ANL-5837
Metallurgy and Ceramics
(TID-4500, 14th Ed.)
AEC Research and
Development Report

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

QUARTERLY REPORT
OCTOBER, NOVEMBER, AND DECEMBER 1957

METALLURGY DIVISION

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Previous Quarterly Reports:

ANL-5797 July, August, September 1957
ANL-5790 April, May, June 1957
ANL-5717 January, February, March 1957

Operated by the University of Chicago
under
Contract W-31-109-eng-38

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METALLURGY DIVISION REPORTS AND PAPERS PUBLISHED
DURING THE QUARTERLY PERIOD
OCTOBER - DECEMBER 1957

- Richard J. Dunworth, "Arc Melting of Zirconium Metal," ANL-5519
(October 1957).
- A. E. Dwight and M. H. Mueller, "Constitution of the Uranium-Rich U-Nb
and U-Nb-Zr Systems," ANL-5581 (October 1957).
- F. L. Brown, L. W. Haaker, S. H. Paine, and R. A. Blomgren, "A Shielded
Metallograph for Remote Metallography," ANL-5635 (October 1957).
- F. L. Yaggee, "A Coated Cast Iron Crucible for Use with Eutectic Al-Si
Alloy in the Temperature Range 575° - 650°C," ANL-5673.
(November 1957).
- J. H. Handwerk, C. L. Hoenig, and R. C. Lied, "Manufacture of the
ThO₂-UO₂ Ceramic Fuel Pellets for BORAX-IV," ANL-5678
(August 1957).
- J. H. Kittel, M. Novick and R. F. Buchanan, "The EBR-I Meltdown -
Physical and Metallurgical Changes in the Core," ANL-5731
(November 1957).
- S. H. Paine, F. L. Brown and J. H. Kittel, "Examination of Irradiated
Stainless Steel-UO₂ Fuel Specimens for Nuclear Development
Associates, Inc.," ANL-5734 (July 1957).
- Floyd L. Brown, "A Study of Mechanical-Electrolytic Polishing on
Uranium Metallographic Specimens," ANL-5752 (January 1957).
- W. J. McGonnagle, "Nondestructive Testing of Nuclear Reactor
Components," *Nucleonics* 15 (10) 78-81 (October 1957).
- K. F. Smith, "The Metallurgy of EBWR," *Metal Prog.* 72 79-83
(November 1957).
- S. T. Zegler, R. M. Mayfield and M. H. Mueller, "Effects of Fabrication
and Heat Treatment Variables," *Metal Prog.* 72 210 (November 1957).
- J. E. Baird, N. J. Carson, Jr., "Melting and Casting of Uranium, Zirconium,
and Niobium Alloys," *Nuclear Met. (AIME)* 4 31 (November 1957).
- N. J. Carson, Jr., "Induction Melting of Uranium Base Alloys," *Nuclear Met.
(AIME)* 4 23-29 (November 1957).

- A. B. Shuck, "Centrifugal Casting of Uranium-Zirconium Alloy Rods," Nuclear Met. (AIME) 4 39-50 (November 1957).
- F. L. Yaggee, J. E. Ayer, and H. F. Jelinek, "Injection Casting of Uranium-Fissium Alloy Pins," Nuclear Met. (AIME) 4 51-62 (November 1957).
- A. B. Shuck, "Remote Fuel Fabrication -- How It Was Done for EBR-II," Nucleonics 15 (12) 50-53 (December 1957).
- H. H. Chiswik, "The Plastic Deformation of Uranium on Thermal Cycling," Trans. ASM 49 622-654 (1957).
- J. H. Kittel, S. H. Paine, and H. H. Chiswik, "Influence of Heat Treatment on Irradiation-Induced Dimensional Changes in Some Uranium-Zirconium Alloys," ASTM Spec. Tech. Pbn. #208, 87-99 (1957).
- W. F. Murphy, S. H. Paine, "Fast Neutron Effects on Tensile and Hardness Properties of Type 347 Stainless Steel," ASTM Spec. Tech. Pbn. #208, 162-174 (1957).
- S. H. Paine, J. H. Kittel, "Irradiation Effects in Uranium and Its Alloys," Problems in Nuc. Engr. 1 107-117, Pergamon Press (1957).
- J. H. Kittel, S. H. Paine, "Effects of Irradiation on Powder Compacts of Uranium and Some Uranium Alloys," Adv's. in Nuc. Engr. 2 260-271, Pergamon Press (1957).
- M. H. Mueller, "Summary of ASM Seminar: 'Mechanisms of Deformation and Fracture,'" Metals Rev. 30 22 (1957).

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QUARTERLY REPORT
OCTOBER, NOVEMBER, AND DECEMBER 1957
METALLURGY DIVISION

ABSTRACT

Advanced Water Reactor Program - Activity 4102

Investigations have been started on possible urania-ceramic fuels with magnesia, alumina, zirconia, magnesia-zirconia and calcia-zirconia. Mixtures of 45 magnesia-45 zirconia and 9 magnesia-81 zirconia by weight appeared to give good preliminary promise.

Work on ThO_2 -10 w/o UO_2 has centered about improvement in density of pellets and elimination of cracking and open porosity. These problems have been met by longer milling time and the use of finer and better distributed shellac in place of Ethocel grain as a bakeout material.

Efforts to increase the percentage of urania in thorium-uranium have met with considerable success up to 70 w/o urania in air-firing tests. A rate oxidation study of thorium-uranium solid solutions has been initiated; samples of fused oxide of theoretical density are to be prepared at Plasmatron Corporation.

Some attempts have been made to prepare UC by reaction of UO_2 with carbon, but so far an incomplete reaction has resulted.

As to metal fuels, a sample of U-3 w/o Ti-1.5 w/o Nb has shown good corrosion resistance in 245°C water, slightly better than the EBWR fuel alloy.

Fast Power Breeder Program - Activity 4104

Installation of process equipment in the Fuel Fabrication Facility (Facility 350) is proceeding after the granting of funds for six contracts to low bidders. Expiration dates call for a completion in early calendar 1959.

An improvement of the average yield of EBR-II-type fuel pin injection castings has been attained, reaching over 90% as compared with yields of 50 to 60% in the recent past. An increase in furnace capacity which will allow simultaneous casting of 120 fuel pins has been provided. Prototype equipment items for casting, demolding, shearing to length, internal flaw detection, diametral and length gauging, weighing, optical inspection, reject chopping and fuel tube loading have been designed and are under construction.

The uranium-plutonium-fissium alloys proposed for the fuel of EBR-II are being given further examination. Trials at injection casting have shown best conditions to be 1200°C melt temperature, 600°C mold temperature, and 7 psi helium pressure. In thermal cycling 200 times in sodium to 500°C, weight changes averaged less than 1/2%, length increases about 1%, and density decreases about 1%. The thermal conductivity of U-20 w/o Pu-10 w/o Fs alloy was determined at 0.053 (cal/sec-cm-°C) at 600°C and thermal expansion at about $16.7 \cdot 10^{-6}$ per °C in the range 20° - 510°C.

Reactor Systems Research and Development - Activity 4203/4253

A calibration test of the ultrasonic inspection technique was made on known defect Croloy tubing to check its effectiveness in the examination of fuel jacketing material. Satisfactory resolution was obtained and results were checked metallographically. Development is continuing on a beta ray method for measuring clad thickness and on the scintillation counting method of measuring uranium content of fuel plates. An improved design of probe coil for eddy current measurement of cladding thickness has made possible the use of pulse signals instead of the sinusoidal type. More information can be sent on the pulse type signal.

Dynamic tests in a new loop are being employed to check the hypothesis that cathodic ions from the loop construction material have been responsible for unusual effects of velocity in the corrosion of aluminum. Powder compacts of aluminum alloy M388 containing an inhibitor have shown disappointing results and it is believed the inhibitor gradually washed away to an ineffectual level. A new high temperature steam corrosion facility will be operating shortly. Corrosion inhibition of magnesium by fluorides is being studied. Parallel to this effort is one to develop alloys which will improve the corrosion resistance of the base metal; to date some promise is shown by aluminum additions in the presence of other alloying elements.

Specimens of graphite-1 w/o U_3O_8 fired at 950°C have been made for density and porosity measurements. The bulk density was determined at 1.53 g/cc for a sample with porosity of 21.2 v/o.

Argonne Low Power Reactor - Activity 4602

An ultrasonic evaluation of the bond quality of 197 fuel elements for ALPR showed only 8 free of defects. A common defect was edge bond separation.

Production, Treatment and Properties of Materials - Activity 5410

Dilatation curves have been obtained for single crystals of uranium in two crystallographic directions, [001] and [010], according to the technique described in ANL-5790. The data for the [001] direction agree well with

those reported for that direction in another crystal (ANL-5797). The data for the $[010]$ direction fall somewhat below those reported for two other crystals in ANL-5790.

Compressive tests have been made at 600°C on an uranium single crystal. An analysis made from X-ray back-reflection diagrams shows the slip planes to be $\{021\}$ and the slip direction to be quite close to the $[\bar{1}12]$. Since the $\{021\}$ planes have denser packing directions, the reason for the $[\bar{1}12]$ is not clear. The densest direction $[100]$, being perpendicular to the direction of compression, was inoperative in this test.

Results of the investigation of recrystallization of heavily cold rolled alpha uranium sheet have shown that three recrystallized preferred orientations can be obtained, depending on the annealing temperature, whether it is (1) below 360°C , (2) $400^{\circ} - 600^{\circ}\text{C}$, or (3) near 650°C .

The beta-gamma transformation in high purity uranium has been determined at $774.8 \pm 1.6^{\circ}\text{C}$, following the alpha-beta determination reported in ANL-5717. A higher than expected transformation temperature for an uranium-carbon alloy containing 325 ppm C has been attributed to the very low rate of precipitation of small amounts of UC from gamma uranium. It is therefore considered that the temperature previously reported in ANL-5790 (771.6°C) with an alloy of 1730 ppm C is more nearly correct.

Phase diagram work continues on uranium systems with individual fission elements: Ruthenium, rhodium, ruthenium-molybdenum, and others. Density, thermal expansion and thermal arrest data of 3 to 10 w/o fission in uranium have been obtained, with densities ranging from 18.4 down to 17.5 grams/cc, and thermal expansions of the order of 14 microinches per inch per $^{\circ}\text{C}$.

Neutron and X-ray diffraction intensities for UN have been measured and compared with calculated values, which confirm the NaCl-type structure for this material.

The fused salt electrolysis cell for the production of high purity plutonium has been completed and a trial run using uranium has been made. The analysis of the product was satisfactory except for high manganese and aluminum content.

A study of a Zr-24 w/o Pu alloy has shown the existence of a two-phase structure, one of the phases being alpha zirconium.

Corrosion work on the titanium-zirconium alloy system is directed at present on explaining the differences in the behavior of these alloys in water and in dry oxygen. The electrical resistance of corrosion films of alloys with increasing ratios of titanium to zirconium has shown a continually decreasing resistivity both in oxygen at 500°C and in water at 350°C .

In the determination of solution potentials of aluminum at 100°C, effort has continued on obtaining reproducibility of potential as a function of polarizing current.

Alloy Theory and the Nature of Solids - Activity 5420

The first phase of the study of the Ti_2Ni -type phase in zirconium and hafnium has been completed. Important features of this phase type are (1) the requirement of oxygen for stability, (2) incomplete stoichiometry, and (3) increasing lattice parameter with increasing B element radius.

In the low temperature magnetic laboratory, the calibration of the circuit containing the induction coil and ballistic galvanometer was continued after an interruption occasioned by the failure of a cryostat component.

I. ADVANCED WATER REACTOR PROGRAM - ACTIVITY 4102

1. Development of Ceramic Fuel Elements

a. Refractories for Reactor Use (J. H. Handwerk)

Preliminary investigations of several oxide systems were started with the view of developing refractory compositions which would be useful as high temperature ceramic fuels. Various compositions of the following systems were investigated: UO_2 - MgO , UO_2 - Al_2O_3 , UO_2 - ZrO_2 , UO_2 - MgO - ZrO_2 , and UO_2 - CaO - ZrO_2 . 10 w/o UO_2 (added as U_3O_8) was mixed with 90 w/o of either MgO , Al_2O_3 or unstabilized ZrO_2 . The mixtures were cold pressed into pellets and sintered in air at 1450°C . The MgO and Al_2O_3 mixtures appeared to form good bodies. However, there appeared to be some loss of urania from the alumina body, as evidenced by discoloration in the refractory boats that contained the pellets during sintering. The discoloration was not noticeable on the containers used in sintering the magnesia pellets. The UO_2 - ZrO_2 body developed several small cracks during sintering, which might be due to the expansion of the unstabilized ZrO_2 .

One of the MgO - UO_2 pellets was corrosion tested in 150°C water overnight; the pellet disintegrated.

Mixtures of UO_2 -45 w/o MgO -45 w/o ZrO_2 and UO_2 -9 w/o MgO -81 w/o ZrO_2 were cold pressed into pellets and sintered in air at 1450°C . These compositions formed good bodies and were free from visible defects. This suggests that MgO will stabilize ZrO_2 in compositions of this type.

b. Thoria-Urania Ceramic Bodies (P. D. Shalek, J. H. Handwerk)

Information obtained during processing an initial batch (Batch I) of closed porosity specimens, which had a base body of 90 w/o ThO_2 -10 w/o UO_2 as U_3O_8 with added 0.5 w/o CaF_2 , indicated three main problems in this project:

1. A more readily sinterable base body, that is, one containing no pore-forming grain, had to be obtained. The highest densities obtained in the initial base bodies were about 90% of theoretical, whereas densities of 95 - 96% of theoretical were needed.
2. The cracking encountered during grain bakeout had to be eliminated since even very small cracks would not heal during sintering.
3. The open porosity of the more porous specimens had to be considerably cut down or eliminated, if possible. Although

closed porosities of up to 17 v/o were obtained, there was usually an accompanying 2 - 4 v/o of open porosity.

A series of trials on two recently prepared batches have led to an almost complete solution of these problems.

