general they are lenticular in shape. Observations at higher magnifications indicate that there are areas of entrapped untwinned material left within the broad twin bands.

In addition to the four major  $(130)$  twin traces there were five minor traces that could only be analyzed by the "locus of poles" method. Such an analysis indicated that traces "e" and "k" (Figure 5) were probably caused by  $(172)$  twins; trace "f," by a  $(112)$  twin; trace "h," by a  $(176)$  twin; and trace "g," by either a  $(112)$  twin or a  $(176)$  twin.

Even though this crystal was compressed at  $600^{\circ}\text{C}$ , there is evidence, as indicated by a Laue photogram, that some strain still exists within the crystal after cooling to room temperature. The nature of the asterism is the same as that found for crystal A, namely rotation about the  $[001]$  direction (ANL-4860).

#### Crystal G (room temperature compression in $[100]$ direction)

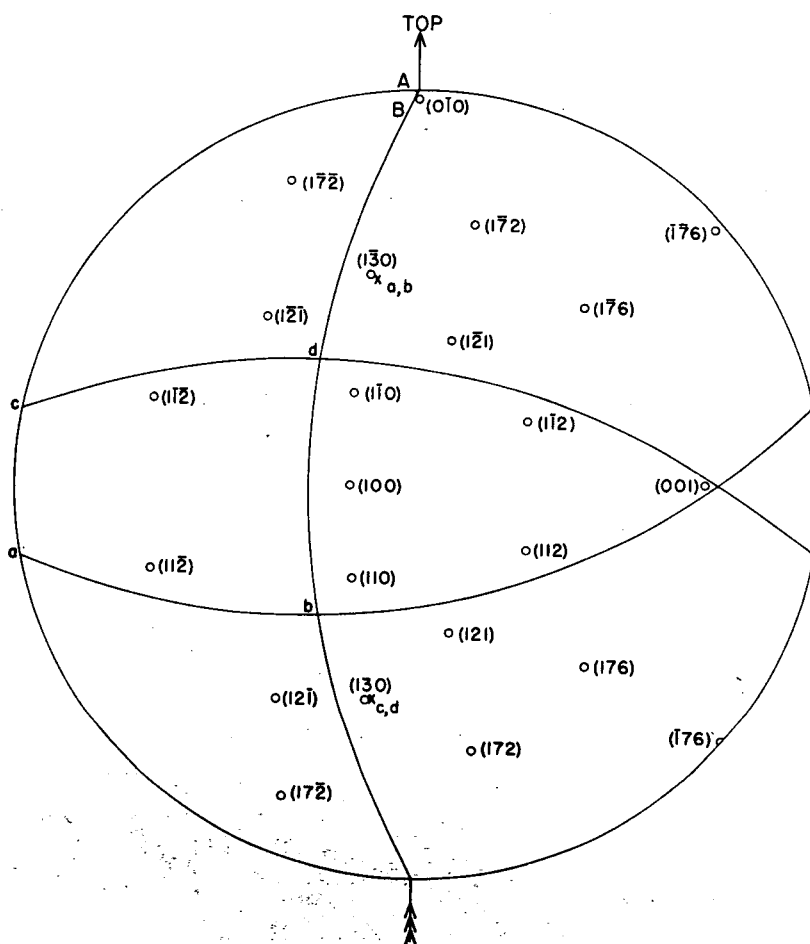
To date, the room temperature compressive studies of alpha uranium single crystals have resulted in "two-surface" identifications of only two twinning systems,  $\{130\}$  and  $\{176\}$ , and one slip system  $(010)$ , as being operative at this temperature. Studies of the reported crystallographic elements of the various twin systems indicate that  $(130)$ ,  $(172)$ ,  $(112)$  and  $(176)$  twinning should not propagate under compressive loads in the  $[100]$  direction;  $(121)$  twinning should. In addition,  $(010)$  slip should not occur because the slip plane and the slip direction are parallel to the  $[100]$  direction. Compression in the  $[100]$  direction, however, should be a favorable direction for kinking involving the  $(010)$  slip plane.

Crystal G was isolated and two parallel compression faces were ground so that they were nearly parallel to the  $(100)$  planes. Subsequent Laue photograms indicated the compression direction to be approximately four degrees from the  $[100]$  direction. Additional surfaces were ground perpendicular to the compression faces so that the crystal was of a regular geometrical shape. Two of these surfaces (inclined at  $132^{\circ}$ ) were metallographically polished for two-surface analysis of traces.

REF ID: A633

252 033

Figure 6. Stereographic Projection on Face A of Crystal F Showing the Two-Surface Analysis of Planes Causing Traces That Could be Followed Over the Common Edge.



Macro #14674

RECORDED

242 03/4

Figure 7. Typical Appearance of Twins in Crystal F After Compression at 600°C.



Micro #14602

Polarized Light

50-X

RECLASSIFIED

242 035

The crystal prior to compression showed a total of eight different traces on the two metallographic faces. These were not profuse in nature but nevertheless existed in the specimen. Four of these traces could be identified by a two-surface analysis: trace "a"\* on face A followed over to trace "b" on face B, and are attributed to  $(\bar{1}30)$  twinning; trace "c" on Face A followed over to trace "d" on Face B, and are attributed to  $(130)$  twinning. Traces "e" and "f" on face A, on the basis of the locus of poles method, are attributed to  $(172)$  plane twins. Traces "g" and "h"\*\* on face B are attributed to  $(112)$  plane twins by the locus of poles method. The latter gave the appearance of the "herringbone" markings often found on uranium surfaces as a result of mechanical polishing.

The crystal was compressed in a Tinius Olsen screw-driven tensile machine. The deformation occurred in a sharp, audible, stepwise fashion. The first deformation occurred near the top of the crystal, and further compression moved the stepwise deformation towards the bottom. Compression was continued until a total of 5 "clicks" occurred. The crystal was removed from the compression fixture and examined macroscopically and microscopically.

Macroscopically the crystal showed a sidewise displacement of one end with respect to the other (the compression fixture was designed to allow such motion to occur). The metallographic surfaces showed irregularities in the deformed portion of the crystal and each surface indicated two angles of tilt with respect to the original surfaces. Attempts to measure these angles of tilt proved unsuccessful because of the apparent rounding of the tilted surfaces.

Microscopically the surface showed the same traces as in the initial condition, plus four new traces as follows: traces "i" and "j" on face A; and traces "k"\*\*\* and "l" on face B (see Figure 8). Of these, three are associated with the stepwise deformation of the crystal: two trace directions on face A ("i" and "j") and one on face B ("l"). Trace "k" appeared adjacent to this stepwise deformation, and on the basis of the locus of poles, analysis is indicated to be a  $(172)$  plane twin. As was pointed out above, this system should not have operated for compression in the  $[100]$  direction. Its presence, however, can probably be attributed to stresses, other than direct compressive stresses, that were set up as a result of the deformation that occurred.

The traces "i," "j," and "l" were extremely close to  $90^\circ$  from the common edge. The exact angular displacement with respect to the common edge was difficult to measure because of the resultant roughening. The

---

\*The trace identification given here is the same as that given in Figure 8.

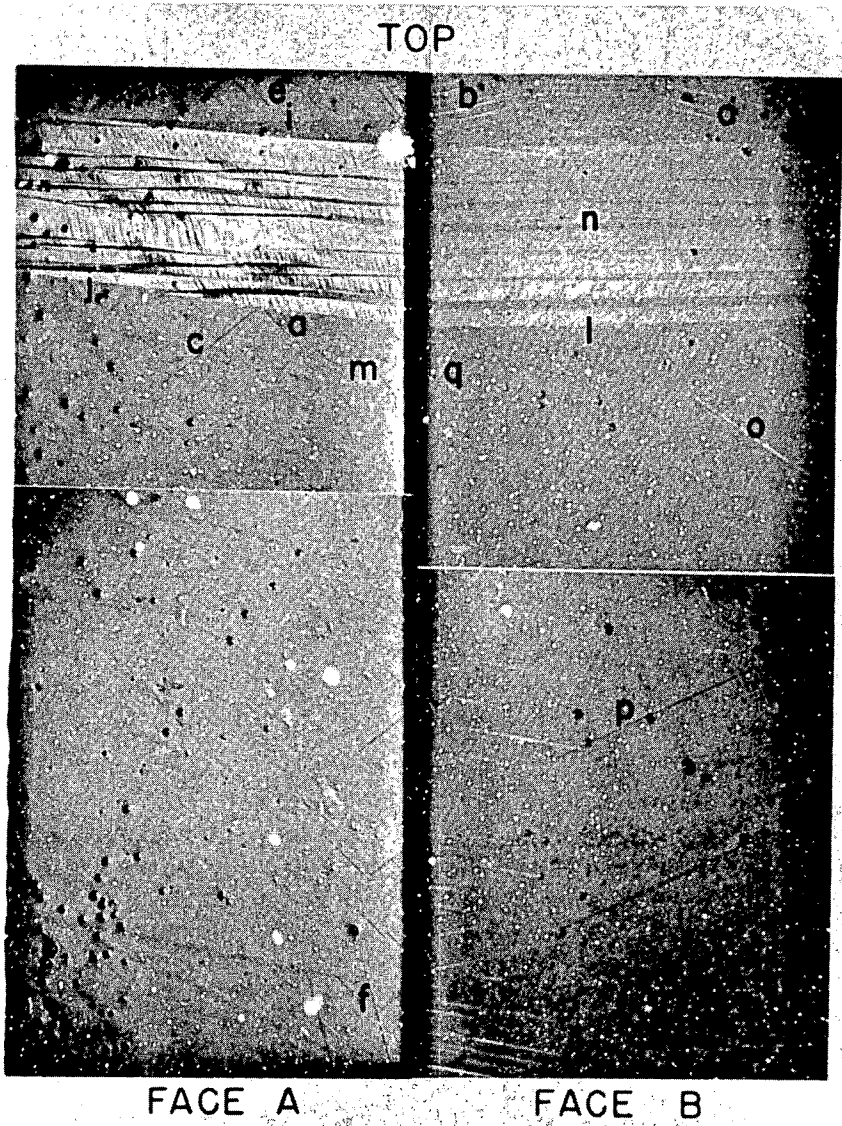
\*\*Traces "g" and "h" do not appear on the crystal in the repolished condition.

