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By

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ISC-389

3

QUARTERLY SUMMARY RESEARCH REPORT

For the period April, May, and June, 1953

This report is prepared from material
submitted by the group leaders of
the Laboratory.

Previous quarterly research reports in this series are:

ISC-287
ISC-314
ISC-346

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429 002

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TABLE OF CONTENTS

Summary.	5
Metal Coating.	6
1. Diffusion Coating	6
2. Copper Plating of Uranium and Zinc Coated Uranium	8
Slug Casting into Metal Cans	11
1. Casting into Zirconium Cans	11
a. Nature of Uranium-Zirconium Bond	11
b. Thermal Treatment of Bonded Specimens.	14
c. Capping and Corrosion Testing of Canned Slugs.	14
2. Casting into Uranium Alloys Cans.	15
Alloy Studies.	17
1. Uranium-Niobium Alloys.	17
a. Preparation of Alloys.	17
b. Hardness of the Arc-Melted Alloys.	18
c. Fabrication.	18
d. Determination of Melting Points.	19
e. Dilatometric Measurements.	19
f. Measurements of Electrical Resistivity	19
g. The Constitutional Diagram	21
2. Uranium-Molybdenum Alloys	21
3. Uranium-Zirconium-Niobium Alloys.	21
4. Other Uranium Ternary Alloys.	23
5. Uranium-Magnesium Alloys.	23
6. Zirconium-Zinc System	27
Physical Properties of Metals.	28
1. Thermal Conductivity of Metals by a Steady State Method.	28
2. Thermal Conductivity of Uranium from Diffusivity Measurements.	28
3. Thermal Conductivity and Tensile Properties of Slug Materials.	33
Preparation of Niobium Metal	33
Production of Cast Uranium Rods.	33

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ISC-389

5

QUARTERLY REPORT

P. Chiotti and O. N. Carlson

Summary

Several changes relative to the uranium coating problem have been made during this report period. Due to difficulties encountered in plating aluminum from a fused NaCl-AlCl_3 bath, work on this problem was discontinued.

Effort has been directed to other more promising coating procedures. The possibility of producing a corrosion-resistant diffusion coat on uranium by heating uranium in a magnesium bath containing the desired metal or metals in solution is being investigated. A thin outer coat containing 20.0 weight per cent zirconium has been produced by heating a uranium specimen in a magnesium bath saturated with zirconium at 850°C for one hour. Diffusion coats produced by dipping uranium into molten baths consisting of Mg-Ni eutectic, Mg-Si, or Mg-Si-Zr are also being investigated. Difficulty in obtaining uniform wetting of the samples has been encountered but it is believed that this problem can be solved.

The use of a thin zinc dip coat on uranium as a base for copper plating has been found to eliminate the rapid undercutting of the copper plate by boiling water. Some samples have withstood the action of boiling water for approximately 200 hours before appreciable pitting was observed. Attempts are being made to seal the pores in the copper coat by annealing in either a fused salt or lead bath. This procedure may prove useful in improving the corrosion resistance of other thin electroplates.

Slug casting into metal cans during this quarter has been confined principally to zirconium cans. Several samples have been sent to Hanford for further testing. Bonding conditions, corrosion resistance, and resistance to thermal cycling of the zirconium canned slugs have been studied. Some work was also done on the bonding of cast uranium to uranium-niobium alloy cans.

Work on the uranium-niobium alloy system was continued. A tentative phase diagram for the uranium-rich end of the system has been constructed. The results of dilatometric measurements, hardness measurements and melting point determinations are presented. Comments on the fabricating properties and the results of electrical resistivity measurements on some of these alloys are also given.

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Work on the uranium-molybdenum, uranium-zirconium-niobium, and zirconium-zinc systems has continued. Some measurements of the change in electrical resistivity with temperature of some uranium-molybdenum alloys have been made. The effects of alloy composition and heat treatment on the corrosion resistance, microstructure and grain size of uranium-zirconium-niobium alloys were studied. Work on the zirconium-zinc system has been confined principally to the preparation of alloys containing from 6 to 50 weight per cent zirconium.