Batch II: The base body was 90 w/o ThO_2 -10 w/o UO_2 as U_3O_8 with added 2 w/o CaF_2 and 4 w/o carbowax 4000 in H_2O solution in the mill as a pressing binder. In order to increase the sinterability of this body three steps were taken:

1. CaF_2 was increased from 0.5 to 2.0 w/o and screened to -325M before adding to the mill to increase its mineralizing action.
2. The U_3O_8 and ThO_2 were screened to -200M; milling time, as for Batch I, was 3 hours.
3. The pellets were formed by preforming at 5000 psi in a 1/4" die followed by isostatic pressing at 55,000 psi. Batch I pellets had been die-pressed at 10 - 40,000 psi.

The pellets, air-fired to 1750°C for 10 hours, showed a slight improvement in density (92% of theoretical). Since this was still short of the goal and, in addition, the fired pellets showed cracking at the point of contact with the boat, further changes were indicated.

In order to eliminate cracking during bakeout, the character of the pore-forming grain was changed. Since Ethocel grain was found to flow under pressure, only shellac grain was used. The grain size of the shellac was reduced to the -140 +170M and -170 +200M size ranges since the elastic deformation of larger grains under pressure was believed to have caused the cracking of Batch I pellets. A few pellets containing grain in the -200 +325M and -325M ranges were also made. Regardless of how carefully the burnout cycle was controlled, the pellets containing -140 +170M and -170 +200M grain invariably started cracking when burnout greater than 83% was reached. One pellet containing -325M grain achieved complete burnout in a rapid cycle without cracking. None of the porous pellets was fired since the base body was unsatisfactory.

Batch III: The base body was 90 w/o ThO_2 -10 w/o UO_2 as U_3O_8 with added 1 w/o CaF_2 and 3% carbowax. Millings of 1, 2, and 3 days were employed to reduce the particle size and improve the size distribution of the body materials. Pellets from all three mills, isostatically pressed at 55,000 psi, sintered to 95 - 96% of theoretical density, with zero open porosity, on air-firing to 1750°C for 10 hours. Longer milling thus solved the first problem.

Pellets were then pressed isostatically at 55,000 psi with 10 v/o of -200 +325M, -200 +400M, -325M and -400M shellac grain and -200 +325M, -200M and -400M Ethocel grain. These pellets were given accelerated 24-hour bakeout cycles, and 90% bakeout was achieved with no cracking. Finer bakeout material in conjunction with finer and improved distribution of the body material solved the second problem.

The above pellets were fired along with base body pellets to 1750°C for 10 hours. The pellets containing Ethocel grain gave disappointing results but the pellets containing shellac grain gave good results as shown below:

<u>Size of Grain</u>	<u>Amt. Added (v/o)</u>	<u>Closed Porosity (v/o)</u>	<u>Open Porosity (v/o)</u>
None (Base Body)	0	4.1	0
-200 +325M	10	9.0	0.5
-325 +400M	10	9.5	0.8
-325M	10	8.9	2.0
-400M	10	8.8	1.1

The -200 +400M size range of grain was best. When -400M grain is introduced, the pore structure appears to open considerably. With added grain up to about 20 v/o a closed porosity range from 4 to 15 v/o should be obtained, with accompanying open porosity grading from 0 to no greater than 1 v/o. A more carefully controlled bakeout cycle plus a slightly more severe firing cycle will be employed in the future.

Enriched pellets for irradiation studies are now being prepared, using the successful procedures developed in the Batch III preparation.

c. Properties of Thoria-Urania Bodies (C. L. Hoenig, J. H. Handwerk)

Increased Urania Compositions: Past research has indicated an upper compositional limit of 30 mole percent UO_2 in UO_2 - ThO_2 bodies that could be fired in air without appreciable cracking. It appeared desirable to attempt to extend this limit to above 50 mole percent.

Several investigators have reported that a cubic fluorite structure is retained in UO_2 - ThO_2 solid solutions fired in air for UO_2 percentages greater than 50 w/o; some place the upper limit at 78%, others at 56%. With percentages greater than these an orthorhombic phase change occurs, and such a phase change would disrupt and crack a body on air-firing.

If, however, the cubic fluorite structures were maintained once a solid solution had been formed, it should be possible to extend the percentage of UO_2 in UO_2 - ThO_2 solid solutions beyond the 30 mole percent limit. The experiments described below were carried out to test this possibility.

1. Two solid solution compositions, 70 w/o UO_2 -30 w/o ThO_2 and 50 w/o UO_2 -50 w/o ThO_2 , have been fired in air (gas and electric kiln) to temperatures from 1400° - 1500°C from 4 to 12 hours with no cracking.

2. Draw trials were conducted at 100° intervals from 1000° to 1500°C in an electric furnace. An X-ray analysis showed an orthorhombic phase to exist after 3 hours at 1200°C but to have disappeared after 3 hours at 1300°C . Bulk density measurements showed that a major portion of the sintering took place from 1200° to 1300°C , the measured bulk density at 1200°C being 5.73 grams/cc and at 1300°C , 8.48 grams/cc.

3. Firing shrinkage data on $1/4$ " pellets of a 70 w/o UO_2 -30 w/o ThO_2 body which was wet-milled for 3 days, calcined at 600°C (this step later found unnecessary), water slurried with 3% carbowax, pressed at 20,000 psi, and fired in gas furnace from 1400° - 1500°C for 17- $1/2$ hours were:

Diametrical shrinkage - 21.74%
Longitudinal shrinkage - 23.50%

4. Solid solution compositions ranging from 30 to 70 w/o UO_2 (added as U_3O_8) were fired in H_2 at 1800°C for a week. X-ray analysis showed evidence of incomplete solid solution. These pellets when reheated at 600°C pulverized completely. Others reheated at 300°C overnight showed no change, but disintegrated after 72 hours at 400°C . In contrast, air-fired solid solutions of the same uranium to thorium ratios showed no dimensional change on reheating to 600°C for 72 hours. A chemical analysis of the hydrogen-fired samples before and after reheating showed that the O/U ratio was very near 2.00 after the hydrogen firing but had increased to 2.48, 2.37, and 2.22 for the 70 w/o UO_2 -30 w/o ThO_2 , 50 w/o UO_2 -50 w/o ThO_2 , and 30 w/o UO_2 -70 w/o ThO_2 , in that order. This indicates that air-fired solid solutions are in an oxidized state, with an O/U ratio between 2.2 and 2.4, and that they resist further oxidation on reheating.

5. The fired bulk density increased with increasing UO_2 . For compositions wet-milled for 3 days, calcined at 600°C , pressed into $3/4$ " pellets isostatically at 40,000 psi, and fired in an electric furnace to 1500°C for 4 hours, the following composition vs. density relationships were obtained (bulk densities):

70 w/o UO_2 -30 w/o ThO_2 : 9.81 grams/cc
50 w/o UO_2 -50 w/o ThO_2 : 8.69 grams/cc
30 w/o UO_2 -70 w/o ThO_2 : 8.35 grams/cc

Rate Oxidation Study of UO_2 - ThO_2 Solid Solutions: A Pyrex-cement-Morganite seal has been developed. This seal and the Morganite tube hold a fore-pump vacuum of 15 microns Hg when the farthest 6" of the tube are heated in a gas kiln to 1750°C . Under these conditions the seal temperature never rises above 40°C . Room temperature air can be quickly admitted to the system at 1750°C and there are no adverse effects on the Morganite tube.

It has been decided that the best sample to use for study of the oxidation of UO_2 - ThO_2 solid solutions is a fused oxide of theoretical density. The following steps have been taken to prepare such samples:

1. Pellets were induction heated in a graphite susceptor to approximately 2500°C . Many specimens showed carbide formation, but in no case did melting occur, nor was theoretical density attained.

2. A vertical graphite arc furnace was unsuccessful because of carbide formation and unstable arc conditions.

3. A 3-phase alternating arc operating in a "Y" type hookup with the ceramic specimen at the center did not work. The electric arc did not rotate from one electrode pair to the next to heat the specimen uniformly on all sides; it arced erratically from one pair to the next. Also, the heat loss from the specimen was too great to permit melting to be initiated.

4. Plasmatron Corporation, Santa Ana, California, has offered to fuse some of our specimens into dense chunks large enough to yield a machined pellet $1\frac{1}{4}" \times 3\frac{3}{4}"$ long and weighing approximately 3 grams. This is being pursued further.

5. Another approach that is being investigated is to dissolve uranyl nitrate and thorium nitrate in water, digest to dryness, calcine at 600°C to drive off the nitric oxide and to form a finely divided homogeneous oxide solid solution. This will then be isostatically pressed into pellets as starting material for fusion in the Plasmatron.

d. Uranium Carbide (R. C. Lied, J. H. Handwerk)

Apparatus has been set up for making UC by reaction of uranium oxide with carbon. Several test firings have been made in vacuum using graphite susceptors. Uranium carbide has been produced by reaction with graphite between 1600° and 1800°C ; however, the carbide is contaminated with UO_2 . Further tests are under way in an effort to produce pure UC.

A reaction chamber has also been set up to prepare UC by reaction of uranium metal with organic gases.

2. Corrosion-Resistant Uranium Alloys (S. Greenberg, G. Dragel)

It has been previously reported that titanium improved the corrosion resistance of uranium considerably. An alloy containing 3 w/o Ti and 1.5 w/o Nb was prepared by arc melting and quenching from 900°C. It has been tested in water at various temperatures up to 260°C. Its behavior has been excellent up through 245°C; samples cracked after extended testing at 260°C. Preliminary work shows slightly better corrosion behavior than the U-5 w/o Zr + 1.5 w/o Nb alloy (EBWR fuel).

II. FAST POWER BREEDER REACTOR PROGRAM - ACTIVITY 4104

1. EBR-II Fuel Fabrication (A. B. Shuck, R. M. Mayfield, J. E. Ayer, F. L. Yaggee, H. F. Jelinek, G. Pokorny)

a. Process Equipment for Facility 350

The preassembly of mechanical feeding devices for rolling mills (PF-11 and PF-19) was started during the quarter for the purpose of coordinated testing of the mill stands (supplied by the Stanat Manufacturing Company), of electrical equipment (supplied by Westinghouse Electric Company), of the control consoles and relay stations constructed by the group, and of mechanical feeding and tensioning devices constructed in ANL shops. Considerable rewiring and circuit additions to the electrical equipment were found necessary. These were worked out with the co-operation of the electrical supplier. Final testing of Rolling Mill PF-19 was held up pending shop completion of the lower feed roll assembly.

b. Installation and Hooding of Process Equipment for Facility 350

Approval and funds were granted for awarding contracts to the six low bidders for the installation, hooding, and services for the process equipment for Facility 350. The effective contract dates and duration are as indicated below.

<u>Subcontracts</u>				
<u>Part</u>	<u>Work</u>	<u>Subcontractor</u>	<u>Effective Date 1957</u>	<u>Duration (Months)</u>
II-A	Hood Fabrication	Nucledyne Corp.	August 13	9
II-B	Erection of Hoods and Equipment	Midwest Machinery Movers, Inc.	September 23	15
II-C	Process Piping	Northwestern Heating and Plumbing Co.	November 15	15
II-D	Ventilation and Controls	Bloomer Heating and Ventilating Co.	November 14	15
II-E	Electrical	Hyre Electric Co.	November 14	15
II-G	Painting	W. R. Simmer Co.	August 16	17-1/2

The delivery of the first hoods was delayed by the failure of the extruded stock to meet dimensional and surface finish specifications and by additional time required for development of satisfactory weld techniques by the fabricator. These difficulties appear to have been resolved and the first hood delivery is scheduled for early February, 1958. This represents a delay of about 3 weeks in the contract schedule for other subcontractors. An effort will be made to make up this time during the course of the contracts.

c. Development of Methods for Remote Fabrication of EBR-II Type Fuel Elements

The objectives of this program are as follows:

1. To develop methods suitable for the remote controlled fabrication of cylindrical shapes measuring $0.144" \pm 0.001"$ diameter x 14.22" long from pyrometallurgically processed billets of fuel alloy containing an equilibrium residual of approximately 7.5 w/o fission elements.
2. To design and construct suitable equipment to fabricate and inspect the cylindrical fuel pieces and to load them into the jacketing tubes.
3. To test the performance of such equipment under simulated remote control conditions.

A technique for precision casting the "fissium alloy" into inverted, refractory coated, high silica glass molds was developed.

Experimental Work: During the quarter, a total of approximately 1000 fuel pins was cast. Each pin was inspected to determine length, conformance to diametral tolerance, internal porosity and surface conditions, and each lot was analyzed. Yield of acceptable pins has improved from 50 or 60% to over 90%. Approximately one-half of the rejects have been due to failure to cast to full length; the others were due to internal porosity or surface conditions.

Total yield of metal in castings to metal charged is low, largely because the prototype furnace produces only about 20 castings per melt from which only about 1400 grams of pins can be finished. The skull remaining in the crucible varies from 400 to 600 grams. Approximately 200 grams of cropped ends must be returned for remelting. An effort to improve the process yield will be made by use of a larger furnace to allow more pins to be cast per melt, improving the casting weight to skull weight ratio, and by investigating the possibility of casting more closely to length.

Full Scale Furnace Development: A second furnace has been constructed which will allow 120 or more pins to be cast at a time. This furnace embodies most of the design features now believed required for remote process cell operation. All organic seals which would be radiation damaged have been eliminated, substituting bellows seals, fusible metallic seals, and malleable metal seals. Water-cooling has been eliminated. Furnace components have been designed for manipulator replacement as single motion "plug in" assemblies. The major components of this furnace were delivered late in December. Work is in progress on completion of the internal parts, on tests on the uncooled furnace coils, and on the various seals and operational parts.

Crucible Development: A crucible resistant to erosion by the fission alloys and to mechanical and thermal shock is needed for in-process-cell use. High thermal conductivity and susceptibility to induced heating are also desired. Graphite possesses the required properties except that it is attacked by the fission alloy. Various coatings and washes on graphite have been tried. The latest of these coatings is a mixture of 50% zirconia and 50% thoria applied by flame spraying. The coating is extremely hard and firmly fixed on the surface of the crucible. Suitability of this coating for repeated use is under test.