\*\*\*Trace "k" does not appear on the crystal in the repolished condition.

DECLASSIFIED

242 036

Figure 8. Composite Photomicrograph of the Two Metallographic Faces of Crystal G Showing the Traces Observed After Repolishing.



Micro #14666

Polarized Light

Approximately 25-X

UNCLASSIFIED

242 037



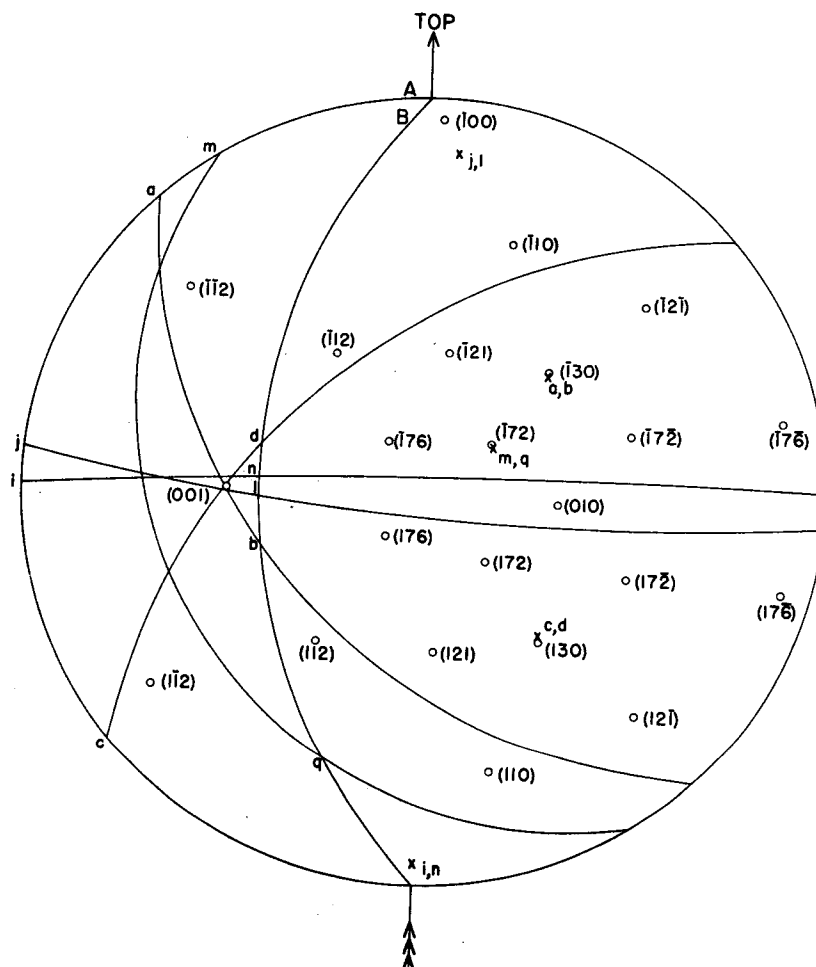
metallographic faces were then reground and repolished, so that more accurate measurements could be made. In the process of repolishing, an attempt was made to keep the new metallographic faces as close to being parallel to the old ones as possible. The angle between these faces after repolishing was 131 degrees. A composite microphotograph of the crystal in this condition is given in Figure 8.

A total of twelve different trace directions are shown in the crystal in this condition. Table X lists these traces together with the angles they made with respect to the common edge and the identity assigned to them. Traces "a," "b," "c," and "d" are (130) plane twins as indicated above. Figure 9 gives the two-surface analysis showing the solution for the location of the poles causing the traces that could be followed over the common edge. Traces "e" and "f" are indicated to be traces of (172) twins by the locus of poles method. Trace "m" on face A can be followed over to trace "q" on face B, and two-surface analysis shows that they are caused by a ( $\bar{1}72$ ) twin. The fact that they appeared after repolishing indicates that they were brought about by some forces other than those in the [100] direction, or they could have been present in the metal before compression and were brought out by the repolishing. Trace "o" on face B is attributed to a (121) plane twin by the locus of poles method. It could possibly have been formed as a result of the compression applied to the crystal.

The remaining four traces ("i," "j" on face A and "l," "n" on face B) are the result of kinking involving the (010) slip plane. They are traces of planes bisecting the angle between the slip planes in the parent crystal and those in the kinked material. The compression direction of this crystal is ideal for the formation of kink bands, for the slip plane (010) is nearly parallel to the compression direction as is the [100] slip direction. At higher magnifications it is possible to see (130) twins that existed in the crystal before deformation that are bent slightly at the boundary of the slip plane bisection. Further substantiation of this interpretation lies in the fact that Laue back reflection X-ray photograms taken from this deformed material on face A show an asterism of the spots which indicates a rotation of the lattice around the [001] direction. This is consistent with the usually accepted concept of the mechanism of kinking.

The two-surface analysis of the poles of these planes is shown in Figure 9. Two kink planes exist, because it is possible for rotation to occur in both a positive and negative sense about the [001] direction. The poles are displaced approximately six degrees from the (100) pole and one to two degrees toward the (001) pole.

Figure 9. Stereographic Projection on Face A of Crystal G Showing Two-Surface Analysis of Planes That Could Be Followed Over the Common Edge.



Macro #14667

DECLASSIFIED

242 039

Table X

## TRACES OBSERVED ON CRYSTAL G AFTER REPOLISH

Face	Trace	Angular Measurement with Respect to Common Edge*	Identity
A	a	43°CC	( $\bar{1}30$ )
B	b	76°C	( $\bar{1}30$ )
A	c	50.5°C	(130)
B	d	79°CC	(130)
A	e	21°C	(17 $\bar{2}$ )
A	f	16°CC	( $\bar{1}7\bar{2}$ )
A	i	90°	
A	j	85°CC	
B	l	87.5°C	
A	m	3.5°CC	( $\bar{1}72$ )
B	n	88°CC	
B	o	56°CC	(121)
B	p	65.5°C	(17 $\bar{2}$ )
B	q	26°C	( $\bar{1}72$ )

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

5. Preferred Orientation in Hot Pressed Uranium (M. H. Mueller, H. W. Knott)

A number of X-ray intensity measurements were made for various reflections from a cross and a longitudinal section of a hot pressed uranium slug. Since this material has been suggested and used as a standard random sample, it was of interest to make a comparison between the observed intensity and the intensity values as calculated by Jacob and Warren.<sup>1</sup>

<sup>1</sup>C.W. Jacob and B. E. Warren, JACS 59, 2588 (1932)

The intensities as observed, in terms of counts per second, were normalized by dividing the raw intensities by 2.05 after subtracting background. The values obtained for the cross and longitudinal section are shown in Table XI. In order to obtain an accurate picture of the degree of randomness the results from several samples should be averaged. However, the results shown here seem to indicate that the material is fairly random. The fact that the (020) intensity is somewhat high could be compatible with the somewhat low intensity from the (002) and (200) which are both  $90^\circ$  from (020). It is difficult to make an accurate comparison of the intensities from low intensity reflection since a slight variation in background causes a considerable change.

Table XI

COMPARISON OF THE CALCULATED INTENSITIES WITH THAT OBSERVED  
IN HOT PRESSED URANIUM MATERIAL

Reflection	(020)	(110)	(021)	(002)	(111)	(112)	(131)	(040)	(023)	(200)	(113)	(042)	(133)	(114)	(223)	(152)
$I_{j \& w}$	6.5	87	125	61	73	50	43	8	19	9.5	13	10	17	11	14	15
$I_{\text{Cross}}$	9.3	87	139	51	75	54	46	6.5	16	6.0	11	7.5	11	12	13	10
$I_{\text{Longitudinal}}$	7.8	122	138	42	92		44			8.3						

## 6. Diffusion in the System Copper-Uranium (R. Weil, S. H. Paine)

A few diffusion experiments were conducted using copper-uranium couples. These couples are interesting because only one new phase forms as a result of diffusion, which makes it possible to calculate a diffusion coefficient if the range of concentration of the new phase is known. The concentration range of the phase, which in the copper-uranium system is  $UCu_5$ , has not yet been determined.