A number of miscellaneous uranium-rich ternary alloys have been prepared and tested in boiling distilled water.

Work on the uranium-magnesium system was concluded during this period and summarized in a final report ISC-377. A summary along with a table giving the solubility of uranium in molten magnesium at various temperatures is given in the present report.

Apparatus for the determination of the thermal conductivity of metals by a steady state method has been completed.

The thermal conductivity of uranium at various temperatures has been calculated from thermal diffusivity measurements. The change in thermal diffusivity with temperature, the temperature dependence of the electrical resistivity, and the change in thermal conductivity with temperature are presented.

Measurements on the thermal conductivity of Hanford slugs by standard engineering methods have also been made.

The preparation of niobium from the oxide by reduction with carbon as well as with a calcium-aluminum mixture is being investigated.

Metal Coating (P. Chiotti)*

1. Diffusion Coating

Magnesium wets but does not react with uranium to form inter-metallic compounds or dissolve in uranium to any appreciable extent. The solubility of uranium in magnesium is also negligible below 1100°C. These observations suggested the possibility of producing a diffusion coat of zirconium or nickel, etc., on the surface of uranium by heating uranium in molten magnesium saturated with the desired metal or metals.

*Name indicates group leader in charge of work.

Diffusion coats produced by dipping uranium into magnesium saturated with zirconium, silicon, silicon and zirconium, and in a bath of magnesium-nickel eutectic are being investigated. Other metals which would be of interest include niobium and molybdenum. The solubility of these metals in magnesium is not known but is believed to be very small in the temperature range of interest.

Some results using a magnesium bath saturated with zirconium at approximately 850°C were given in the previous quarterly report, ISC-346. Further work has been carried out using this bath. In these tests the bath was contained in a magnesia crucible under an atmosphere of helium. Four specimens dipped in this bath for one hour at 850°C, partially cooled in helium to permit excess magnesium to drain from the specimen, and then quenched in oil were corrosion tested in boiling distilled water. The average corrosion rate for a 48 hour period was found to be 0.1 to 0.3 mg/cm²/hr. All samples had a dark gray surface. These results represent the corrosion resistance of the magnesium-zirconium outer coat. An attempt was made to evaluate the corrosion resistance of the diffusion coat by dissolving the outer material with dilute nitric acid. The surface exposed by this treatment was quite bright and metallic. Only one such specimen has been tested in boiling water. This specimen failed after a relatively short period.

At the point of failure the alloy coat was rapidly undercut separating a thin foil of corrosion resistant alloy from a part of the specimen surface. The remainder of the coat remained adherent, bright, and untarnished. The foil, together with some of the corrosion products, was weighed (0.0500 gr.) and analysed, and was found to contain 20.0 weight per cent zirconium. The weight of the remainder of the sample was 37.6929 grams, of which approximately 6.340 grams were dissolved in a mixture of nitric and hydrofluoric acid and also analysed for zirconium. This portion contained 0.44 weight per cent zirconium. Dissolution of another 11.9 gram portion of the specimen analysed 74 ppm zirconium. The total zirconium in the sample was roughly 1300 ppm. Qualitative tests for magnesium on the portions of the sample analysed were negative.

A sample from another test weighing 16.947 grams after removal of the outer magnesium coat was found to contain a total of 86 ppm zirconium. The area per unit mass of this sample was slightly greater than that of the above sample. The zirconium content in this case is lower by a factor of about 15. Chemical analyses of the bath material showed it to contain 0.55 weight-per cent zirconium which is in fair agreement with the known solubility of zirconium in magnesium at 850°C. This discrepancy is believed to be due to the formation of films of either oxide or other impurities on the uranium surface during immersion of the specimens. Although a helium atmosphere has been used it has been observed that oxides

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or other impurities form a film on the surface of the bath. The film tends to adhere to the specimen surface as it is submerged into the bath. These impurities possibly form a diffusion barrier and are also believed to be responsible for the non-uniform wetting observed in many cases.