Production of Metallurgical Test Specimens: A series of five fission alloy compositions were premelted and injection cast to yield 8 pins of each composition for metallurgical property studies, metallography, and for analytical and spectrographic analysis standards. The assumption was made that zirconium would not be removed in the pyrometallurgical processing. The percentage of each alloying element was held in the following constant proportions, while the percentage of uranium was varied:

<u>Element</u>	<u>Weight Percent of Total Residual Fission Elements</u>
Zirconium	34.5
Molybdenum	32.7
Ruthenium	26.5
Rhodium	3.8
Palladium	2.5

There is an indication that the inclusion of zirconium induces a degree of brittleness not observed with similar alloys not containing zirconium. This brittleness caused difficulty in shearing pins from the 8, 10, and 15 w/o fission alloy compositions.

Production of Enriched Fission Alloy Pins: Approximately 110 of the proposed 130 fission alloy irradiation specimens have been cast in 10 and 20% U^{235} enrichment. Included are 5, 7.5, 10, and 15 w/o fission

alloys of the high zirconium composition. Those yet to be cast are low Zr-5 w/o F's compositions of the two enrichments.

Design of Equipment: Prototype and test equipment for casting, demolding, shearing to length, internal flaw detection, diametral and length gauging, weighing, optical inspection, reject chopping, and fuel tube loading have been designed. Prototype equipment is under construction in ANL Central Shops and on purchase contract.

It is assumed that the simulated condition test of this equipment will necessitate major changes in its construction. It was not necessary, therefore, to include all of the special radiation resistant components on this prototype equipment, which will be used for mock-up testing and perhaps for the first fuel loading.

Design of the in-cell equipment will begin during the next quarter.

2. Uranium-Fissium-Plutonium Alloys

a. Casting of Uranium-Plutonium-Fissium Alloys (O. L. Kruger)

Uranium-plutonium-fissium alloys were injection cast in the Vycor tube furnace described in ANL-5717. The alloys, casting temperatures, mold temperatures, and some of the casting defects are listed in Table I. The charge was melted in a graphite crucible which had been coated with a mixture of 30 v/o thoria in magnesium zirconate. The Vycor tube mold (15-1/2" long by 0.145" I.D.) was coated with a mixture of 30 v/o thoria in aquadag. The mold was heated by a graphite sleeve to approximately 600°C at the top. When the rods were cast, the furnace vacuum was about 1×10^{-4} mm mercury. Helium at a pressure of 7 psi filled the furnace in 4 seconds and forced the metal into the mold.

The best castings were obtained under the following conditions:

1. Melt temperature about 1150° to 1250°C.
2. Temperature approximately 600°C at the top of the mold.
3. Helium pressure of 7 psi.

The first castings contained a number of cold shuts and blowholes. An increase in the melt temperature to 1340°C did not help because the Vycor mold collapsed. By raising the temperature of the top of the mold from 500° to 600°C, cold shuts were eliminated and blowholes were concentrated in the top 2" of the casting.

TABLE I.

Casting Data for Uranium-Plutonium-Fissium Alloys.

Composition	Melt Temp. (°C)	Estimated Temp. at Top of Mold(°C)	Attack on Crucible Wash			Length of Rod	Observations
			Slight	Moderate	Severe		
U-10 w/o Pu-10 w/o Fs	1160	500	X			15-5/8"	5" of casting had severe cold shuts.
U-20 w/o Pu-10 w/o Fs	1340	550			X	The mold did not fill; it was bent and fused at the bottom.	
U-20 w/o Pu-10 w/o Fs	1230	525			X	14-3/4"	Cold shut 1" from top; wash burned into surface on lower 4-1/2" of the casting.
U-20 w/o Pu-10 w/o Fs	1230	525			X	Blowholes thruout rod.	Blowholes probably due to wash in the melt.
U-20 w/o Pu-10 w/o Fs	1160	500			X	15-3/16"	Top 5" of casting has severe cold shuts.
U-20 w/o Pu-10 w/o Fs	1200	600*			X	15-5/8"	Rod broke on cleaning; suspect carbon or contamination.
U-20 w/o Pu-10 w/o Fs	1190	600*			X	15-5/8"	Blowholes in top 1-1/4" of casting; excellent surface.
U-25 w/o Pu-10 w/o Fs	1140	600*			X	15-5/8"	Blowholes in top 1" of casting; excellent surface.
U-20 w/o Pu-15 w/o Fs	1180	600*		X		15-5/8"	Blowholes in top 1-3/8" of casting; excellent surface.
U-20 w/o Pu-15 w/o Fs	1200	600*		X		15-5/8"	Slight cold shut 2-1/2" from top; blowholes in top 1/2"; excellent surface.

*A 3" graphite sleeve was added to increase the temperature of the top of the mold.

b. Thermal Cycling of Plutonium Alloy Pins (H. V. Rhude)

Sixteen plutonium alloy pins (Table II) were thermally cycled 200 times in sodium between 50° and 500°C. The weight changes varied from -0.48 to +0.04%, the length changes from +0.05 to +1.72%, and the density changes of 13 pins from -0.03 to -1.50% (the densities of three remaining pins were not measured after cycling). The data are listed in Table III.

The various alloys were prepared by induction melting in vacuo, using a thoria crucible, and top-pouring into a graphite mold. The mold was designed to yield an extrusion billet and three pins in one casting.

The eight as-cast pins were machined to size on a jeweler's lathe. After the initial measurements, the eight pins were loaded into a bundle of eight molybdenum tubes. The molybdenum tubes were beveled at each end, had an O.D. of 0.187", an I.D. of 0.159", and were 1-1/4" long. The over-all annulus around the pins was 0.009". The tubes were closed by a perforated molybdenum plate at each end of the bundle to prevent the specimens from contacting the stainless steel. The bundle was inserted into a stainless steel capsule which was filled with sodium under a helium atmosphere. The capsule closure was welded in a helium atmosphere. The capsule was taken out of the helium glovebox, placed in a second stainless steel container which in turn was filled with NaK, and thermally cycled.

Only four of the alloys listed in Table II were extruded. The uranium-plutonium alloys had partially disintegrated after having been stored in the helium glovebox for several weeks, and therefore were not extruded. The thorium-plutonium alloys galled in the extrusion die and had to be rejected. The remaining four alloys were extruded bare in a heated die between 390° and 590°C at a reduction of 7 to 1. The extruded pins were machined, measured, encapsulated, and thermally cycled in the same manner as the as-cast pins.

Only one pin, 126A1, was attacked by molten sodium; the attack was slight. Pin 121A was badly warped and showed some surface bumping, pin 125A was slightly warped, and pin 126A was badly warped. The remaining pins had no discernible warp. Pin 123D3 developed a small pimple.

TABLE II.

Properties of Specimens Before Thermal Cycling Test.

Pin No.	Nominal Compositions (w/o)	Condition	Weight (gm)	Density (gm/cc)	Dimensions		Hardness (R _A)
					Length (in)	Diameter Range (in)	
121A	90 U-10 Pu	As Cast	4.1649	18.812	0.8598	0.1412-0.1422	59.2-64.0
122A	75 U-20 Pu-5 Mo	As Cast	4.3230	17.945	0.9406	0.1407-0.1420	73.0-74.5 ^(a)
123A	74.6 U-20 Pu-5.4 Fs	As Cast	2.8594	17.590	0.6604	0.1388-0.1390	73.0-79.5 ^(a)
124A	69.2 U-20 Pu-10.8 Fs	As Cast	3.7191	16.537	0.8849	0.1403-0.1422	74.2-77.0 ^(a)
125A	71 U-20 Pu-5.4 Fs-3.6 Mo	As Cast	3.7576	17.088	0.8535	0.1416-0.1420	65.0-70.0 ^(a)
126A	80 U-20 Pu	As Cast	3.4112	18.636	0.7117	0.1425-0.1433	64.0-65.2 ^(a)
127A	95 Th-5 Pu	As Cast	2.5326	11.644	0.8576	0.1413-0.1433	-
128A	90 Th-10 Pu	As Cast	2.5589	11.858	0.8510	0.1413-0.1436	-
122D2	75 U-20 Pu-5 Mo	As Extruded	4.4886	18.004	0.9852	0.1400-0.1417	77.3-79.8
122D3	75 U-20 Pu-5 Mo	As Extruded	4.4705	17.966	0.9873	0.1404-0.1404	80.0-81.9
123C1	74.6 U-20 Pu-5.4 Fs	As Extruded	4.3514	17.677	0.9952	0.1378-0.1412	68.1-71.2
123C2	74.6 U-20 Pu-5.4 Fs	As Extruded	4.5130	17.657	1.0002	0.1408-0.1415	68.8-71.1
124C1	69.2 U-20 Pu-10.8 Fs	As Extruded	4.1200	16.901	0.9847	0.1396-0.1411	71.8-74.1
124C2	69.2 U-20 Pu-10.8 Fs	As Extruded	4.1989	16.902	0.9888	0.1400-0.1413	74.0-75.0
125C1	71 U-20 Pu-5.4 Fs-3.6 Mo	As Extruded	4.3574	17.188	0.9989	0.1396-0.1413	70.0-71.2
125C2	71 U-20 Pu-5.4 Fs-3.6 Mo	As Extruded	4.2757	17.222	0.9851	0.1389-0.1414	72.2-74.2

(a) Readings made on duplicate as cast pins.

TABLE III.

Properties of Specimens After Thermal Cycling Test.

Pin No.	Weight (gm)	Weight Difference (gm)	Wt. Change (%)	Length (in)	Diameter Range (in)	Length Change (%)	Density (gm/cc)	Density Change (%)
121A	4.1494	-0.0155	-0.37	0.8650	0.1412-0.1435	+0.60	-	-
122A	4.2893	-0.0337	-0.79(a)	0.9426	0.1412-0.1433	+0.21	17.899	-0.26
123A	2.8457	-0.0137	-0.48	(b)	0.1385-0.1412	-	-	-
124A	3.7145	-0.0046	-0.12	0.8855	0.1409-0.1422	+0.07	16.520	-0.10
125A	3.7536	-0.0040	-0.11	0.8576	0.1418-0.1445	+0.48	16.997	-0.54
126A	3.3997	-0.0115	-0.34	0.7240	0.1439-0.1463	+1.72	-	-
127A	2.5336	+0.0010	+0.04	0.8580	0.1405-0.1436	+0.05	11.637	-0.06
128A	2.5552	-0.0037	-0.14	0.8526	0.1405-0.1431	+0.19	11.810	-0.41
122D2	4.4886	0.0000	0.00	0.9893	0.1406-0.1455	+0.42	17.738	-1.50
122D3	4.4698	-0.0007	-0.02	0.9893	0.1408-0.1442(c)	+0.20	17.752	-1.21
123C1	4.3502	-0.0012	-0.03	0.9981	0.1376-0.1428	+0.29	17.567	-0.63
123C2	4.5107	-0.0027	-0.06	1.0039	0.1405-0.1445	+0.40	17.609	-0.03
124C1	4.1210	+0.0010	-0.02	0.9878	0.1407-0.1436	+0.31	16.748	-0.91
124C2	4.1997	+0.0008	-0.02	0.9919	0.1402-0.1446	+0.31	16.764	-0.82
125C1	4.3576	+0.0002	-0.01	1.0015	0.1400-0.1460	+0.26	17.082	-0.62
125C2	4.2757	0.0000	0.00	0.9879	0.1410-0.1438	+0.28	17.079	-0.84

(a) Small piece had broken off.

(b) Pin was dropped and broken in two.

(c) 0.1509" across pimple.

c. Thermal Conductivity of Uranium-20 w/o Plutonium-10 w/o Fissium Alloy (W. H. Livernash)

The thermal conductivity values of a cast U-20 w/o Pu-10 w/o Fs alloy are listed in Table IV and plotted in Figure 1. The data were obtained by a comparison method using Inconel X as the reference material. The maximum error is estimated to be 10%. The specimen (0.250" in diameter and 2.142" long) was machined from the lower part of a 0.290" diameter by 7-3/4" long injection casting. The maximum specimen temperature was 607°C. The specimen was slightly deformed by the longitudinal pressure at temperature, but not enough to ruin the symmetry of the experiment or to cause appreciable errors in calculations. The maximum bow near the center of the specimen was about 0.015". The run was made in a vacuum of about 0.1 microns, and upon completion of the experiment the specimen surface was bright with only a slight discoloration at the hot end.

TABLE IV.

Thermal Conductivity of an Uranium-20
w/o Plutonium- 10 w/o Fissium Alloy

Temperature (°C)	K (cal/sec-cm-°C)
205.6	0.0347 Heating
312.5	0.0387 Heating
432.6	0.0486 Cooling
534.1	0.0537 Cooling
552.6	0.0568 Heating
594.7	0.0530 Heating

FIG 1 THERMAL CONDUCTIVITY OF A 70 w/o URANIUM -
20 w/o PLUTONIUM-10 w/o FISSIUM ALLOY

d. Thermal Expansion of an Injection Cast Uranium-20 w/o Plutonium- 10 w/o Fissium Alloy (O. L. Kruger)

The thermal expansion of an injection cast U-20 w/o Pu-10 w/o Fs alloy was measured by a dial gauge, quartz push-rod dilatometer. A specimen, 1.500" long by 0.120" in diameter, was heated in a vacuum and held at temperature until the reading of the dial gauge remained constant. In Figure 2 the expansion of the specimen in mils/inch is plotted against temperature for the first five cycles. The curves are displaced 2 to 4 mils to prevent overlapping. Each cycle starts at zero on its expansion scale.

A sharp break in the heating curve occurred on the first cycle at 508°C. The transformation took about 100 minutes, and the specimen contracted 0.6 mils/inch. This contraction did not occur on successive cycles, and it might have been caused by the transformation of a metastable phase, quenched-in during casting. In the region of 550° to 600°C the expansion curves changed in slope which indicated that a transformation occurred. Above 600°C, the slope of the curves was constant. When cooled, the specimen contracted and did not follow the heating curve. Holding the specimen at temperatures between 500° and 550°C resulted in a sharp break on the cooling curves. This transformation took approximately 100 minutes and the specimen contracted about 1 mil/inch. On the fourth cycle the specimen was held at 520° and 508°C on cooling. On the fifth cycle the specimen was held at 562°C for 20 minutes, but the transformation did not take place. When the temperature was lowered to 548°C the transformation started. The temperature was then lowered to 535°C and held while the specimen transformed. The transformation seemed to be time-temperature dependent and was more rapid at the lower temperatures.