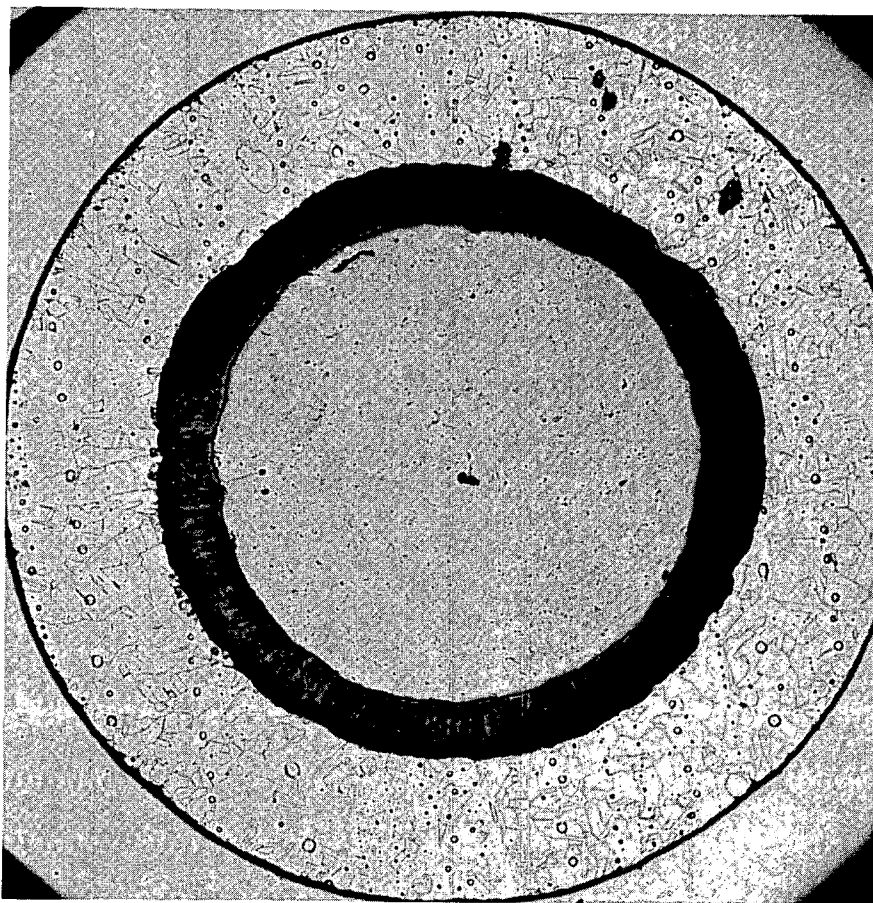
The diffusion couple consisted of a uranium wire which had been copper plated after the usual treatment of uranium for electroplating. After diffusion, the  $UCu_5$  layer is clearly visible, as illustrated by Figure 10 which shows a cross section of a diffusion couple.

The data obtained from four-day experiments at various temperatures is shown in Figure 11. The solid line represents the result of a least-squares analysis of the data. Data from two-day experiments indicated that the square of the thickness of the  $UCu_5$  layer is proportional to the diffusion time. Given the slope of the curve in Figure 11, an activation energy of 11,750 calories/mole was calculated.

RECEIVED

212 041

Figure 10. Cross Section of Uranium-Copper Diffusion Couple.

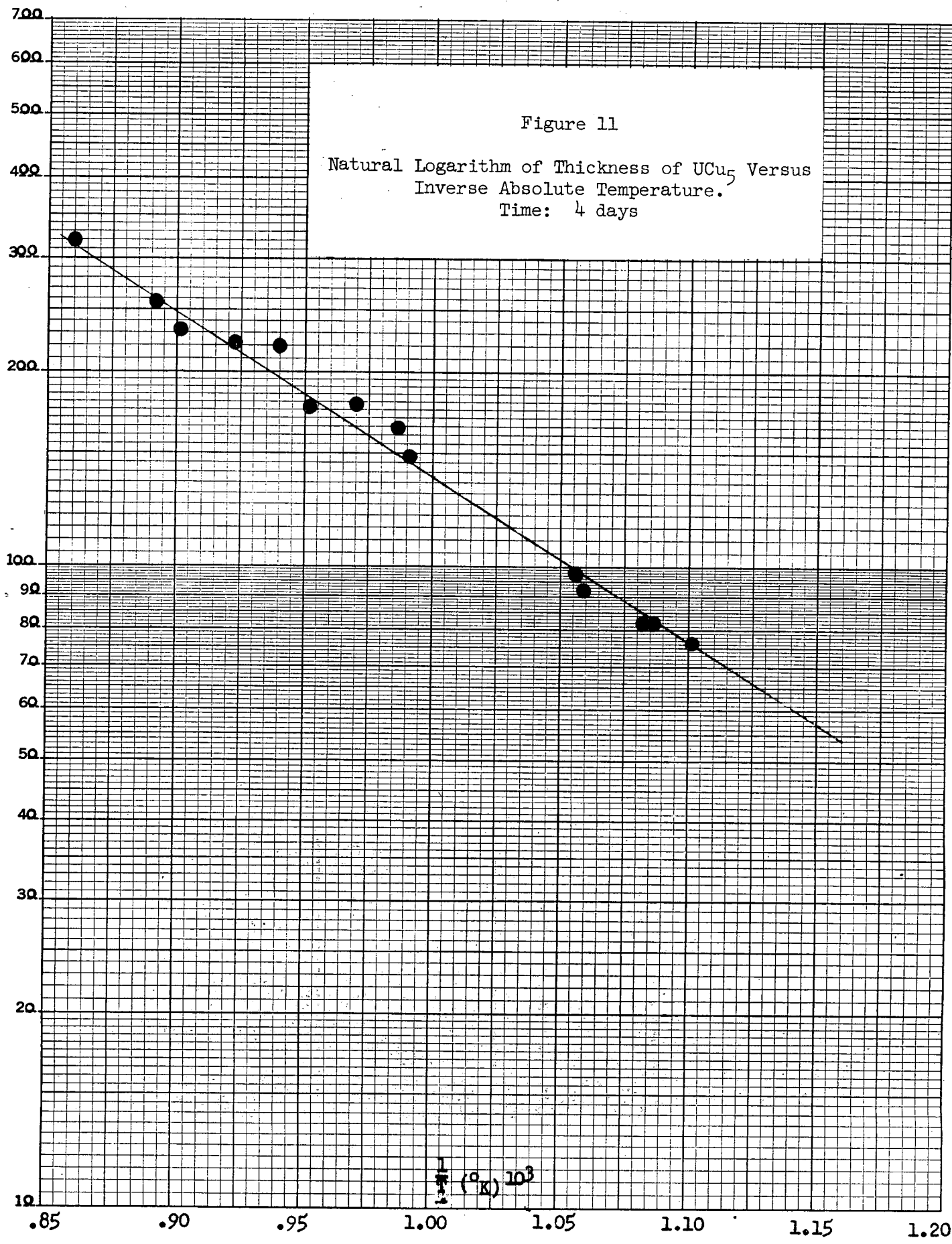


Micro #14549

75-X

DECLASSIFIED

242 042



DECLASSIFIED

242 043

## V. APPLIED METALLURGY

### 1. Casting of High Purity Uranium Billets (R. J. Dunworth, R. E. Macherey)

Three large, high purity uranium billets were made from electrolytic crystals. These billets weighed 4, 6 and 7 kg. The crucible was brought to a temperature of 1350°C and held at temperature until the pressure had decreased to  $2 \times 10^{-6}$  mm. Then the electrolytic crystals were fed into the crucible from a Syntron feeder. As the crystals melt the pressure rises in bursts to  $1 \times 10^{-4}$  mm. The gas evolved from the crystals is probably hydrogen from the pickling operation. Both ThO<sub>2</sub> and UO<sub>2</sub> crucibles were used. The analyses of castings made from ThO<sub>2</sub> crucibles show a pickup of 0.2 to 0.3 ppm of boron. Other impurity elements are the same as for the UO<sub>2</sub> melted castings. Reference to Table XII (Analyses of Crucibles, Section V-3 of this report) would suggest that the aluminum, iron, and silicon contents, as well as the boron content, of billets melted in thoria might be expected to increase. The fact that no such increases are reported might be ascribed to relatively low sensitivity for aluminum, iron and silicon in the spectrographic analysis. When biscuit uranium, however, is melted in high purity magnesia and in Magnorite crucibles (from Norton Company) with much higher aluminum, boron, iron and silicon contents, the castings show only a large pickup of boron. It may be concluded that uranium is particularly sensitive to boron contamination and relatively insensitive to other crucible impurities. A special mass spectrographic analysis was made for thorium in uranium melted in thoria crucibles, and the value reported was  $2 \frac{+1}{-2}$  ppm thorium. The high purity billets contained 23 ppm carbon and less than 10 ppm nitrogen. No difference was found metallographically or in analysis between billets melted in 15 minutes or 4 hours. The amount of skull in the crucible was about 5% of the crystals charged. The production of large, high purity billets has been demonstrated and is limited mainly by the amount of electrolytic crystals available.