Attempts are being made to eliminate the above difficulties. The use of a KCl-LiCl flux has not eliminated our problem. Since a thin coat of zinc can be readily applied to uranium the application of such a coat prior to submersion in the magnesium-zirconium bath might be helpful. This procedure will be tried.

Some experiments have also been conducted with a magnesium-nickel eutectic bath. With this bath the time required to produce a diffusion layer is much shorter. Specimens dipped in this bath from 4 to 28 minutes at 700°C show the formation of diffusion bands. The diffusion layer formed on a specimen after eight minutes is shown in Figure 1. The outer magnesium-rich coat is out of focus due to the more rapid removal of this material during polishing. At temperatures near 800°C the uranium reacts with the bath and forms a separate liquid layer on the bottom of the crucible. This material has a eutectic structure. The composition has not yet been determined.

Some samples have also been dipped in a magnesium bath saturated with silicon and with silicon plus zirconium.

Without the removal of the magnesium-rich outer coat none of these samples have shown superior corrosion resistance to boiling distilled water. The magnesium-nickel eutectic reacts readily with water. The other magnesium-rich coats have corrosion rates varying from 0.1 to 3.0 mg/cm²/hr.

In order to evaluate the corrosion resistance of the diffusion coat the magnesium-rich layer must be removed. Dilute nitric acid has been used; this may not be the best procedure since pitting of the diffusion coat by the acid might weaken the corrosion resistance of the diffusion coat. Removal of the excess magnesium under vacuum will also be tried.

2. Copper Plating of Uranium and Zinc Coated Uranium

Copper has been plated on uranium to serve as a base for aluminum plating. Copper has also been plated on the inside surface of uranium-alloy cans for the casting operations described elsewhere in this report. In the latter case the copper plate has proven useful in improving the bond between the alloy can and the uranium metal cast into the can. Copper plating has not, however, been entirely satisfactory as a base for aluminum plating from a NaCl-AlCl₃ fused salt bath. These composite plates failed rapidly in boiling distilled water by undercutting at the copper uranium interface.

Figure 1

Diffusion band formed on uranium after 8 minutes in a magnesium-nickel eutectic bath at 700°C. X-250.

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Porosity of the electroplates and small amounts of entrapped salts are believed to be primarily responsible for the rapid failure. Attempts to plate aluminum from this bath have been discontinued.

In general thin electroplates of nickel and chromium are also rapidly undercut by boiling water. Annealing reduces the porosity of these coats but as long as some porosity remains which permits the water to come in contact with the uranium, rapid failure may be expected due to the more noble character of the coat. It has been observed, however, that "hot-dip" zinc coats are quite resistant to the action of boiling distilled water and are not undercut at pinholes or points of failure. Since thin zinc coats can be readily applied on uranium by hot-dipping, this method has been used to apply a zinc base coat on which copper or other metals may be plated. Heat treatment of the composite coat in lead or a fused salt bath has been tried in an attempt to reduce the porosity of the electroplate and to produce a strong bond between the electroplate and the zinc.

Clean uranium specimens weighing approximately 40 grams were dipped in zinc at about 475°C for 60 seconds. The excess zinc was removed by centrifuging and the samples were then quenched in water or oil. The oil quench gave a smoother surface than the water quench. The specimen surface was then cleaned and plated with copper in the usual way. A quite uniform composite coat from one to two mils in thickness can be applied in this way. Without any further treatment these samples have withstood the action of boiling distilled water for 192 hours before pitting and blistering were evident. Failure first occurred along the sharp edges of the samples. No serious undercutting was observed either at the uranium-zinc interface or the copper-zinc interface. Copper plates approximately one mil thick prepared in the same way without the zinc base failed in from 12 to 24 hours. The effectiveness of the copper plate on zinc-coated uranium in reducing the corrosion rate is uncertain since some "hot-dip" zinc coats have also withstood the action of boiling water for 192 hours before appreciable pitting was evident.