The coefficients of expansion calculated from the heating curves before and after the transformation are listed in Table V. After the first cycle the average coefficient of expansion was 16.7×10^{-6} per °C from 20° to 510°C and 18.8×10^{-6} per °C from 200° to 500°C. Above 610°C, however, the coefficient of expansion increases with successive cycles.

A test was made to determine the effect of the dial gauge pressure on the specimen length at various temperatures. The results are shown in Figure 3. The dial gauge pressure was determined to be 15 psi. Under this pressure an increase in temperature above 735°C resulted in compression of the specimen. The amount of compression increased rapidly at temperatures above 809°C.

FIGURE 2
 SUCCESSIVE THERMAL EXPANSION CURVES OF AN INJECTION CAST
 70 W/O URANIUM-20 W/O PLUTONIUM-10 W/O FISSION ALLOY

TABLE V.

Coefficients of Expansion of U-20 w/o Pu-10 w/o Fs
Calculated from the Heating Curves (per °C).

Cycle	20° - 510°C	200° - 510°C	610° - 710°C
1	14.9×10^{-6}	15.6×10^{-6}	17.2×10^{-6}
2	16.8	18.5	19.9
3	16.9	19.4	20.1
4	16.6	18.3	20.8
5	16.7	18.9	21.3

FIG 3 THE COMPRESSION OF AN URANIUM-20 w/o PLUTONIUM-10 w/o FISSION ALLOY
AT VARIOUS TEMPERATURES UNDER A LOAD OF 15 psi

III. REACTOR SYSTEMS RESEARCH AND DEVELOPMENT - ACTIVITY 4203/4253

1. Nondestructive Testing

a. Ultrasonic Testing of Croloy Tubing (W. N. Beck)

An ultrasonic inspection was made of 60 feet of 3/4" Croloy 27-4-1 (Type 329) low nickel seamless tubing. The test was performed by an immersion, two crystal reflection technique. The sensitivity of the test was established by scanning a sample section of tubing provided with various manufactured defects of diversified depths. By this means a resolution was determined for defects equivalent to 2% of the tubing wall thickness. In the 60 feet of tubing, 76 defects were found. A metallographic inspection of defective areas revealed the presence of laps, inclusions, and tears.

b. Beta Back Scanner for Measurement of Cladding Thickness (W. J. McGonnagle, N. P. Lapinski)

Experimentation is continuing on the use of beta ray back scattering for measuring clad thickness. Increased sensitivity, especially in the measurement of aluminum cladding in the range of 0.030" - 0.040", has been achieved by better positioning of source and detector. Improvements have also been made in the electronic circuitry. Variations of 0.001" in cladding have been successfully detected and recorded.

c. Measurement of Uranium Content of Fuel Elements (W. J. McGonnagle, R. B. Perry)

Work is continuing on the nondestructive measurement of uranium content of reactor fuel plates. A 2" sodium iodide scintillator crystal has been substituted for the 1" crystal with an increase in sensitivity. A single scintillation crystal is being used to detect both the 90 Kev and the 180 Kev gamma ray. The effect of geometry of the specimen on the results is being investigated.

d. Eddy Current Instrument Development (R. G. Myers, C. J. Renken)

A probe coil of much better definition than earlier types has been developed. The diameter of this coil is 1/16", and this reduced the area of measurement to about 0.003 square inches. A reduction in the area of measurement improved the present eddy current instruments in two ways: smaller flaws can be detected, or cladding measurements can be made over a smaller integrated area. It is also now possible to test smaller specimens.

A new type of probe called a "coaxial probe" which has two coaxial coils wound on a ferrite cup core has been developed. One coil was wound on the outside of the core. Several experiments have resulted in an optimum design. The advantages of this probe are: much better definition is achieved and coil heating is reduced to a minimum. Changes in ambient temperature are still a problem in some of the better eddy current systems. To minimize this difficulty, experiments for determining the best method for constant temperature have been started.

The development of a new series of eddy current testing instruments has been started. These instruments utilize the coaxial probe described above. There are several advantages in this system: (1) pulsed eddy currents are used instead of sinusoidal eddy currents; more information is carried by the pulses since the pulse amplitude can be much larger than the sinusoidal amplitude with no probe coil heating; (2) the stability of the new type instrument is greatly increased over older instruments; (3) much more difficult testing jobs can be handled with this instrument.

A system for measuring the zirconium cladding on uranium-molybdenum alloy fuel pins was developed. These pins had a nominal cladding thickness of 0.004" and a nominal outside diameter of 0.158". The accuracy of the measurements was within ± 0.0002 ". A dual frequency instrument was used for making the measurement.

2. Corrosion

a. Corrosion-Resistant Aluminum Alloys (W. E. Ruther, D. J. Dorman)

Dynamic Testing at 260°C: Ions of metals cathodic to aluminum are suspected of causing the unusual effects of velocity and surface to volume ratio found in dynamic aluminum corrosion. A dynamic corrosion test was therefore planned to add trace amounts ($\sim 1/2$ ppm) of Ni^{++} , Fe^{++} or Co^{++} to the loop feed solution at a sufficiently low pH to prevent the deposition of these ions as an insoluble basic salt when the temperature was raised. Another corrosion test at the same pH but without the presence of the trace ions would then serve to test the hypothesis.

The pH of a $1/2$ ppm Ni^{++} (NiSO_4) was reduced to a point just sufficient to hold the nickel in solution ($\sim \text{pH } 4$) at 260°C. Unfortunately, when the deliberate addition of nickel to the loop feed water was stopped, it was found that the effluent (no samples in loop) still contained almost as much nickel ion, presumably due to increased loop corrosion. Analysis also showed the presence in the effluent solution of a slightly greater amount of iron.

To survey the field a series of 1-day tests were conducted with Ni^{++} - and Fe^{++} -free feed solutions at different pH levels. The loop effluent concentrations of these ions were measured at a feed rate of 36 ml/minute. The gas concentration was maintained at about 100 cc H_2 /kg H_2O by adjusting the feed tank pressure. The results are shown in Table VI.

TABLE VI

Nickel and Iron Content of Solutions Leaving Loop.

Approximate pH	Actual pH at Room Temp.	Ni^{++} (ppm)	Fe (ppm)
6.0	6.1 (H_2SO_4)	0.01	0.02
5.0	5.2 (H_2SO_4)	0.02	0.01
	5.1 (H_3PO_4)	0.13	0.14
4.5	4.5 (H_2SO_4)	0.06	0.12
	4.6 (H_3PO_4)	0.04	0.04
4.0	3.9 (H_2SO_4)	0.55	0.56
	4.2 (H_3PO_4)	0.16	0.23
	3.8 (H_3PO_4)	1.27	2.20
3.5	3.55 (H_2SO_4)	1.27	2.41
	3.6 (H_3PO_4)	1.80	3.70

The relatively high concentrations obtained for pH 5.1 H_3PO_4 are probably due to nonequilibrium conditions, since the previous run was pH 3.55 H_2SO_4 .

These results were discouraging from two points of view. First, the proposed test of the cathodic ion hypothesis could not be run in this equipment. Second, the relatively high iron concentration in pH 3.5 H_3PO_4 might result from stainless steel corrosion that is rapid enough to rule out the use of this solution for inhibiting aluminum alloy corrosion in stainless steel systems.

To further investigate the corrosion of the stainless steel loop material, a test has been started with stainless steel samples (Types 316 and 347) in pH 3.5 H_3PO_4 . At the end of 2 weeks the weight changes of the samples are very small and thin interference color films are present. So far it appears that the corrosion of stainless steels in this acid is quite slow, and an unusual corrosion phenomenon must be sought to explain the build-up in the loop water.

Powder Metallurgy: As discussed in the last quarterly report, it was hoped that extruded powder compacts of X8001* aluminum containing

*X8001 = M388 = 1100 aluminum + 1% nickel.

corrosion inhibitors might prove superior in strength and corrosion resistance to wrought alloy products. To date, 8 aluminum extrusions have been made. Corrosion testing was done in two steps. First, the extrusion was given a 48-hour test in 350°C water. If the extrusion did not suffer accelerated attack in this exposure, more extensive corrosion testing was performed in 290°C, refreshed water autoclave systems. The results to date are summarized in Table VII.

TABLE VII

Corrosion of Mixed Powder Aluminum Alloy Extrusions.

Extrusion No.	Composition		Corrosion in Water	
			350°C 2 Days	290°C Average Rate from 5 to ~50 Days
1	X8001 Powder 96% AlPO ₄ 4%		Pass	6 mdd*
2	1100 Powder 96% Nicrobraz-10 4%		Fail	-
3	X8001 Powder 96% Bi ₂ O ₃ Powder 4%		Fail	-
4	X8001 Powder 96% SiO ₂ Powder 4%		Pass	5
6	X8001 Powder 96% AlPO ₄ Powder 2% SiO ₂ Powder 2%		Pass	Not finished but similar to Extr. 1
7	X8001 Powder 100%		Pass	4
8	X8001 Powder 96% As ₂ O ₃ Powder 2% AlPO ₄ Powder 2%		Pass	Not finished but similar to Extr. 4
9	X8001 Powder 96% αAl ₂ O ₃ Powder 4%		Pass	Not finished but similar to Extr. 4

*mdd = mg/decimeter²-day.

To date, no extrusion has exhibited improved corrosion resistance over wrought X8001, although the high temperature strength was much improved as indicated by simple loading tests at 350°C. The extrusion corrosion samples gave slightly more scattered data than those of the wrought alloys. The average corrosion rates from 5 to 50 days were in the range of 4 - 6 mdd (wrought X8001 ~3.3 mdd).

It has been noted that the appearance of some of these extrusions after exposure in small nonrefreshed autoclaves is considerably different and generally better than samples exposed to refreshed water. It is now suspected that the inhibitors in the extrusions are washed away and diluted to an ineffectual level in the refreshed autoclaves.

High Temperature Steam Corrosion (S. Greenberg, G. Dragel):

A facility has been set up to expose materials of interest to superheated steam in the vicinity of 540°C and 600 psia. The facility is a static one and suffers from the disadvantages of build-up of corrosion product hydrogen and difficulty in precise control of pressure. A new facility, incorporating constant additions of steam and removal of hydrogen (and allowing for more precise control of pressure) has been designed and will be operating shortly.

Two aluminum-base materials have been tested. Their nominal compositions (w/o) are:

<u>Alloy</u>	<u>Fe</u>	<u>Ni</u>	<u>Ti</u>
A198	-	1.0	0.1
A203	0.28	5.65	0.1

One sample of each alloy was tested in superheated steam at 540°C. Alloy A198 showed signs of internal deterioration after 10.6 days, and had badly swollen after 16.5 days. Alloy A203 was still in test, covered with a thin gray oxide, after 49 days. Weight changes on this sample were quite small, indicating negligible corrosion rate after completion of the first several days of exposure. It appears likely that the higher nickel content and/or the presence of iron is necessary for resistance to superheated steam.

In addition to the sample of A203 described above, other samples of presumably the same composition (different castings) have been tested under the same conditions. Most were not as good as the sample described. Behavior ranged from complete reduction to oxide in one day to blistering in a relatively short time. Studies are now under way to determine the causes for this variation in behavior. It is suspected that titanium concentration may be a key factor.

- b. Magnesium Alloys (S. Greenberg, W. E. Ruther, G. Dragel, D. Dorman)

Fluoride Inhibition: The studies this quarter have been concerned with the rate of fluoride consumption during corrosion of magnesium in dilute fluoride solutions. The objectives have been to learn the nature of the inhibition mechanism and to establish minimum requirements for fluoride concentration. Some progress has been made toward the latter objective.

Samples of alloy AZ31 (3 w/o Al, 1 w/o Zn) (annealed at 260°C) of 11 cm² surface area were tested at 150°C in autoclaves containing 50 cc of solution at an initial concentration of 104 ppm F⁻ (as sodium fluoride). Weights, determined by stripping in boiling 10 w/o Cr₂O₃ solution, and fluoride concentrations were determined periodically. As a control, one autoclave was run for the complete test period with the same initial concentration of fluoride solution but no magnesium, in order to determine the effect of stainless steel on fluoride concentration.

There were approximately equal induction periods before magnesium began to corrode significantly, and before the fluoride ion was depleted. In the absence of magnesium samples a slow but uniform depletion of fluoride was observed.

The corrosion rate of the magnesium alloy is only slightly sensitive to fluoride concentration, except perhaps at very low fluoride concentrations. Once the fluoride is exhausted from solution, the corrosion product produced in its presence no longer exerts an inhibitive effect and the corrosion rate reverts to the normal rate in distilled water, of the order of 14 mg/cm²-day.

Fluoride consumption rates, as derived from this test and the exposed areas of magnesium and stainless steel are as follows:

Magnesium alloy AZ31	32.0 mg F ⁻ /dm ² -day
Stainless steel 304	0.12 mg F ⁻ /dm ² -day.

Concurrently with the test discussed above, another series of tests using alloy AZ31 was run in which a sodium fluoride solution of given composition was fed in at a rate of 8 cc/minute. Based on the statements above and the geometry of the system, a feed concentration of ~2 ppm F⁻ would be required to balance fluoride consumption by magnesium samples and stainless steel system.

Tests were run at feed concentrations of 1, 5, 10, and 50 ppm F⁻. At the beginning of each test, the autoclave was filled with solution of the same composition as the feed solution. The feed rate was such that there were 8.6 changes of autoclave volume per day. As shown in Table VIII, corrosion rates were only slightly sensitive to fluoride concentration. However, there does appear to be a minimum in the vicinity of 10 ppm F⁻.

Induction periods decreased with decreasing fluoride concentration and may be nonexistent at 1 ppm. However, even at this low concentration there was a marked inhibition of corrosion.

TABLE VIII

Corrosion of AZ31 Magnesium in NaF Solution

Fluoride Concentration (ppm)			Constant Corrosion Rate	
Nominal	In	Out	mcd	mils/day
1	1.1	0.7	4.30	1.00
5	5.0	4.3	4.45	1.03
10	10.2	10.0	3.52	0.82
50	49.5	48.0	4.86	1.13

The fact that appreciable induction periods exist, coupled with the rapid exhaustion of fluoride from small closed systems, makes it impossible to obtain true corrosion rates for fluoride solutions in such systems. To obtain such rates, it is obviously necessary to maintain a constant composition and to be in a period of constant rate. Relatively constant composition was maintained in the above tests, as shown in Table VIII.