### 2. Casting of Uranium Rich Alloys (R. J. Dunworth, R. E. Macherey)

Over thirty uranium alloy castings were made in 6 kg size and five in 30 kg size. All the alloys were poured into water-cooled copper molds to minimize segregation. Some binary and ternary zirconium and niobium alloys were made for corrosion studies, but the bulk of the castings were made for EBR loading and roll cladding experiments. Sufficient data have been obtained to determine methods of making these alloys. A defect common to all billets is the pinholes found at the top and the sides of the castings. This defect is presumed to be associated with the condensation of some volatile material inside the water-cooled mold prior to casting. The volatile material vaporizes on casting with the formation of pinholes near the surface of the casting.

In the 1 w/o and 2 w/o zirconium alloys, the zirconium sheets dissolved completely at 1300°C and 1350°C. In making the 5%, 7-1/2% and 10% alloys, however, about 25% of the zirconium added did not alloy. These

044

alloys may not have had sufficient time, or may not have been at a high enough temperature, to put the zirconium entirely into solution. Supporting this view was the observation that the zirconium sheets were packed tightly in the bottom of the crucible, giving the effect of a solid block of zirconium instead of  $1/16$ " sheets. A new method of making the 2% alloy was tried in the high vacuum furnace. Zirconium shot,  $1/4$ " x  $1/4$ ", was put in the Syntron feeder and added to the molten uranium at a temperature of  $1400^{\circ}\text{C}$ . Solution of the zirconium was rapid and complete. It may be noted, however, that a vacuum of  $5 \times 10^{-6}$  mm is probably required for this method, since any oxide scum floating on the surface would prevent the zirconium pieces from coming into direct contact with the molten uranium.

The segregation of zirconium with carbon in the 2 w/o Zr alloy has received additional confirmation with the receipt of more analyses. The presence of a segregation pipe at the top of the casting has also been confirmed - both in the 2" and 3" diameter billets. About 15% of the 3" diameter billet must be cropped to remove this pipe. Typical values of zirconium near the top of these 3" billets are: top center - 2.86%, top outside - 2.53%, bottom - 1.95%. These large castings contain about 100 ppm carbon compared to the 12 ppm found in the 2" size. Even in the 2" size the values vary from 5 ppm carbon and 2.05% zirconium at the bottom to 20 ppm carbon and 2.25% zirconium at the top. It is expected that remelting will reduce this segregation. It has been shown that remelting is necessary to make an acceptable casting in the 3" size.

The difficulties in the analysis for nitrogen have been mainly associated with the use of plastic test tubes for dissolving the 2 w/o Zr alloy. Because a few drops of HF were added to the solution, plastic tubes were used exclusively for this alloy. As a consequence all values reported have been high by factors of 4 to 20. Through the use of glass test tubes, the values now reported are quite precise (although somewhat high, 50 - 200 ppm), and it is hoped that the effect of nitrogen on the segregation of zirconium in this alloy may be determined. Because of many very low values for carbon at the bottom of these castings (2 - 5 ppm) it has been suggested that these values may be in error due to incomplete combustion of ZrC. Since no easy way exists to introduce a definite quantity of ZrC into the 2% alloy, no early answer to this problem seems probable.

The solution of niobium in uranium has been complete in the 1- $1/2$ %, 2%, 3%, and 6% alloys. Both  $1/16$ " sheet, and coarse,  $1/16$ " mesh powder have been used to make the 3% alloy with no apparent difference in solution rate. The chief difficulty with this alloy has been the high temperature ( $1650^{\circ}\text{C}$ ) required for alloying. This temperature is quite destructive to crucibles, stopper rods and furnace parts, and in addition more volatile material is deposited inside the mold. The casting, then, has many more pinholes than do the zirconium alloys. At the top of several 2" diameter castings a large blowhole ( $1-1/2$ " diameter x  $2-1/2$ " deep) was found. Some of the metal was

DECLASSIFIED

242 045



blown from the mold and solidified inside the ceramic crucible stand. This particular defect was found only when using a particular biscuit, and it was presumed that this biscuit had more volatiles than usual.

The analysis for niobium in the alloy is difficult, but the values have a precision of  $\pm 0.02\%$ . The values for carbon range from 20 - 30 ppm, and for nitrogen from 50 - 150 ppm. These values seem reasonable and the precision is good. No segregation of niobium with carbon or nitrogen is evident, and the top and bottom analyses agree quite closely.

### 3. Crucibles for Uranium Melting (R. J. Dunworth, R. E. Macherey)

In Table XII the crucibles are listed in order of decreasing desirability for maintaining purity in the uranium castings. Although all of these crucibles have been used for making alloy castings, about 75% of the castings were made from the high purity MgO crucibles. These crucibles generally last four or five heats. Molten uranium, however, attacks these crucibles excessively at temperatures above 1500°C. A sprayed on thoria wash protected the crucibles to a considerable degree. It was necessary to use the Magnorite crucibles (MgO of lower purity than the high purity crucibles), as these are the only crucibles large enough to contain 30 kg of metal. The boron contamination from the Magnorite is rather high - 2 ppm at 1300°C, 8 ppm at 1450°C. Although large zircon and zirconia crucibles are available the silicon pickup is about 500 ppm. Urania crucibles are no longer available but these crucibles lasted only for one melt. About half of the thoria crucibles failed in the first heat (at the 1650°C necessary for niobium alloys). The method of loading thoria crucibles might contribute to the failures and this is being investigated. The use of ceramic crucibles of any kind is quite expensive and means of preventing early failures are being studied.

### 4. Effect of Irradiation Upon Normal Uranium (J. H. Kittel, F. R. Taraba, S. H. Paine, P. Tedeschi, F. Pausche)

Irradiations of natural uranium in the MTR have continued. Specimens have been studied with total atom burnups as high as 0.88% (7500 MWD/T). Other specimens, still in the reactor, have burnups well above 1% (10,000 MWD/T). Although the specimens are not enriched, burnups above 0.7% are possible because of the fissions from plutonium atoms that have formed from the  $U^{238}$ . The specimens with the highest burnups are reported by the Chemical Engineering Division to have plutonium contents on the order of 5000 - 6000 g/T, or about 1/2%.

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

A group of partially enriched (10%  $U^{235}$ ) uranium-zirconium alloys containing 1 w/o and 2 w/o zirconium are being irradiated in the MTR beryllium stringers. Six of the specimens have been examined after total

DECLASSIFIED

222 046

48

Table XII

IMPURITIES IN CRUCIBLES FOR MELTING URANIUM ALLOYS  
(ANALYSES IN ppm EXCEPT AS NOTED)

Crucible <sup>(1)</sup>	C	Al	B	Ca	Cr	Cu	Fe	Mg	Mn	Na	Pb	Si	Cost	Contamination in Casting Detected
UO <sub>2</sub>	--	70	0.3	50	2	1	50	20	0.5	< 1	< 1	100	ANL Made	None
ThO <sub>2</sub>	17	200	10	200	3	5	300	50	< 1	50	10	300	\$100	B 0.2
High Purity (MgO)	--	< 100	< 100	5000	< 100	< 100	800	> 1%	< 100	< 100	< 100	1%	\$ 25	B 0.2
Magnorite (MgO)	--	200	200	5000	< 100	< 100	6000	> 1%	< 100	< 100	< 100	1%	\$ 8 <sup>(2)</sup>	B 2-8 <sup>(3)</sup>

(1) All crucibles except those of Magnorite were 4" O.D. x 8" high.

(2) Estimated; Magnorite crucibles cost \$25 for 7" diameter x 12" high size.

(3) 2 ppm boron contamination at 1300°C, 8 ppm boron contamination at 1450°C.

Note: Elements not listed are below spectrographic limits.

362  
047

atom burnups ranging from 0.18 to 1.0%. The thermal histories of the specimens, the conditions under which they were irradiated, and the changes observed due to irradiation are summarized in Tables XIII and XIV. Photographs of the specimens before and after irradiation are shown in Figures 12 through 18.