In spite of acceptable corrosion rates (which, however, are very high), the corrosion product is very voluminous and could introduce serious problems in heat transfer. The appearance of the samples before removal of corrosion product is shown in Figure 4.

Although Figure 4 may be somewhat misleading because of some unavoidable loss of corrosion product during handling, it is a good representation of the scale problem involved. Based on sample appearance, it would appear desirable to use 1 ppm fluoride. At present, another test is under way using 0.1 ppm F^- in order to determine a lower limit of effectiveness.

An attempt to study the nature of fluoride inhibition by means of X-ray diffraction has been started. The corrosion product formed by high purity magnesium at 100°C has been investigated. In distilled water, as expected, hexagonal $Mg(OH)_2$ is produced. However, in water containing 100 ppm F^- (as NaF), a face centered cubic structure (not MgO) is produced. Preliminary results indicate that fluoride consumption at 100°C is much lower than at 150°C.

Alloys: Parallel with the program on inhibitors, an effort is under way to develop magnesium alloys superior to AZ31. A simple and rapid method has been developed for producing 100-gram magnesium alloy castings by induction melting. As a result of screening tests in water at 150°C, considerable progress is being made toward producing a satisfactory alloy. Several conclusions may be tentatively drawn from the results of these tests.

Figure 4. Corrosion of AZ31 at 150°C in Fluoride Solution.

1 ppm F^-

Macro 22755

Days: 2 6 9 14

5 ppm F^-

Macro 22756

Days: 3 5 9 13

10 ppm F^-

Macro 22484

Days: 3 6 10 14

50 ppm F^-

Macro 22485

Days: 3 6 9 14

1. The presence of aluminum in magnesium changes the nature of the corrosion process in such a manner that cathodic alloying elements, e.g., copper or nickel, are beneficial rather than harmful.
2. The presence of zinc is apparently beneficial. However, zinc by itself is not very useful; it may be that increased aluminum is as useful as an equivalent total of aluminum plus zinc.
3. The corrosion rate decreases with increasing aluminum content. However, high aluminum alloys are not readily workable.
4. Copper appears to be superior to nickel as the cathodic additive.
5. Manganese is present in commercial magnesium alloys chiefly to remove cathodic materials such as iron, copper, and nickel. It also serves as a grain refiner. It may be that its presence is useless, or even detrimental from the corrosion viewpoint (150°C water).

It is planned to produce material containing fluoride as a corrosion inhibitor by powder metallurgy techniques. The preferred method is hot extrusion. Preliminary attempts (pending procurement of necessary equipment for extrusion) using hot pressing followed by sintering, did not produce material that was corrosion resistant at 150°C.

3. Graphite-Urania Fuel Elements for the TREAT Reactor (J. H. Handwerk, R. C. Lied)

Graphite-1.0 w/o U_3O_8 pellets were fired to 950°C in graphite crucibles. The bulk density and the uranium oxide dispersion of the fired pieces were considered satisfactory. Based on this experience, right cylinders were fabricated from a mixture of graphite, petroleum pitch, and enriched U_3O_8 . These irradiation samples were made in two sizes: 1" diameter for the Reactor Engineering Division, and 3/8" diameter for the Metallurgy Division. For Reactor Engineering three groups of samples were made with U_3O_8 concentrations of 0.1, 0.3, and 0.6 w/o. Four concentrations were fabricated for Metallurgy: 0.2, 0.4, 0.6, and 1.0 w/o U_3O_8 .

One set of specimens was used for density and porosity measurements. Bulk density is 1.53 grams/cc, apparent density, 1.93 grams/cc. Porosity was found to be 21.2 v/o.

Heat capacities of graphite-urania samples fabricated at ANL were measured along with samples fabricated by outside suppliers. Heat capacities are reported in cal/gram-atom/°C.

Temp. (°C)	Los Alamos	ANL	United Carbon Corporation	Great Lakes
0	1.92	2.10	1.72	1.82
100	1.84	1.84	2.10	1.88
200	2.00	2.04	2.10	1.88
300	2.20	2.04	2.10	2.12

IV. ARGONNE LOW POWER REACTOR - ACTIVITY 4602

1. ALPR Fuel Element Evaluation (W. N. Beck)

An evaluation of the bond characteristics of the Argonne Low Power Reactor type fuel plates was performed ultrasonically. The transmission technique at a frequency of one megacycle was used. Metallographic examination of sample fuel plates identified and established the type of nonbonding which was considered detrimental to the element. With this information, a standard of acceptance was established which was used throughout the test program. A permanent, two-dimensional recording was made of each fuel element.

A total of 197 fuel elements was tested ultrasonically. Of these, 8 elements were found to be free of defects. Thirty-three fuel plates were put into corrosion after ultrasonic inspection. After corrosion they were ultrasonically inspected again. This second test revealed the presence of edge bond separations which were not readily discernible before the corrosion test. These 33 plates were then blister tested and again inspected ultrasonically. The edge bond separation noted on previous testing had increased in area. The plates indicated little appreciable change in bond characteristics after the corrosion and blister tests.

V. PRODUCTION, TREATMENT, AND PROPERTIES OF MATERIALS - ACTIVITY 5410

1. Uranium and Its Alloys

a. Thermal Expansion of Alpha Uranium Single Crystals (L. T. Lloyd)

During the past quarter dilatation curves have been obtained along principal crystallographic directions of two additional alpha uranium pseudo unit cell single crystals. The techniques of specimen preparation and testing are described in ANL-5790.

Crystal T_E was tested for dilatation in the [100] direction. A second crystal, T_C, was tested first in the [001] direction and then in the [010] direction. In each case the dilatation direction was within 0.5° of the principal crystallographic direction, as determined from Laue back-reflection photograms. The original lengths at 25°C for the three directions were 0.1398", 0.1680", and 0.1457", respectively. Consecutive curves were measured for each direction. Table IX and Figures 5 and 6 record the data,

TABLE IX
Expansion of Alpha Uranium in the [010] and [001] Directions^(a)

Temperature (°C)	Expansion in the [010] Direction (inch/inch $\times 10^4$)		Expansion in the [001] Direction (inch/inch $\times 10^4$)	
	Measured from Crystal T _C	Calculated from Equation(b)	Measured from Crystal T _C	Calculated from Equation(b)
50	0.09	0.08	5.91	4.97
75	0.20	0.11	11.05	10.08
100	- 0.13	0.07	17.74	15.29
125	- 0.47	- 0.08	24.06	20.70
150	- 1.24	- 0.34	30.76	26.24
175	- 2.02	- 0.72	37.47	32.01
200	- 3.23	- 1.36	44.18	38.00
225	- 4.89	- 1.96	50.50	44.24
250	- 6.10	- 2.85	58.38	50.74
275	- 7.76	- 3.93	65.87	57.54
300	-10.31	- 5.23	73.37	64.65
325	-12.40	- 6.77	81.64	72.10
350	-14.95	- 8.56	90.31	79.88
375	-17.91	-10.61	98.58	88.05
400	-21.37	-12.96	108.02	96.62
425	-25.25	-15.60	117.46	105.61
450	-29.58	-18.57	126.90	115.01
475	-33.47	-21.87	137.11	124.93
500	-38.24	-25.53	148.81	135.32
525	-42.13	-29.56	159.09	146.22
550	-47.35	-33.98	171.63	157.62
575	-52.59	-38.81	183.78	169.59
600	-58.26	-44.06	196.31	182.14
625	-65.28	-49.75	209.23	195.27
650	-73.20	-55.90	221.76	209.02

(a) Based upon 1" specimen length at 25°C.

(b) The equations for expansion in the [010] and [001] directions, as derived from the data of Bridge, Schwartz and Vaughan, are:

$$[010] - L_T = L_0 \left(1 + 0.61 \times 10^{-6} T - 2.17 \times 10^{-9} T^2 - 18.41 \times 10^{-12} T^3 \right)$$

$$[001] - L_T = L_0 \left(1 + 19.37 \times 10^{-6} T + 5.71 \times 10^{-9} T^2 + 23.26 \times 10^{-12} T^3 \right)$$

where: L = length and T is expressed in °C.

Figure 5. Expansion of Alpha Uranium in the [010] Direction as a Function of Temperature.

Macro 23006

Figure 6. Expansion of Alpha Uranium in the [001] Direction as a Function of Temperature.

Macro 23007

corrected for the expansion of quartz over the specimen length, obtained from the reproducible curves of the [010] and [001] directions of crystal T_C. Data calculated from the equations fitted to the X-ray diffraction lattice parameter measurements as a function of temperature, reported by Bridge, Schwartz and Vaughan,¹ are included for comparison.

Consecutive expansion curves obtained from the [100] direction of crystal T_E were not reproducible. The cause for this behavior became obvious when metallographic observations subsequent to testing revealed recrystallized grains on the sample's surfaces. The data obtained from this crystal have been discarded. Metallographic observations of crystal T_C after both series of dilatation tests indicated that no appreciable changes had occurred in the structure.

The data obtained in the [001] direction of crystal T_C agree well with those reported for crystal T_D tested in the same direction (ANL-5797). Both of these curves lie above the expansion curve calculated from the data of Bridge, Schwartz and Vaughan. The data for the [010] direction of crystal T_C fall somewhat below those reported for crystals T_A and T_B in ANL-5790. These [010] direction expansion curves are, however, consistent in that they all fall below the curve calculated from the X-ray lattice parameter measurement data.

b. Plastic Deformation Mechanisms in Alpha Uranium Single Crystals (L. T. Lloyd)

The deformation mechanisms have been studied in an additional alpha uranium single crystal (D₆) compressed at $600^{\circ} \pm 5^{\circ}\text{C}$. Equipment employed to protect the crystal during testing and to perform the elevated temperature compression is briefly described in ANL-5790.

First Compression Test: Crystal D₆ was oriented for testing in a direction near the [001] direction. The actual compression direction was 89.5° from the [100] direction, 88.0° from the [010] direction, and 2.5° from the [001] direction. Two parallel compression faces and five additional surfaces perpendicular to the compression faces were prepared on the crystal; two of the latter surfaces, inclined at an angle of 119° , were used as metallographic faces. The initial specimen length between compression faces was 3.63 mm.

Prior to testing, a few $\{130\}$ type twins were observed parallel to and lying near the left-hand edge of face A; the rest of the sample did not show evidence of prior straining. After the first compressive deformation of approximately 1%, the metallographic surfaces appeared as shown

¹J. R. Bridge, C. M. Schwartz, and D. A. Vaughan, "X-Ray Diffraction Determination of the Coefficients of Expansion of Alpha-Uranium," Trans. AIME 206, 1282 (1956).

in Figure 7; both faces show slip deformations. The angular location of these with respect to the common edge are given in Table X. Since the crystal was oriented for compression in a direction that excluded, or at least minimized, slip on previously reported systems of $(010) - [100]$,^{2,3} $(001) - [100]$ ² and $\{110\} - \langle 110 \rangle$,³ the operative slip system must be heretofore unidentified. The metallographic observations did not permit positive association of traces 4 or 5 on face B with trace 3 on face A; however, a pole-loci analysis of the three traces yielded a common intersection near the $\{021\}$ plane pole.

Figure 7. Composite Photomicrograph of Crystal D₆ After First Compressive Deformation of Approximately 1% at $600^\circ \pm 5^\circ\text{C}$.

Macro 22979

Polarized Light

33-X

²L. T. Lloyd and H. H. Chiswick, "Deformation Mechanisms of Alpha-Uranium Single Crystals," Trans. AIME 203, 1206-1214 (1955).

³R. W. Cahn, "Plastic Deformation of Alpha-Uranium; Twinning and Slip," Acta Metallurgica 1, 49-70 (1953).

TABLE X

Deformation Traces Observed on Metallographic Faces
of Crystal D₆ Compressed at 600° ± 5°C

Metallographic Face	Trace Number	Angular Location With Respect to Common Edge(a)	Identity	Method of Identification
After First Compression				
A	3	31.5°CC	(0 $\bar{2}$ 1) slip	Pole-Locus Analysis
B	4	43° CC	(0 $\bar{2}$ 1) slip	Pole-Locus Analysis
B	5	40° C	(021) slip	Pole-Locus Analysis
After Second Compression(b)				
A	3	34° CC	(0 $\bar{2}$ 1) slip	Two-surface Analysis
B	4	45° CC	(0 $\bar{2}$ 1) slip	
B	5	40° C	(0 $\bar{2}$ 1) slip	Two-surface Analysis
A	6	31° C	(0 $\bar{2}$ 1) slip	
After Second Compression and Mechanical Repolish				
A	9	27.0°CC	~($\bar{1}\bar{7}2$) twin	Two-surface Analysis
B	12	24.5°CC	~(17 $\bar{2}$) twin	
B	10	8.0°C	~(172) twin	Pole-Locus Analysis
B	11	46° CC	~($\bar{1}\bar{7}\bar{2}$) twin	Pole-Locus Analysis
A	14	6.5°CC	?	-

(a) C designates that the angle was measured clockwise from the common edge and CC designates counterclockwise measurement.

(b) For angular measurements of traces observed on the metallographic faces of the crystal in this condition the common edge was defined as a line perpendicular to the compression faces.

Second Compression Test: After cleaning the crystal by electropolishing, it was subjected to a second compressive test at 600° ± 5°C to increase the quantity of the slip deformation and, thereby, permit association of the slip traces across the common edge formed by the intersection of the two metallographic faces. By making the deformation relatively large it was hoped that some conclusion could be drawn as to the identity of the slip direction. Figure 8 is a composite photomicrograph of the metallographic faces after this second compression to a total of approximately 6.5% deformation. It is quite obvious that trace 3 on face A is related to trace 4 on face B. Slip traces designated by 5 again are present on face B and a small amount of a second trace direction (6) may be noted at the left top and near the common edge on face A. The slip deformation in the crystal appears to be predominantly by the plane defined by traces 3 and 4. The angular locations of the four slip traces with respect to the

Figure 8. Composite Photomicrograph of Crystal D₆ After Second Compressive Deformation to Approximately 6.5% at 600° ± 5°C.

common edge, in this case defined as a normal to the compression faces, are given in Table X. Figure 9 is a two-surface stereographic analysis of the plane poles designated by these slip trace directions; traces 3 and 4 correspond to slip on the $(0\bar{2}1)$ plane and traces 5 and 6 correspond to slip on the $(0\bar{2}\bar{1})$ plane.

In addition to the slip traces observed on the metallographic faces after the second compression, face B showed markings at angles of approximately 90° to the common edge. In certain instances these appeared as sharp lines of separation between $(0\bar{2}1)$ and $(0\bar{2}\bar{1})$ plane slips. The marking appearing just below the center of face B and extending across its entire width appears to have width of its own and could represent kinking associated with the $(0\bar{2}1)$ plane slip.

To further observe these markings and to aid in determining the slip direction, the crystal was repolished mechanically so that new metallographic surfaces, again perpendicular to the compression faces, were developed. Figure 10 is a composite photomicrograph of the

Figure 9. Two-Surface Metallographic Analysis of All Plane Faces 3, 4, 5 and 6 Observed on Metallographic Faces of Crystal D₆ After Second Compression at $600^{\circ} \pm 5^{\circ}\text{C}$.

Macro 22980

Figure 10. Composite Photomicrograph of Crystal D₆ After Second Compression at $600^{\circ} \pm 5^{\circ}\text{C}$ and Mechanical Repolishing.

metallographic faces in this condition. Face B shows bands of subgrains that appear to be disoriented with respect to each other in a systematic manner, and slight evidence for the same sort of behavior may be noted in the lower portion of face A. Since these markings are only distinct on face B, they do not lend themselves to a two-surface analysis of their origin.

The crystal in this condition no longer shows the $\{130\}$ type twins that were originally present on face A. Apparently they were absorbed during the second compressive test. Several new twin traces are present in the crystal. Two-surface and pole-loci analyses identified all but one of these as $\sim\{172\}$ type twins^{2,3} (see Table X). The direction of compression was such that this type of twinning should not have occurred; however, the complex stress pattern resulting from the kinking deformation may have permitted their formation at temperature or during cooling from the testing temperature. There is also the possibility that they were created by clamping during the repolishing process; however, this is not believed to be the case.

Slip Direction Analyses: Because the platens of the compression equipment are designed so that the lower one is relatively free to move in a plane perpendicular to the compression axis (see ANL-5790), the ends of the crystal should be free to displace themselves, one with respect to the other, as dictated by the deformation occurring in the crystal. For slip deformation, this displacement direction should be the projection of the slip direction into the compression planes. By polishing the two new metallographic faces perpendicular to the compression planes and making tracings of the shapes of these compression planes, the direction of the relative displacement of the crystal's compression faces can be determined. If the two tracings are superimposed so that the two lines representing the newly polished metallographic surfaces coincide, then the two corners defined by the other three surfaces originally perpendicular to the compression faces will be displaced relative to each other in the direction of displacement of the two compression faces. This analysis, of course, requires that the original compression faces have the same shape and area; the method of preparing the crystals for testing results in such a condition. This type of analysis was performed for crystal D₆ subsequent to its second compression and repolish. The direction of displacement of one compression face with respect to the other, when projected into the $(0\bar{2}1)$ slip plane, indicated a slip direction lying between the $[\bar{2}12]$ and $[\bar{1}12]$ directions. The fact that the crystal deformed by two slip planes means that the gross displacement of the crystal's compression faces is effected by both of these slips and, therefore, the present results cannot yield a unique solution for either slip direction. In this crystal, however, slip was predominantly on the $(0\bar{2}1)$ plane, thus the above directions are undoubtedly close to the true slip direction for this plane.

A second slip direction analysis based upon information obtained from X-ray Laue back-reflection photograms was also performed. After repolishing, the crystal Laue photograms were obtained from the upper left and lower left corners of face B. While obtaining these photograms, the crystal was held in a fixed position on an X-ray specimen holder, which provided for motion parallel to the crystal's common edge, so that no error was introduced by dismounting the sample and remounting it for the second photogram. Both photograms gave Laue spots with asterism, but of insufficient quantity to permit an analysis of the rotational axis for each individual photogram. Comparison of the photogram taken from the top of face B with respect to that obtained from the bottom of face B indicated that the latter area was rotated downward and to the left of the former. For the purposes of stereographic analysis the opposing extremities of the two sets of distorted Laue spots were plotted on a common projection (Figure 11)

Figure 11. Stereographic Analysis of $(02\bar{1})$ Plane Slip Direction.

Crystal orientations are plotted in the plane of face B after second compression and mechanical repolish. Line segments represent range of orientations from top to bottom of the face. Solid points and bottom of line segments represent orientations obtained from Laue back-reflection photogram taken at bottom of face B. Open circles and top of line segments represent orientations obtained from Laue back-reflection photogram taken at top of face B. The slip direction, perpendicular to the intersection of the two $(02\bar{1})$ plane traces and lying in the $(02\bar{1})$ planes, is represented by X.

Macro 22983

and the traces for the $(0\bar{2}1)$ planes of each orientation were constructed. The line of intersection of these two planes was assumed to represent the axis of lattice rotation resulting from slip on the $(02\bar{1})$ plane. Such a rotational axis is, of course, an axis lying in the slip plane and 90° from the slip direction. The analysis yields a slip direction (represented by X in Figure 11) that is quite close to the $[\bar{1}12]$ direction, and it seems logical to conclude this to be the true slip direction for the $(02\bar{1})$ plane in this crystal.

Since there are two $\langle 112 \rangle$ directions in the $(02\bar{1})$ plane the question then poses itself as to why the $[\bar{1}12]$ direction operates in preference to the $[112]$ direction. The possible answer for this is that the $[\bar{1}12]$ direction originally was at 35.5° from the compression axis and the $[112]$ direction was at 35.0° ; thus, the former is slightly favored for operation over the latter. More important is the question as to why the most densely packed direction, the $[100]$, does not operate as the slip direction. The original orientation of the crystal was such that the $[100]$ was nearly 90° from the compression axis and, therefore, it would not be expected to operate as a slip element in this particular case. There is another type of direction in $\{021\}$ planes that would also have a denser packing of the atoms than the $\langle 112 \rangle$ directions - the $\langle 012 \rangle$ directions. The reason for the inoperability of the latter direction is not understood.

No value for the critical resolved shear stress for this $\{021\}$ - $\langle 112 \rangle$ slip system can be presented at this time because of experimental difficulties encountered during the first compressive test. The load-contraction curve was erratic and it was impossible to determine the load at which the curve deviated from linearity.

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

The investigation of recrystallization in room temperature, heavily rolled alpha uranium sheet has been continued during this quarter. Cabane and Petit⁴ reported that such material could be recrystallized without a preferred orientation change. The present portion of the investigation, now concluded, has been concerned with the confirmation of this phenomenon in high purity material fabricated identically to that studied by the above investigators.

The preparation of the high purity sheet, reduced 80% in thickness at room temperature, along with a metallographic study of annealed samples, was reported in ANL-5623. This study showed that various bands of the deformed material behaved quite differently during annealing. A metallographic investigation of specimens annealed for short times at

⁴G. Cabane and J. Petit, "Study of Annealing of Rolled Uranium" *Revue de Metallurgie* 51, 603-613 (1954)

400°C and for long times at 320° and 360°C was reported in ANL-5717. In the first stages of recrystallization very fine grains appeared throughout the greater portion of all the specimens; however in the later stages these fine grains were absorbed by relatively large grains

Dilatation studies reported in previous Quarterlies showed that the changes in mean thermal expansion coefficient between 200° and 300°C for annealed specimens over that measured for the as cold rolled specimens were not a simple function of the measured volume percent recrystallization. For samples annealed at 400°C there is essentially no change in the mean expansion coefficient up to 80% recrystallization; however, the expansion changed rapidly upon further recrystallization. The specimens annealed for long times at 320° and 360°C had only a small and gradual change in mean expansion coefficient up to 98% recrystallization.

The results indicate that heavily cold rolled alpha uranium sheet can be recrystallized at low temperatures without appreciable preferred orientation change, whereas recrystallization at higher temperatures causes the preferred orientation to change markedly. A definitive test of this behavior would be to anneal samples at higher temperatures following their first low temperature treatment and to observe the relative effects of the two treatments upon the change in mean expansion coefficient. Tests of this nature are described below.

A specimen that had previously been annealed for 400 hours at 320°C and had showed essentially no preferred orientation change over that of the as rolled condition was reannealed at 400°C for 15 hours. As shown by Table XI, the second anneal resulted in an appreciable change in the mean expansion coefficient. A second specimen, previously annealed for 15 minutes at 400°C, was also reannealed for 15 hours at 400°C as a check. It too had a substantial increase in mean expansion coefficient. The values for both specimens were similar to those obtained from other samples given a single 15-hour anneal at 400°C.

Two other specimens previously annealed at lower temperatures were annealed at 650°C for 48 hours to determine if secondary recrystallization (grain coarsening) would also occur. As shown in Table XI, the first of these specimens had an increase in mean expansion coefficient significantly greater than that of similar specimens given a single anneal at temperatures up to 600°C, while the second sample yielded results of comparable value. This discrepancy between the two specimens is not surprising since both experience a large amount of grain coarsening; thus, because the samples are relatively small they probably do not yield a mean expansion coefficient that is representative of the over-all preferred orientation. Many coarse grains grew about one-half the distance across the width of the specimens and one was found that grew completely across the specimen (Figure 12-a). The entire sample did not experience grain coarsening,

TABLE XI

Volume Percent Recrystallization and Change in Mean Expansion Coefficients^(a) of Heavily Cold Rolled Uranium Sheet After First and Second Annealing Treatments on the Same Specimen

First Annealing Treatment				
Spec. No.	Temp. (°C)	Time	Volume Percent Recrystallization ^(b)	Change of Mean Expansion Coefficient (in/in-°C × 10 ⁶)
T13	400	15 min	81	0.89
T31	320	400 hrs	75	-0.21
T14	400	30 min	88	3.07
T6	320	200 hrs	72	0.43
Second Annealing Treatment				
T13	400	15 hrs	~100	5.38
T31	400	15 hrs	~100	4.77
T14	650	48 hrs	100	6.89
T6	650	48 hrs	100	5.22

- (a) Change in mean expansion coefficient between 200° and 300°C over the average of that obtained from 2 cold rolled specimens. Dilatation tests were made in a direction perpendicular to the rolling direction and lying in the rolling plane.
- (b) The values of volume percent recrystallization were obtained from specimens given the same treatment as the specimens used in this reannealing study.

as is shown in Figures 12-b and 12-c; a few large grains are visible in Figure 12-b with some small grains completely imbedded in them, and Figure 12-c shows an area that has not coarsened.

The results indicate that three recrystallized preferred orientations can be obtained in heavily cold rolled alpha uranium sheet depending upon the annealing temperature. One preferred orientation, which is essentially the same as that of the as rolled material, results from annealing at 360°C or lower; a second preferred orientation is created upon annealing at temperatures between 400° and 600°C; and a third preferred orientation accompanies grain coarsening at temperatures of approximately 650°C.

Figure 12. Grain Coarsening in Heavily Cold Rolled Sheet.

Specimen #T6 after second annealing
treatment of 650°C for 48 hours.

12-a. Macrophotograph of Etched Specimen.

12-b. Partially Coarsened Area in Rolling Plane.

Micro 22466 Polarized Light 50-X

12-c. Uncoarsened Area in Rolling Plane.

Micro 22453 Polarized Light 50-X

d. The Uranium-Carbon System (B. Blumenthal)

The Beta-Gamma Transformation of High Purity Uranium: The beta $\rightleftharpoons$ gamma transformation temperature of high purity uranium has been determined by the method described in ANL-5717. The two samples, B-728T and B-734, with 6 and 9 ppm carbon, respectively, underwent superheating in a manner comparable to that observed for the alpha $\rightarrow$ beta transformation. The transformation temperatures on heating, T_H , versus the logarithm of the rate of heating, r , can be expressed by the relationship:

$$T_H = a_1 + b_1 \log r$$

where a_1 and b_1 are constants. The pertinent equations are:

$$\text{B-728T} \dots T_H = 778.34 + 2.34 \log r$$

$$\text{B-734} \dots T_H = 779.11 + 2.19 \log r$$

The slight difference in the slope for the two equations is probably an effect of the residual impurity content of the metal. No supercooling of the kind that was observed for the beta $\rightarrow$ alpha transformation took place on cooling. Recalescence was noted in several, but not all, cycles; this indicates that the gamma $\rightarrow$ beta transformation is one of nucleation and growth. Thus, the cooling data are best represented by the arithmetic mean of the observed values which graphically present a straight line parallel to the x-axis ($\log r$). The intersection of the lines for heating and cooling, and therefore the equilibrium transformation temperature, is identical with the mean of the cooling curve data. They are:

$$\text{B-728T} \dots T_C = 774.4 \pm 2.2^\circ\text{C}$$

$$\text{B-734} \dots T_C = 775.3 \pm 0.7^\circ\text{C}$$

The beta $\rightarrow$ gamma transformation temperature of high purity uranium is $774.8 \pm 1.6^\circ\text{C}$.

Uranium-Carbon Alloys: The beta $\rightarrow$ gamma transformation temperature of 771.6°C for an uranium-carbon alloy containing 1730 ppm carbon has been reported previously in ANL-5790. The determination was repeated with an alloy containing 325 ppm carbon. Although an alloy with such carbon content should have given a clear indication of the eutectoid temperature, no equivalent arrest was found upon thermal analysis. Unexpectedly, the experimental data agreed rather closely with those obtained for the beta $\rightleftharpoons$ gamma transformation of high purity metal. The relationship between thermal arrest and heating rate is given by the function:

$$\text{B-733} \dots T_H = 777.59 + 2.02 \log r$$

For cooling the mean value is:

$$T_C = 775.6 \pm 1.1^\circ\text{C}$$

The abnormal behavior is probably due to the very low rate of precipitation of small amounts of uranium carbide from gamma uranium. This effect was observed when the response to heat treatment of the precipitate in high purity uranium was studied in conjunction with the preparation of the high purity metal (see ANL-5019). The ease with which the precipitation can be suppressed by quenching or fast cooling, and the long time required for reprecipitation from the supersaturated alpha solution obtained by quenching from a gamma temperature, point in that direction. Thus, it is concluded that the true transformation temperature was measured in the earlier experiment where a large excess of carbon was present. The beta $\rightleftharpoons$ gamma transformation of uranium-carbon alloys is of the eutectoid type:

It occurs at 771.6°C , which is 3.2°C below the transformation point of the pure metal.

e. Phase Diagrams of Uranium-Fissium Alloys (A. E. Dwight)

Uranium-Ruthenium System: Investigation of the structure and properties of the intermetallic compounds in this system continues. The U_2Ru_4 phase exists from 35 to 36 w/o Ru, and has sufficient ductility to be hot rolled approximately 70% at 900°C . The microstructure at room temperature exhibits banding that is characteristic of a quenching transformation. The U_4Ru_3 phase exists at $38\frac{2}{3}$ w/o Ru and has no measurable homogeneity range. The phase is the most brittle of the six compounds in the system.