Table XIII

## ZIRCONIUM-URANIUM ALLOYS: IRRADIATION CONDITIONS

Specimen	Zr (w/o)	Heat Treatment	Total Atom Burnup, %	Calculated Maximum Temp. °C
AA- 6	1	As cast	0.40	370
AA-16	1	Gamma quenched	0.78	610
AA-36	1	Beta quenched	0.18	170
AA-22	2	As cast	0.27	270
AA-26	2	Air cooled from gamma	1.0	720
AA-32	2	Isothermally transformed at 500°C	0.57	510

Table XIV

## ZIRCONIUM-URANIUM ALLOYS: IRRADIATION CHANGES

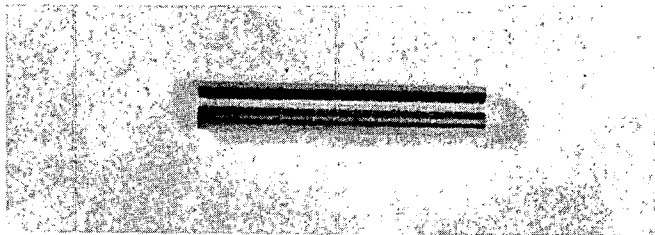
Specimen	Length Increase, %	Ln L/L <sub>0</sub> /Burnup	Density Decrease, %	Hardness Increase, R <sub>A</sub>
AA- 6	6.7	17	2.1	4
AA-16	40	43	6.7	6
AA-36	13	68	2.0	4
AA-22	4.8	18	1.9	3
AA-26	61	48	7.4	10
AA-32	48	69	2.8	10

In general, it was found that none of the heat treatments reduced growth rates to those exhibited by the as cast materials, of which the 2 w/o zirconium was found to be much more satisfactory than the 1 w/o.

RECEIVED

242 - 048

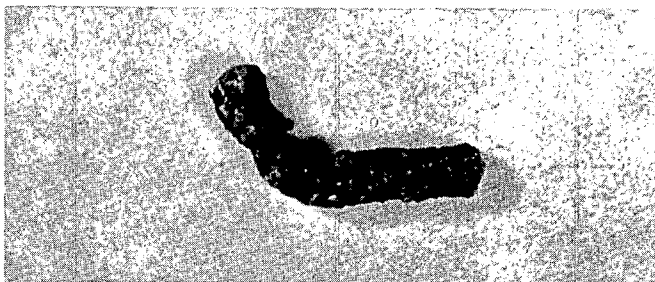
Figure 12. Appearance of Typical Specimen Before Irradiation.



Macro #M-14625

2-X

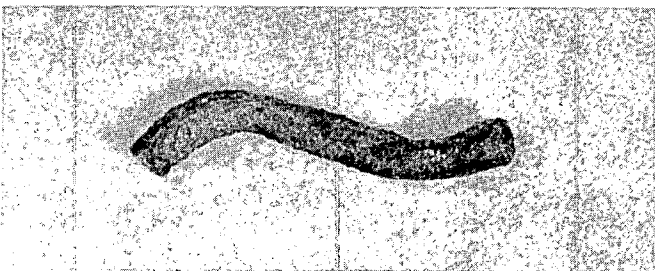
Figure 13. Specimen AA-6, 1 w/o Zr, As Cast, After Total Atom Burnup of 0.40%.



Macro #M-14626

2-X

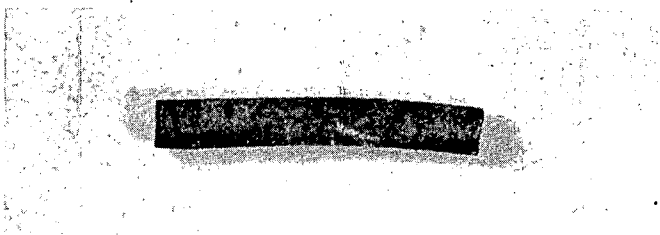
Figure 14. Specimen AA-16, 1 w/o Zr, Gamma Quenched, After a Total Atom Burnup of 0.78%.



Macro #M-14627

2-X

Figure 15. Specimen AA-36, 1 w/o Zr, Beta Quenched, After a Total Atom Burnup of 0.18%.



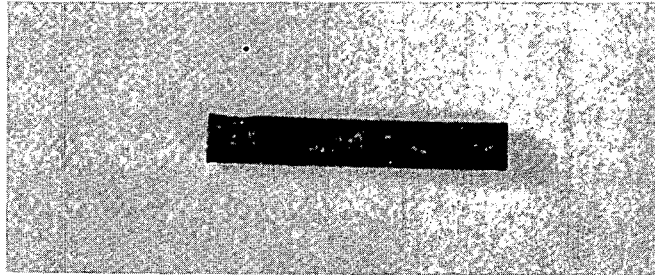
Macro #M-14631

2-X

DECLASSIFIED

242 049

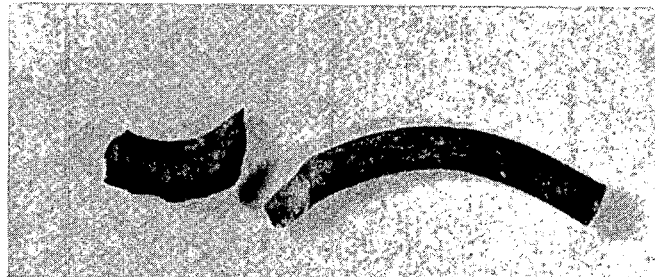
Figure 16. Specimen AA-22, 2 w/o Zr, As Cast, After a Total Atom Burnup of 0.27%.



Macro #M-14628

2-X

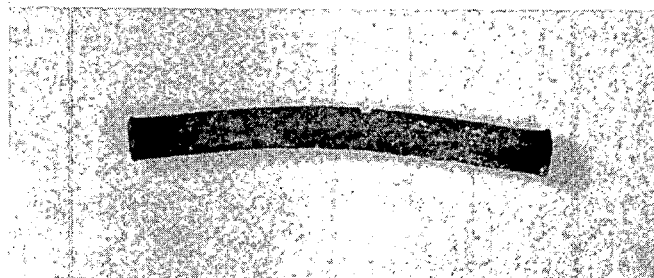
Figure 17. Specimen AA-26, 2 w/o Zr, Air Cooled from Gamma, After a Total Atom Burnup of 1.0%.



Macro #M-14629

2-X

Figure 18. Specimen AA-32, 2 w/o Zr, Isothermally Transformed at 500°C, After a Total Atom Burnup of 0.57%.



Macro #M-14630

2-X

242 050

DECLASSIFIED

Although the 2 w/o as cast specimen was the best of the group, it also grew at a greater rate than anticipated. Density decreases occurred at about the same rate as has been observed in unalloyed uranium. All specimens increased in hardness, and specimens AA-6 and AA-26 broke with brittle fractures during normal handling.

Previous thermal cycling tests of similar materials indicated that 2 w/o isothermally transformed alloy, represented by specimen AA-32, would be relatively stable dimensionally under irradiation. The first irradiation results reported herein indicate that it grows at a rate several times that shown by ordinary beta quenched unalloyed uranium. However, it has recently been found that not all specimens of the 2% Zr alloy respond properly to heat treatment. Thermal cycling growth rates as high as 80 microinches/inch/cycle have been observed in some cases. Unfortunately, thermal cycling specimens identical to the irradiation specimens are not available, and in order to obtain more information on this material, additional specimens have been prepared for irradiation and the results will be compared with thermally cycled specimens cut from the same rod.

DECLASSIFIED

242 051

## VI. AQUEOUS CORROSION

### 1. Metal Thickness Gauge (J. E. Draley and W. E. Ruther)

Improvement of the alternating current supply and of the instrumentation have been made. The gauge is apparently stable enough to provide reliable readings of metal thickness to a sensitivity of about 0.7 microinch (for 2S aluminum). Further improvement in the sensitivity is limited by several factors, notably the difficulty in obtaining an adequately sensitive bridge balance.

Work is continuing on improvement of the characteristics of the gauge, and corrosion curves are being measured with it.

### 2. Corrosion of Aluminum in Dilute Aqueous Solutions (J. E. Draley and Nancy Williams)

Several varieties of tests are being run in an effort to explain the characteristics of the curve of the corrosion of aluminum versus exposure time. Such curves characteristically show an initial rapid rate of reaction followed after a day or a few days by a linear low rate of corrosion. The total amount of corrosion which takes place before the straight line portion of the curve begins is very large compared to the amount of metal required to form the oxide film which is believed to be the protective one.

It is as an attempt to explain this large initial amount of reaction that work is directed. Curves of solution resistivity versus time and close checks of the amount of metal corroded as a function of time are now available. Other work will include an attempt to determine the pH of the water immediately adjacent to the metal sample during this initial reaction period. Among the possible explanations is the supposition that the water immediately adjacent to the metal becomes alkaline as a result of initial reaction, and that this alkaline medium prevents the formation of the highly protective film which can form after the water becomes more nearly neutral. Another factor which might be significant is the possibility that the metal must be etched to a preferred condition prior to its ability to support the particular type of thin protective film required to limit the corrosion rate to quite low values. Work being done and planned has as an objective the evaluation of the importance of these factors.