Uranium-Rhodium System: The gamma uranium phase may contain nearly 5 w/o Rh in solution at 800°C . An eutectic exists between 800° and 900°C . The gamma phase is stabilized by rhodium to $708^\circ \pm 12^\circ\text{C}$.

Uranium-Ruthenium-Molybdenum System: A vertical section through the uranium-molybdenum-ruthenium system is being determined in which the ratio of Mo:Ru is held constant at 2.5:2 by weight. This ratio closely approximates the proportions in which molybdenum and ruthenium are expected to appear in "fissium" in reprocessed EBR-II fuels. The present status of this vertical section is shown in Figure 13. The location of the eutectoid valley at 650°C and 3.6 w/o alloy content indicates that the line joining the U-2 w/o Ru eutectoid and the U-12 w/o Mo eutectoid is nearly straight.

Figure 13. Vertical Section Through Uranium-Molybdenum-Ruthenium Ternary System.

Macro 23008

In the higher ruthenium part of the ternary system, a two-phase field has been found joining the U_3Ru_4 phase with the molybdenum corner of the system. Similar two-phase fields were found between molybdenum and U_2Ru_3 , molybdenum and U_3Ru_5 and molybdenum and uranium-ruthenium. This virtually eliminates the possibility of a new ternary phase, and indicates that the three phases, U_3Ru_4 , U_2Ru_3 and U_3Ru_5 have only a slight solubility for molybdenum.

Supporting Work on Other Ternary Systems: An equiatomic zirconium-ruthenium-molybdenum alloy gave a diffraction pattern containing the lines of the CsCl-type zirconium-ruthenium phase and of pure molybdenum. This indicates the zirconium-ruthenium phase forms in preference to $ZrMo_2$ or $ZrRu_2$. An equiatomic uranium-zirconium-ruthenium alloy also gave a diffraction pattern containing the zirconium-ruthenium CsCl-type phase, indicating a preference for zirconium-ruthenium over the various uranium-ruthenium intermetallic compounds. An equiatomic uranium-zirconium-molybdenum alloy gave a diffraction pattern containing gamma uranium and the $ZrMo_2$ Laves-type phase, indicating that a Laves-type phase will be formed in the absence of ruthenium. A quaternary uranium-zirconium-molybdenum-ruthenium alloy gave a diffraction pattern containing the zirconium-ruthenium CsCl-type phase as a minor constituent.

The above-mentioned investigations indicate that, as the fissionium content (including zirconium) is allowed to build up, eventually the zirconium-ruthenium CsCl-type phase will appear as an equilibrium phase.

f. Properties of Uranium-Fissionium Alloys (S. T. Ziegler, M. V. Nevitt)

Density, thermal expansion, and thermal arrest data have been obtained for uranium-fissionium alloys containing from 3 to 10 w/o fissionium.

The alloys studied were in the form of arc melted and cast buttons prepared from 99.98 w/o pure uranium and fissionium element powders. Three buttons, 1.0" in diameter x 0.27" thick, of each of the nominal compositions given in Table XII were prepared.

TABLE XII

Nominal Compositions of Uranium-Fissionium Alloys

Fissionium Element	U-3 w/o Fs (w/o)	U-5 w/o Fs (w/o)	U-8 w/o Fs (w/o)	U-10 w/o Fs (w/o)	U-5 w/o Fs + 2.5 w/o Zr (w/o)
Mo	1.485	2.475	3.960	4.950	2.475
Ru	1.185	1.975	3.160	3.950	1.975
Rh	0.174	0.290	0.464	0.580	0.290
Pd	0.114	0.190	0.304	0.380	0.190
Zr	0.036	0.060	0.096	0.120	2.560
Nb	0.006	0.010	0.016	0.020	0.010
Total w/o Fs	3.000	5.000	8.000	10.000	7.500

Densities: Density measurements were made by the carbon tetrachloride displacement method. Measurements were made first of whole "as-cast" buttons and later of two saw-cut halves of the same buttons. The averages of the three measurements are given in Table XIII. In most cases the calculated standard deviations of the averages were 0.008 g/cc or less. For a 95% confidence level the standard deviations were 0.017 g/cc or less.

TABLE XIII

Densities of As Cast Uranium-Fissionium Alloys

U-3 w/o Fs		U-5 w/o Fs		U-8 w/o Fs		U-10 w/o Fs		U-5 w/o Fs + 2.5 w/o Zr	
Cast No.	Density (g/cc)	Cast No.	Density (g/cc)	Cast No.	Density (g/cc)	Cast No.	Density (g/cc)	Cast No.	Density (g/cc)
3-1	18.373	5-1	17.988	8-1	17.629	10-1	17.408	5-4	17.467
3-2	18.383	5-2	17.996	8-2	17.652	10-2	17.397	5-5	17.465
3-3	18.389	5-3	17.983	8-3	17.640	10-3	17.373	5-6	17.498

Thermal Expansion: Thermal expansion data (Table XIV) were obtained for only the 3 w/o fissium (Cast No. 3-2) and 5 w/o fissium (Cast No. 5-2) alloys. The data were obtained with specimens 0.200" in diameter x 0.9" long, machined from as cast buttons. Length measurements were made upon two repeated heating and cooling cycles between room temperature and 650°C.

TABLE XIV.

Thermal Expansion Coefficients of As Cast
Uranium-Fissium Alloys

Alloy	Cycle	Temperature Range (°C)	Mean Thermal Expansion Coefficient (inch/inch/°C)
U-3 w/o Fissium (Cast No. 3-2)	First	22 - 100	14.49
		22 - 200	13.82
		22 - 300	13.99
	Second	22 - 100	14.49
		22 - 200	15.00
		22 - 300	15.18
		22 - 400	15.24
		22 - 500	16.15
		22 - 600	17.63
		22 - 650	20.81
U-5 w/o Fissium (Cast No. 5-2)	First	34 - 100	13.37
		34 - 200	14.17
		34 - 300	14.37
		34 - 376	13.33
	Second	34 - 100	15.66
		34 - 200	15.12
		34 - 300	14.99
		34 - 400	15.73
		34 - 500	16.79
		34 - 600	18.52

On the first cycle both alloys showed marked shrinkages in length upon heating between approximately 300° and 450°C. This behavior was not observed on the second cycle; it is probably related to the decomposition of metastable phases. X-ray data showed both alloy castings to be essentially single phase: the 3 w/o fissium alloy, supersaturated alpha uranium and the 5 w/o fissium alloy, retained high temperature gamma phase (b.c.c.).

Thermal Arrests: Thermal arrest data were obtained for the U-3 w/o fissium (Cast No. 3-1) alloy on cooling from 825°C. Table XV details the cooling rates and the temperatures and types of arrests. The data evidence two transformations, both of which are depressed to lower temperatures with increasing cooling rates.

TABLE XV.

Thermal Analysis Data for Uranium-3 w/o Fissium Alloy.
(Cast No. 3-1)

Thermal Treatment	Cooling Rate on Approach to Arrest (°C/minute)	Arrest Temperature (°C)	Type of Arrest
Heated to 825°C, held 15 minutes; furnace cooled to room temperature.	9.0	678	Slope Change
	7.33	607	Isothermal
Reheated to 825°C, held 30 minutes, slow cooled to room temperature.	2.66	713	Slope Change
	2.20	627	Isothermal

g. Neutron Diffraction Study of UN (M. H. Mueller, H. W. Knott)

UN and UC have been reported⁵ to be cubic with a NaCl rather than a ZnS-type crystal structure. Although the contribution of the nitrogen or carbon to the diffracted X-ray intensity is small, it was calculated previously that for the NaCl-type structure, the intensity of the (420) for UC should be greater than the (331) by about 14%, while for the zinc-blend structure the intensity of the (331) should be greater than the (420) by about 7%. These relative intensities were obtained from a comparison of the appropriate structure factors for these reflections without any correction of the intensity due to factors which are angle dependent. Slightly greater differences were calculated for UN due to increased scattering of the nitrogen. Sufficient differences of intensity were observed⁵ on powder patterns within this pair of lines and several others to support the NaCl-type structure for UN and UC.

Recently, additional X-ray and neutron diffraction data were obtained definitely confirming the NaCl-type structure for UN.

The sample used for this study was obtained by two different methods. Part of the sample was made by the decomposition of UH_3 at 400°C with further heating at 1000°C under 1 atmosphere of nitrogen. Another part was made by heating massive uranium metal in a nitrogen atmosphere at 800°C followed by additional heating at 1200°C.

The X-ray diffraction intensity data were obtained with an X-ray diffractometer using a sample spinner. The holder for this spinner consisted of an $1/8$ " thick aluminum disc with a $3/4$ " diameter hole in the center. A cell for holding the powder in the center of this disc was made by placing a window of coil winding paper, approximately 0.0003" in

⁵R. E. Rundle, N. C. Baenziger, A. S. Wilson, and R. A. McDonald, J. of the Am. Chem. Soc. 70 99 (1948).

thickness, on the front side of this disc. This window was held in place by the use of a doughnut-shaped piece of double coated, pressure sensitive tape. The finely powdered sample was then loaded into the cell from the rear in order to avoid orientation effects. After completely filling the cell, an aluminum back-up plate was slid over the hole in order to remove the excess material and to hold the sample in place. This sample holder was then secured to the face plate of the sample spinner.

The thin paper was found to be strong and suitable as a window, since one thickness decreased the intensity of the $\text{CuK}\alpha$ beam by less than 1% and did not contribute an appreciable diffraction pattern in itself. The window also made it possible to form a smooth compact surface on the sample, thus minimizing absorption errors.

A summary of the observed and calculated X-ray intensities for UN is given in Table XVI. It can be noted that there is better agreement between the observed and the calculated intensities for the NaCl than for the ZnS-type structure as evidenced by an R factor of 0.085 and 0.141, respectively, for these two structures.

TABLE XVI.

Observed and Calculated Relative X-ray Intensities for
UN Using Cu Radiation with an X-ray Diffractometer.

(hkl)	Observed I/I_0	Calculated ⁽¹⁾	
		NaCl-Type	ZnS-Type
111	100.0	100.0	100.0
200	69.4	63.6	45.8
220	45.6	44.5	39.7
311	46.4	44.5	43.4
222	14.4	15.3	11.6
400	9.6	7.1	6.3
331	18.9	19.1	18.4
420	20.8	21.1	16.2
422	19.6	18.3	16.2
333, 511	21.1	21.1	20.2
440	9.2	10.8	9.7
531	35.8	47.3	45.2
442, 600	25.6	37.8	29.4

$$(1) \quad I \propto |F|^2 p \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta}$$

An accurate lattice parameter was obtained for this same material from a Debye Scherrer powder pattern using a modified Cohen least squares method. A value of 4.890Å was obtained, which is in good agreement with the previously reported value of 4.880Å,⁵ if it is assumed that this latter value was in terms of KX units.

In order to confirm the structure unequivocally, a neutron diffraction pattern was obtained with the diffractometer described previously.⁶ A relatively small sample of UN was used which filled a vanadium tube, 1/8" in diameter x 1-1/2" in length. A summary of the relative neutron intensities together with calculated values for the NaCl and ZnS-type structures are given in Table XVII. The value of 2B was determined from the slope of the plot of logarithm of I_o/I_c versus $\sin^2 \theta / \lambda^2$ using only those reflections whose calculated intensity was the same for both structures. There is considerable difference in the calculated relative intensities for many of the reflections for the two types of structures and it is therefore apparent that the best agreement is with the NaCl-type. The R factor for this type structure is 0.024.

TABLE XVII.

Observed and Calculated Relative Neutron Diffraction Intensities for UN with $\lambda = 1.09\text{\AA}$.

(hkl)	Observed I/I_o	Calculated ⁽¹⁾	
		NaCl-Type	ZnS-Type
111	0.0	0.4	8.3
200	101.4	101.8	0.3
220	100.0	100.0	100.0
311	0.0	0.4	77.5
222	44.7	46.3	0.1
400	25.5	25.2	25.2
331	0.0	0.2	4.2
420	79.4	79.9	0.2
422	66.7	66.2	66.2
333, 511	0.0	0.2	12.7
440	20.4	24.4	24.4
531	0.0	0.2	43.5
442, 600	56.6	53.7	0.1
620	39.3	39.2	39.2

$$^{(1)} I \propto |F|^2 p \frac{1}{\sin^2 \theta \cos \theta} \exp (-2B \sin^2 \theta / \lambda^2)$$

⁶ S. S. Sidhu, LeRoy Heaton and D. D. Zaubers, Acta Cryst. 9 607 (1956).

2. Plutonium and Its Alloys

a. Preparation of High Purity Plutonium (B. Blumenthal)

Cell Design: High purity uranium has been prepared in the electrolysis cell designed for plutonium. Its analysis was satisfactory except for a high manganese and aluminum content. A short breaking-in period and intermittent operation were considered responsible for the residual contamination.

The cell is shown in Figure 14. It was designed to meet the requirements of glovebox operation and differs from uranium cells in several ways. The cell is closed. A Lavite head seals the Hastelloy C cell with O-rings. The electrodes are adjustable through O-ring seals. Tank helium is passed through the cell at a rate of 0.5 cc/minute. The Cl_2 and small HCl content of the helium are absorbed in an Ascarite column. The reactions

purify the gas to the extent that after several weeks of operation while bubbling the gas through water, no change in the pH of the water was observed. Charcoal filters at room temperature were less effective to remove the active gases. Therefore, the gas released from the absorption column is not expected to corrode the gloveboxes, the brass fittings, and the copper piping of the system. The electric resistance furnace for heating the cell is water-cooled to minimize the heating effect on the glovebox atmosphere. It is heavily shielded to reduce the high temperature areas with which the neoprene gloves might come in contact, and can be completely disassembled inside the glovebox for repair and replacement of parts. Data on power requirements for the furnace, on power input vs. cell temperature, were obtained. The cell will be run on a battery rather than a rectifier since the use of a battery was found to give better control of crystal size and operating periods between pulls. The cell is ready to be placed into the glovebox.

Glovebox Conversion: Two adjacent gloveboxes have been converted from air to helium. The scheme of the once-through system is shown in Figure 15. A negative pressure of 0.75 to 1.0 inch of water is maintained. A flow rate of 2700 cc/minute of helium, which is equivalent to approximately 0.1 ft³/minute, results in a consumption of six tanks of helium every 10 days. The pressure is normally controlled by setting the valve on the inlet side and adjusting the baffle that connects the open outlet with the plenum. If the pressure in the boxes should drop below the specified minimum of -1", a pressure switch opens a solenoid valve and lets high pressure gas (5 pounds/in²) enter the boxes. If the pressure is too high (-0.75" maximum) another solenoid valve is opened automatically, providing a direct connection to the -4" plenum. Because of the necessity of tying into

Figure 14. FUSED SALT ELECTROLYSIS CELL

JES
BB
1-16-58

Figure 15. SCHEME OF PRESSURE CONTROL SYSTEM
ONCE-THROUGH HELIUM FLOW THROUGH
GLOVE BOX AND ELECTROLYSIS CELL

J.E.S.
B.B.
1-15-66

an existing system, a number of compromises had to be made which would not have been necessary if a new system could have been built. There is, for instance, the danger that air will be pulled into the glovebox from the high pressure outlet side (-1.5") if the solenoid valve that opens the system to the -4" plenum fails to close. Even though the probability of such an event is very small, it would have been desirable to have eliminated this potential hazard. After purging the two gloveboxes for 2 weeks at a rate of 400 cc/minute, and then at a rate of 2700 cc/minute, the oxygen content of the gas was 400 to 500 ppm by volume. No data on the humidity were obtained as yet. The humidity is expected to be high since one of the gloveboxes will be used for washing crystals and for electrolytic polishing.

Criticality Hazard: The criticality hazard was evaluated by the Criticality Committee of the laboratory and permission was obtained to operate the cell with a total plutonium content not exceeding 300 grams. If the total plutonium content should approach this limit a new evaluation would be necessary.

Chemical Analyses: In addition to the previously reported chemical analytical data for carbon and hydrogen, we have obtained from R. F. Buchanan of the Chemistry Division, some nitrogen analyses of biscuit plutonium and of the liquated ingot. The data are listed in Table XVIII. The data are inconclusive regarding the separation of PuN by liquation. The order of magnitude of the nitrogen content of plutonium is comparable to that of high purity uranium.

TABLE XVIII.

Nitrogen Content of Plutonium.

Specimen No.	Sample Location	Nitrogen (ppm)
3-424/4C3A	Top Center	13
3-424/2A1B	Edge	39
3-424/2A8B	Edge	44
3-424/4B6A	Bottom Center	27
3-424/4E1B	Bottom Center	10
3-423/15B	Top	29
[Liquated] [Ingot]		

b. Plutonium Phase Diagram Studies (E. M. Benson)

The zirconium-plutonium alloy Al4, with a nominal composition of 24 w/o (11 a/o) plutonium, was examined by metallography, X-ray diffraction, and dilatometry. The alloy was previously homogenized at 600°C for 1 week and slowly cooled.

The room temperature microstructure is shown in Figure 16. The alloy contains two phases. In addition, a number of small spheres in random distribution are observed in the "as polished" condition. The specimen was mechanically polished through 1 micron diamond and etched in a solution of one part HNO₃, two parts HF, and 20 parts of glycerine.

Figure 16. Microstructure of Zirconium-Plutonium Alloy Al4.

PU-217

150-X

Analysis of room temperature Debye-Scherrer patterns, taken with Cu-K alpha radiation, confirms the presence of two phases. The principal phase is alpha zirconium; the second phase has not yet been identified. It could possibly be PuZr₂, which was reported by British investigators at Harwell.

Three dilatometric curves obtained from a single cylindrical specimen, 0.500" long by 0.122" in diameter, are shown in Figure 17.

A dial gauge dilatometer was used. The approximate heating and cooling rates are shown in Table XIX.

FIG. 17 DILATOMETRIC CURVES OF ZIRCONIUM-PLUTONIUM ALLOY A14

TABLE XIX.

Heating and Cooling Rates Used in the Dilatometric Studies of Zirconium-Plutonium Alloy A14.

Run	Heating Rate (°C/min)		Cooling Rate (°C/min)
	Room Temp. to 600°C	600°C to Max. Temp.	Max. Temp. to 500°C
I	10	10	Very rapid
II	4	2	6
III	3	1	2

On heating, a break occurred at 675°C during Run I and Run III and might have been caused by the alpha-beta transformation of the zirconium phase. The same break was displaced to 750°C during Run II. A second break, occurring at 848°C during Run II, was not observed during the other runs. On cooling, breaks occurred at 855°C (Run II) and 815°C (Run III). Since the specimen was rapidly cooled after Run I, the displacement of curve II may be due to the existence of nonequilibrium conditions. During Run III the specimen was held overnight at 742°C, resulting in a 1-mil contraction of the specimen.

3. Corrosion Mechanisms

a. Mechanism of Zirconium Corrosion (R. D. Misch, F. H. Gunzel)

Studies thus far have shown that the binary alloys of titanium-zirconium exhibit several interesting contrasts between corrosion in water and corrosion in dry O_2 . The purpose of this work is to explain these differences on the basis of oxide structure and conductivity.

In dry O_2 , the corrosion rate of zirconium alloys increases steadily with increasing titanium to about 50 w/o Ti. The rate then decreases and reaches another minimum at 100 w/o Ti. In water, the corrosion rate rises to a maximum at several percent titanium and then drops slowly and steadily until it reaches a minimum at 100 w/o Ti. In dry O_2 , the corrosion scale is black; in water the corrosion product is either dark and coherent, when the corrosion rate is low, or white and nonprotective when the rate is high.

Films in Dry O_2 : Titanium, zirconium and a 50 w/o alloy have been oxidized in dry, purified O_2 at 500°C. The specimens were then aluminized with the usual 1/8" diameter spots and the film resistance was measured. The data are presented in Table XX. The calculation of resistivity requires data on the density of the film. In this report the data of Ksendzov⁷ for solid solution of TiO_2 and ZrO_2 was used. It is evident that titanium increases the conductivity of the film on zirconium. Additional compositions are being examined to investigate the influence of smaller titanium additions in zirconium.

TABLE XX.

Corrosion and Resistivity Data for Specimens Oxidized
in Dry O_2 (1 atmosphere at 500°C).

Material	Exposure Time (hr)	Weight Gain (mg/dm ²)	Film Resistivity (ohm-cm)
Zirconium	15	29.4	1.0×10^{14}
50 w/o Ti, 50 w/o Zr	1	17.0	3.2×10^9
Titanium	15	8.0	3.3×10^5

⁷ Ya. M. Ksendzov and V. G. Prokhvatilov, Zhur. Fiz. Khimii 31 321-7 (1957).

Films in Water: A range of alloys which varied from 10 to 100 w/o Ti was examined. Four of the higher titanium alloys were corroded in steam at 400°C because adequate film thicknesses could not be produced in 350°C water. The film thicknesses for these specimens were barely adequate to obtain a meaningful resistance measurement and the reproducibility was poor.

The corrosion exposures were not uniform because the main purpose was to obtain suitable film thicknesses. This is generally true when the oxide appears black. The most reliable data are those in the range from 10 to 50 w/o Ti. Here, the resistivity was highest for 10 w/o Ti, reached a minimum for the 20 and 30 w/o specimens, and then increased in the 40 and 50 w/o Ti specimens. The 10 w/o specimens exhibited slight emf's which is confirmation of a high resistance film. For the compositions from 65 to 100 w/o Ti, the resistivity did not show a consistent variation. These films were very thin (approximately 0.1 micron) as compared to thicknesses of 0.3 to 2.8 microns for the specimens with less titanium. The oxide on titanium does not appear to have the very high resistance characteristic of that on zirconium.

The corrosion weight gains do not agree with the data of Carver and Hayes⁸ who found that the 85 w/o Ti alloy had a much higher corrosion rate than the 65 w/o Ti alloy. The data of the present study should be closer to the true corrosion picture because the alloys were made from crystal bar materials of low impurity content.

b. Aluminum Solution Potentials (F. E. DeBoer, C. A. Youngdahl)

Effort has been continued with the objective of determining reproducible curves of solution potential as a function of polarizing current in pure water at 100°C. For both aluminum and platinum a considerable sensitivity to impurity content of the water has been observed. This is being studied by pre-electrolyzing the water before using it to test samples. In addition, the effect of changing sample surface preparation has caused changes in polarizing behavior. Considerable progress has been made in combatting the causes of poor reproducibility.

⁸ M. D. Carver and E. T. Hayes, "The Effect of Microstructure on the Corrosion Rate of Alloys of Zirconium," USBM-U-123, (June 1, 1956).

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

1. A Study of Transition Metal Intermediate Phases (A. E. Dwight, M. V. Nevitt)

Ti₂Ni-Type Phases: The first stage of the study of this phase in alloys of zirconium and hafnium is complete and a paper for publication has been prepared. During the past quarter single phase compositions have been determined, including the approximate oxygen requirements for stability, and lattice parameters have been refined. Table XXI summarizes the information obtained. The most significant features of these phases are these:

1. There is evidence that most of them require oxygen for their stability.
2. Most of them deviate from A₂B stoichiometry. This composition variability has led to the tentative conclusion that they are a type of electron compound in which oxygen acts as an electron donor or acceptor.
3. Lattice parameters generally increase with increasing B element radius.

A study of ordering is now under way on Hf₂Rh by means of X-ray diffraction intensity measurements and, in cooperation with M. H. Mueller, on Ti₂Ni by neutron diffraction.

TABLE XXI

Ti₂Ni-Type Phases Containing Zirconium or Hafnium

System	Composition (a, o)	Oxygen Requirement	a ₀ (Å) (a)
Zr-Rh	20 - 23 Rh	Minimum required is between 400 and 6000 ppm	12.476 ± 0.001
Zr-Ir	Approx. 25 Ir	Minimum required > 400 ppm	12.471
Zr-Pt	20 Pt	Minimum required is between 250 and 6000 ppm	12.574 ± 0.006
Hf-Rh	33 Rh	Minimum required > 500 ppm	12.3255 ± 0.0002
Hf-Pd	23 Pd	Minimum required is between 800 and 7000 ppm	12.3605 ± 0.0003
Hf-Ir	30 Ir	Minimum required > 600 ppm	12.352 ± 0.001
Hf-Pt	30 Pt	Minimum required > 300 ppm	12.461 ± 0.001

(a) a₀ for the Zr-Ir phase was determined by a Nelson-Riley⁹ extrapolation. For the other phases, a₀ was determined by least squares solution¹⁰ and standard error was determined by the method of Jette and Foote.¹¹

⁹J. B. Nelson and D. P. Riley, Proc. Phys. Soc. 57 160 [London] (1955).

¹⁰M. V. Cohen, Rev. Sci. Instr. 6 68 (1936).

¹¹E. R. Jette and F. Foote, J. Chem. Phys. 3 605 (1935).

Laves-Type Phases: Three new Laves phases were found, as shown in Table XXII. An alloy corresponding to the composition HfIr₂ failed to exhibit the Laves-type phase. An HfIr₂ phase had been expected, due to the existence of previously reported ZrIr₂, ThIr₂ and UIr₂ Laves-type phases.

TABLE XXII

Lattice Parameters of Laves-Type Phases

Phase	Structure	a_0 (Å)	c_0 (Å)	c/a
HfOs ₂	C 14 - MgZn ₂	5.194	8.491	1.635
HfRe ₂	C 14 - MgZn ₂	5.249	8.594	1.637
ThRe ₂	C 14 - MgZn ₂	5.492	9.097	1.657

2. Occurrence and Magnetic Behavior of Cr₃O-Type and Sigma Phases (M. V. Nevitt)

This program was inactive during the first half of the past quarter because of a delay in getting replacement parts for a failed cryostat vacuum component. During this time the component was redesigned to lessen the possibility of similar future failures. After receipt and assembly of the parts the calibration of the induction coil-ballistic galvanometer circuit was continued during the second half of the quarter. The standardizing sample consisted of 9 w/o carbonyl nickel of approximately 5 micron particle size in a heavy silicon jelly. Standardizing runs were made at 43.5°K and 77.3°K in fields ranging from 15,000 $\pm$ 22,000 oersteds. At each temperature the galvanometer deflection at infinite field, $D_{\infty,T}$, was extrapolated from the relation:

$$D_{H,T} = D_{\infty,T} \left(1 - \frac{a}{H^2} \right)$$

which is the appropriate relation for dilute, approximately spherical, non-interacting, ferromagnetic particles in a nonmagnetic matrix. At fields of about 20,000 oersteds and above, the values of $D_{H,T}$ fit a straight line when plotted against $1/H^2$, and the slopes of the lines for the two temperatures are about equal. This is the expected result, since the coefficient, a , is not believed to be temperature dependent in this small temperature range. The values of a derived from the plots are larger than values derived from published work, and there is an abrupt change in a as the field is decreased below 20,000 oersteds. Both of these effects are believed to be due to severe strain in the nickel powder. This will be checked by repeating certain of the measurements of annealed material.

The calibration with nickel powder will be completed by making a similar set of measurements at 4.2°K. The deflection at infinite field and 0°K, $D_{\infty,0}$, will then be extrapolated from the Bloch relation:

$$D_{\infty,T} = D_{\infty,0} (1 - C(T)^{3/2})$$

Since the saturation magnetization of nickel, $\sigma_{\infty,0}$, is known, the calibration of the system is thereby achieved.