### 3. Aqueous Corrosion of Aluminum at Elevated Temperature (W. E. Ruther and J. E. Draley)

Testing is continuing in this system to determine the maximum permissible operating temperature for aluminum in aqueous solution. At present it appears that sulfuric acid solution at pH 3.5 provides genuine beneficial

effect on the metal so that its corrosion rate is considerably reduced and the incidence of intergranular attack is made much less probable, perhaps eliminated. At 200°C, samples appear to be in excellent condition after several weeks of exposure. The addition of 5 ppm chloride ion to the acid medium caused the formation of a few tiny pits per sample. The growth of these pits, however, was very slow, and it is indicated that the sensitivity of aluminum to the presence of chloride ion in the water is lower at elevated temperatures than at ordinary temperatures.

#### 4. Mechanism of Aqueous Corrosion of Zirconium (R. D. Misch)

In continuation of previous work on the rate of oxidation of zirconium as a function of grain orientation (see ANL-5097), several more single grains of zirconium have been anodized, making a total of 24 grains. All areas were wet polished, etched in hydrofluoric-nitric acid, rinsed, anodized in 70 w/o HNO<sub>3</sub> at 5°C for 3-1/2 hours at 0.025 mm/cm<sup>2</sup>. The rate of oxide film growth is indicated qualitatively by the degree of darkening of individual grains. These ranged in appearance from a lustrous appearance (essentially unchanged by the anodizing) to completely black (the color of the oxide layer produced under these conditions). Intermediate shadings were grey or blue. The latter may have been an interference color, but this was not definitely established.

To illustrate the distribution of the data over all possible orientations the results are given on a reciprocal pole figure based on the (001) plane (see Figure 19). The orientations for maximum film growth lie 20° to 45° from the basal plane. The location of points is such as to focus attention on the (102) plane.

Several hypotheses have been considered to explain the different rates of oxide growth on various planes of the zirconium crystal lattice. It is difficult to evaluate these without a knowledge of the orientation of the oxide. Work to establish this point is being conducted. Results of Chirigos and Thomas at WAPD have indicated the orientation of the oxide with respect to the metal structure, when reaction in gaseous oxygen takes place. Similar results might be anticipated for aqueous corrosion.

#### 5. Aqueous Corrosion of Uranium Alloys at Elevated Temperatures (J. E. Draley, W. E. Ruther)

Low niobium alloys of uranium show maximum resistance to corrosion in distilled water at elevated temperature when quenched from the gamma phase. Their corrosion resistance is considerably reduced by aging subsequent to the gamma quenching. For an alloy containing 3 w/o niobium, no effect of aging has been observed after nearly 2000 hours at 260°C. (Corrosion rate 0.18 mg/cm<sup>2</sup>/hour, Reactor Engineering Division.) About 900 hours were required in distilled water at 300°C to cause fracture and edge corrosion of another sample. The data for this test are shown in Figure 20, where uncleaned sample weight changes are shown as a function of time on test.

DECLASSIFIED

242 053



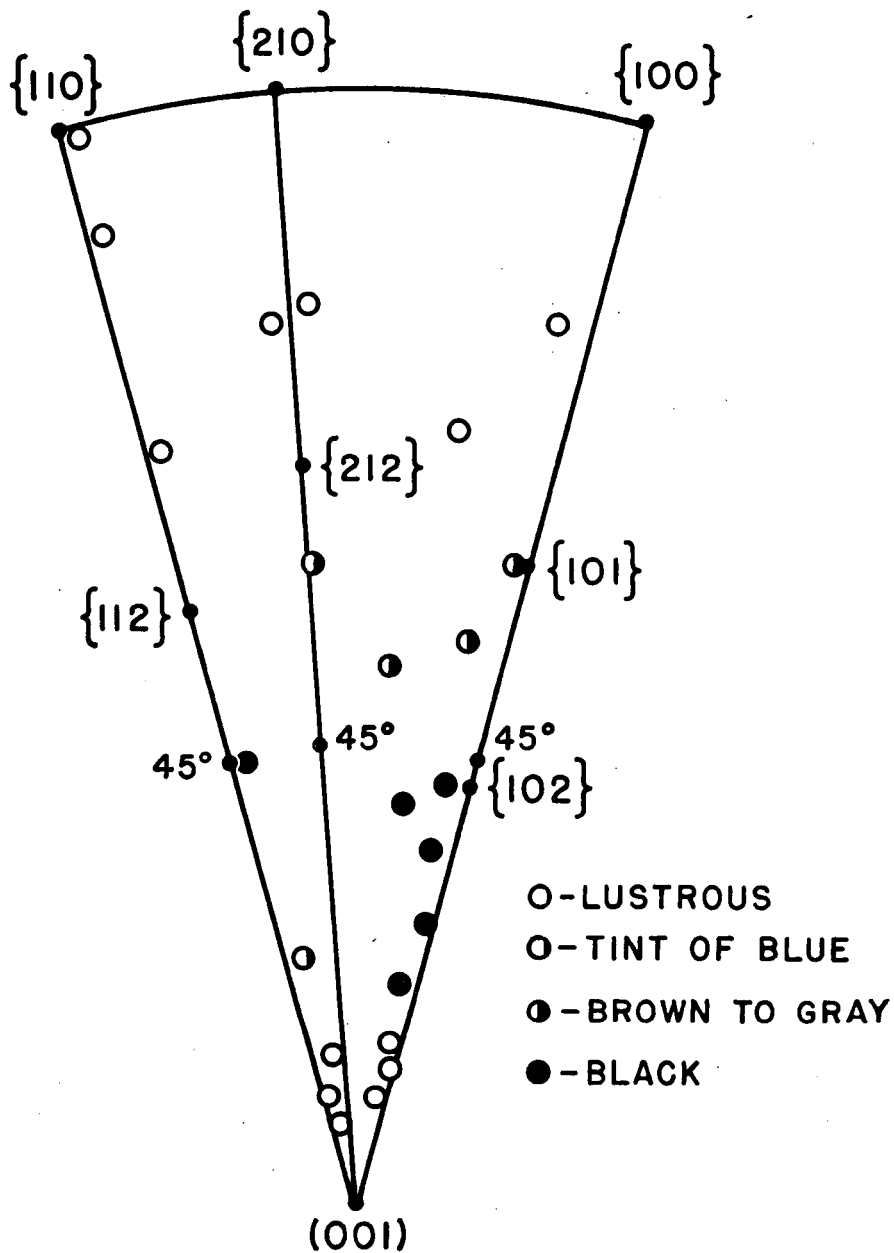


FIGURE 19  
 LOCATIONS OF NORMALS TO GRAIN FACES  
 ON A BASAL PLANE STANDARD PROJECTION

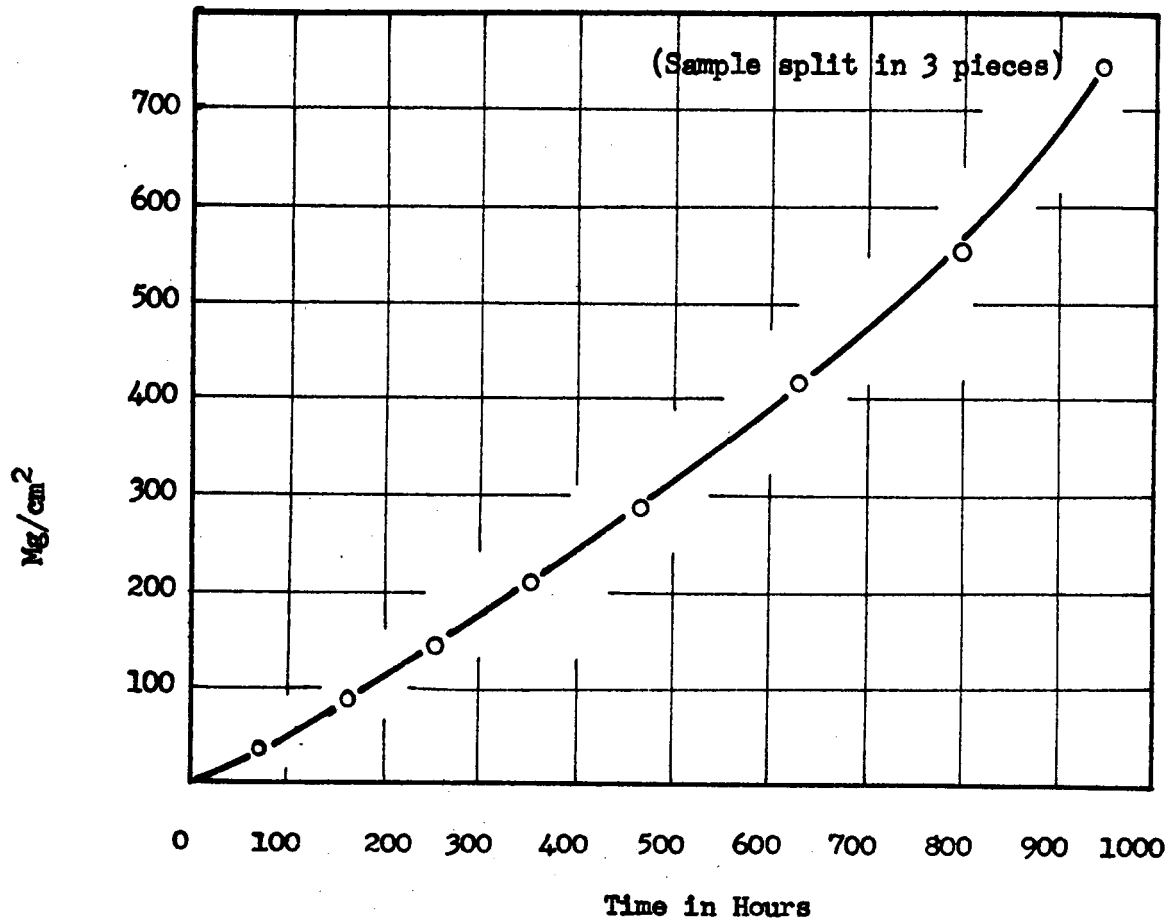


Figure 20

CORROSION OF URANIUM - 3% NIOBIUM ALLOY H187  
IN DEGASSED DISTILLED WATER AT 300°C

Corrosion tests at about 325°C showed sample failure (crumbling) after two weeks, but not after one week exposure. It is suspected that the corrosion failure was enhanced by the aging effect. Three days aging at 350°C is sufficient to spoil the resistance of the alloy to corrosion by distilled water at 300°C as demonstrated by 3 day corrosion tests.

Quenching the 3% niobium alloy from 800° and from 1000°C apparently caused a difference in the rate of aging exhibited during a 300° corrosion test. A sample quenched from 1000° appears excellent after testing together with one quenched from 800° until the latter failed (disintegrated). The testing time required was 555 hours. The good sample has been returned to test.

An alloy containing 6 w/o niobium requires a somewhat longer time for aging at a given temperature than the 3% niobium alloy. The same general phenomena are observed, except that even after aging the 6% alloy does not fail at 260°C (500°F). Its corrosion rate is apparently increased by a factor of two or three. At 325° and 360°C, sample failure does occur.

After quenching from about 800°C, alloys containing 1-1/2 w/o niobium + 5 w/o zirconium and 2 w/o niobium + 4 w/o zirconium showed diminishing rates of unclean sample weight loss for the first several days in distilled water at 260°C. Tests have not progressed long enough to know what corrosion rates will be exhibited, but indications are that they will be about the same as for the 3% niobium alloy. Several other alloy compositions have been investigated but have shown little or no promise as corrosion resistant alloys.

The alloy containing 2% niobium + 4% zirconium possesses approximately the same sensitivity to aging as does the 3% niobium alloy in the as quenched condition. The 1-1/2% niobium + 5% zirconium alloy, however, has shown no deleterious effect of aging at 350°C up to 237 hours. However, aging for as little as 4-1/2 hours at 400°C has destroyed its corrosion resistance to water at 300°C. At the moment this alloy appears to possess more desirable properties for high temperature reactor use than any other. However, testing is only in the preliminary stages and no definite statements can be made.

#### 6. Corrosion of Zircaloy Clad Uranium-Niobium Sandwich Specimens (W. E. Ruther)

Short sections of uranium-3% niobium alloy have been roll clad with Zircaloy II and tested in distilled water at 300°C. The exposed ends of the uranium alloy corroded at about the same rate as is normally exhibited by bare samples of this alloy. A tendency toward corrosion at the interface of the Zircaloy cladding and the uranium alloy core seems to be minimized by

using the highest rolling temperature tried to date, which was 800°C. A sample which had niobium foil rolled between the Zircaloy and the uranium alloy shows no apparent tendency to such localized corrosion and swelling after three weeks testing.

#### 7. Microstructural Features of An Uranium-3 Percent Niobium Alloy (H. H. Chiswik and S. M. Vescovi)

An uranium-3 w/o niobium alloy was examined metallographically after the following heat treatments: (1) as quenched from 1100°C; (2) quenched and annealed for 84 hours at 350°C; and (3) quenched and annealed for 24 hours at 500°C. The annealing heat treatments were undertaken to investigate the possible relationships of the microstructure to the corrosion behavior of the alloy at elevated temperatures. The alloy contained 3 w/o columbium, 95 ppm carbon and 120 - 355 ppm N<sub>2</sub>, with the remaining elements of the order of magnitude usually found in biscuit uranium (the alloy was made from biscuit metal). To study the nature of the inclusions present the specimens were examined "as mechanically" polished and after various stages of electropolishing.

As Quenched Alloy (see Figure 21) - In the "as mechanically" polished condition one can note the presence of some gray angular inclusions along with some smaller white inclusions that often take on a plate-like shape (see Figure 21-a). The shapes of these inclusions are better defined after a five second electropolish (Figure 21-b). After five seconds electropolishing, one may also note the faint appearance of some fine, microscopically unresolvable particles, which may or may not be the same as the small white inclusions noted above. After five minutes electropolishing, grain boundaries make their appearance, revealing a rather large grain size (Figure 21-c), and the large resolvable inclusions are attacked, leaving voids in their places. However, one can also note an increased quantity of the unresolvable particles that were noted only with difficulty after five seconds electropolishing. Continued electropolishing to 10 minutes did not change the main features of the microstructure, except for an increased activity of the electrolyte around the grain boundaries and the inclusions (Figure 21-d). The grain structure was revealed under bright field illumination and the grains did not change color under polarized light with the rotation of the stage, as is usual with alpha uranium.

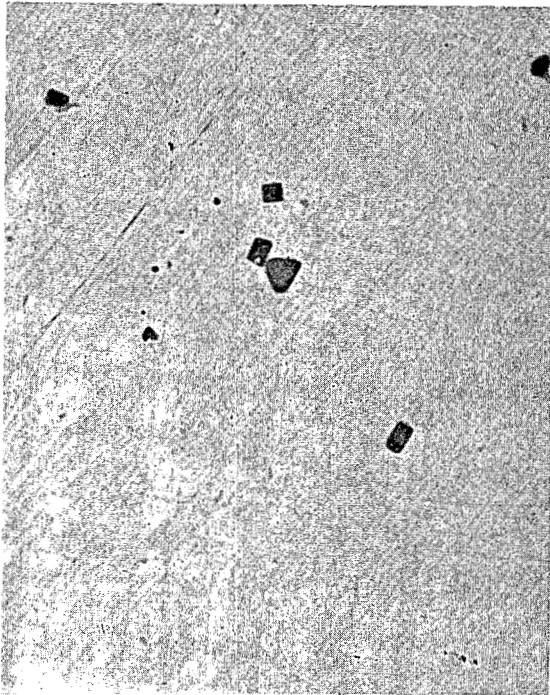
Annealing for 84 Hours at 350°C, (Figure 22) - Annealing at 350°C did not change the major features of the microstructure as noted above, except for two effects: a reaction may be noted in the matrix surrounding the inclusions (Figure 22-b); and the etching effect of the electrolyte at the grain boundaries and around the inclusions is greater (compare Figures 22-c and 21-c, both after five minutes electropolishing). These effects suggest that some reaction or decomposition has started at this temperature, apparently preferentially at the grain boundaries and at the inclusion interfaces, and the results may have an influence on the corrosion behavior of the alloy at this temperature.

DECLASSIFIED

262 057

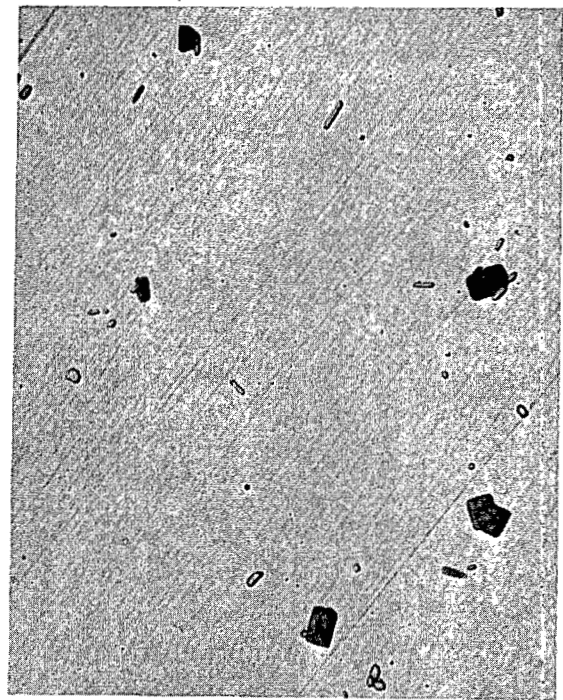
Figure 21. Microstructures of As Quenched U-3 w/o Nb Alloy.

21-a. Mechanically Polished.



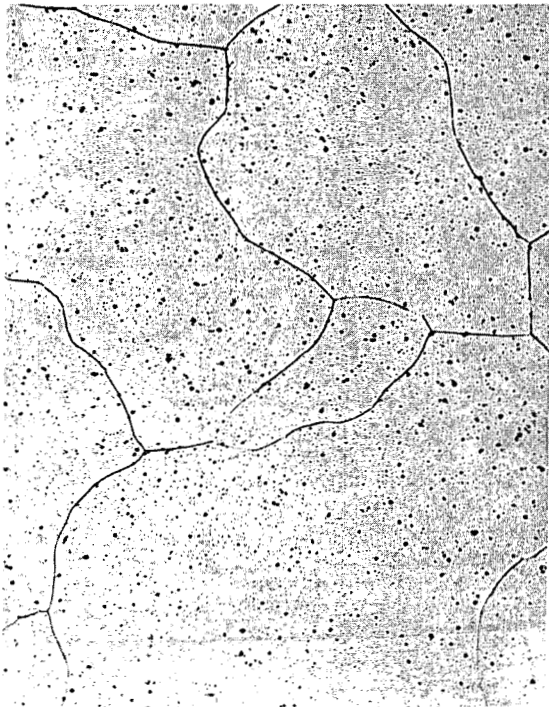
Micro #14355 Bright Field 1000-X

21-b. 5 Second Electropolish



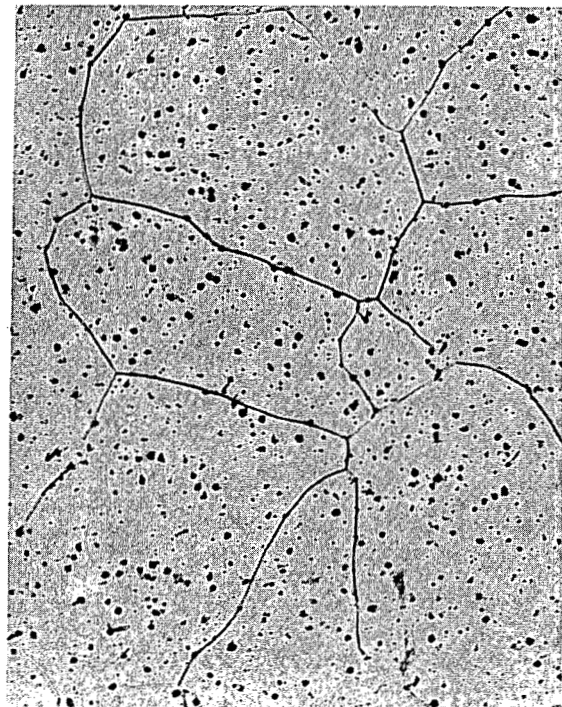
Micro #14356 Bright Field 1000-X

21-c. 5 Minute Electropolish.



Micro #14357 Bright Field 75-X

21-d. 10 Minute Electropolish.



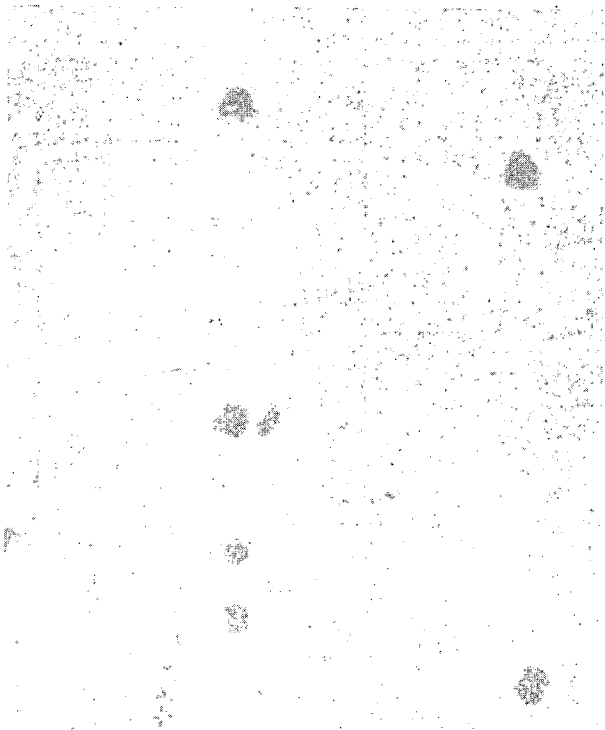
Micro #14348 Bright Field 100-X

DECLASSIFIED

242 058

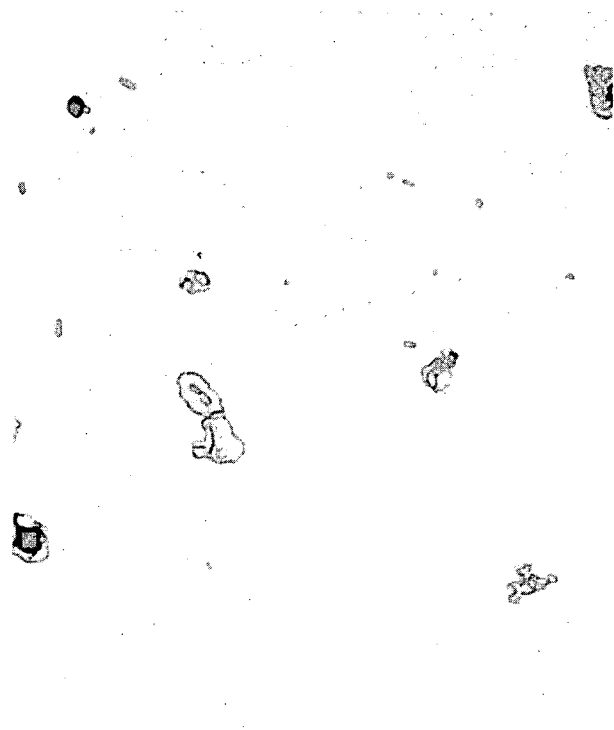
Figure 22. Microstructure of U-3 w/o Nb Alloy After Annealing for 84 Hours at 350°C.

22-a. Mechanically Polished.



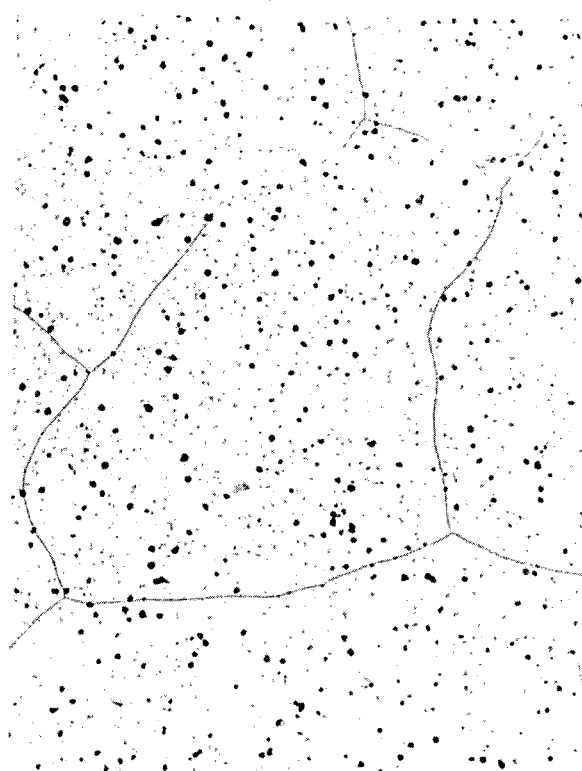
Micro #14438 Bright Field 1000-X

22-b. 5 Second Electropolish.



Micro #14440 Bright Field 1000-X

22-c. 5 Minute Electropolish.



Micro #14441 Bright Field 100-X

REPRODUCED

Annealing for 24 Hours at 500°C, (Figure 23) - The slight activity that was noted around the inclusions at 350°C has now progressed sufficiently to reveal general decomposition of the matrix, (Figure 23-b). The nature of the inclusions appears to be unchanged. The original grain boundary outlines are still evident (Figure 23-c), but on continued electropolishing they are masked by the fine precipitate.

Hardness - The Vickers and RC hardness values of the specimens in the three heat treated conditions were as follows:

<u>Heat Treatment</u>	<u>VPN (30 kg load)</u>	<u>Rockwell C</u>
As Quenched	325 - 355	36.0
Annealed at 350°C (84 hours)	470 - 493	49.0
Annealed at 500°C (24 hours)	425 - 439	40.0

The results indicate a precipitation hardening phenomenon with the annealing at 500°C resulting in overaging in conformity with the microscopic observations.





ARGONNE NATIONAL LABORATORY  
P. O. Box 299  
Lemont, Illinois

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 is to be marked:

"Delete - See ANL-5855

ANL-4316	p. 40	"Effects of Pile Irradiation Upon Dimensional Properties of Enriched Uranium," by R. F. Plott.
ANL-4736	p. 77	Item 9 through <u>A</u> .

Harold D. Young

10-13-58

ARGONNE NATIONAL LABORATORY  
P.. O. Box 299  
Lemont, Illinois

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 is to be marked:

"Delete - see ANL-5538"

ANL-4712	pp. 49-52	Item 5.
ANL-4736	pp. 77-78	Item 9, Part B.
ANL-4825	pp. 34, 36-40	Item 6, Parts B, C and D. Do not delete Figure 10, p. 35
ANL-4966	pp. 61-64	Item 6, Parts A and B.

*Hayden D. Jones*

---

June 24, 1958