Attempts have been made to reduce the porosity of the copper plate by annealing in either a fused salt bath or in molten lead at temperatures both above and below the melting point of zinc (420°C). A fused salt bath consisting of an equal molar mixture of NaCl-KCl-LiCl at temperatures above 420°C undercut the entire coat in approximately five minutes. The fused salt apparently entered flaws in the copper-zinc coat and reacted with the uranium. At temperatures below the melting point of zinc, the coat was not destroyed, however, preliminary tests indicate that the corrosion resistance of the annealed coats is inferior to the unannealed coats. Some work has also been done with a fused KCl-LiCl bath containing a small amount of Cu_2Cl_2 in the hope that pores in the copper plate would be sealed as a result of the displacement and deposition of copper by the zinc base. This procedure has not

been particularly successful. The use of a lead bath anneal to improve the bonding between the copper and zinc and to seal the pores in the copper plate is being investigated.

Slug Casting into Metal Cans (O. N. Carlson and P. E. Armstrong)

1. Casting into Zirconium Cans

The experimental casting of uranium into metal cans was continued, with work in this period being devoted principally to zirconium cans.

Six drawn zirconium cans, manufactured by Bridgeport Brass, were obtained for use in this work. The cans were of one inch inside diameter with a 15-mil wall thickness. The uranium was melted by induction heating and cast into the preheated zirconium cans. Can sections of two, four, and eight inches in length were used to establish bonding temperatures.

Several pourings were made in which the conditions of bonding were varied as indicated in Table I. Having succeeded in preparing several uranium slugs canned in zirconium under varying conditions, it became necessary to evaluate them. All those examined appeared to have good bonds between the uranium and zirconium. Thermal cycling tests were carried out on sections of these to determine how they might be expected to stand up in pile tests or during beta heat treatment for grain refining. Likewise preliminary information concerning the corrosion resistance of these canned slugs was considered of importance. Before it was possible to corrosion test them, however, a capping technique had to be developed.

a. Nature of Uranium-Zirconium Bond

One characteristic of the uranium-zirconium bond area that has been discussed in previous reports is the presence of a narrow, brittle band existing in the diffusion area at the uranium-zirconium interface. This band is now believed to be the epsilon intermediate phase reported by some investigators to exist below 600°C in the uranium-zirconium binary system. Several bonded specimens which exhibited this bright phase were annealed and quenched from 1100°C. Microscopic examination showed that in these specimens the bright epsilon band had disappeared and only a clear diffusion area remained. The as-cast and quenched bond area are shown in Figures 2 and 3, respectively. The diffusion area in Figure 3 is more prominent than expected, but this feature is probably due to the greater hardness of the diffusion area. This behavior is consistent with the phase diagram. It is now believed, however, that the presence of the epsilon band does not have a particularly adverse effect upon the strength of the uranium to zirconium bond.

Table I

Casting of Uranium into Drawn Zirconium Cans
at Various Temperatures

Run	Length of Can, inches	Uranium Pouring Temp., °C	Can Preheat Temp., °C	Thermal Treatment After Pouring	Bond Condition
1	2	1250	1125	Held at preheat temp. for 2 min.	Narrow, regular bond area
2	2	1250	1225	Held at preheat temp. for 30 sec.	Wide, irregular bond area
3	2	1250	1225	Held at preheat temp. for 30 sec.	Wide, irregular bond area
4	2	1250	1250	Held at preheat temp. for 15 sec.	Penetration into Zr, clear areas in bond
5	2	1250	1250	Held at preheat temp. for 30 sec.	Deep diffusion in Zr, pronounced clear bond areas
6	4	1295	800	Furnace cooled immediately after pouring	Thin pipe down center, not sectioned
7	4	1250	1060	Furnace cooled immediately after pouring	Narrow, regular bond area
8	4	1250	1125	Furnace cooled immediately after pouring	Thin pipe down center, not sectioned
9	8	1275	935	Furnace cooled immediately after pouring	Even pipe in center, not sectioned

Figure 2

Zirconium-uranium bond area of a furnace cooled cast slug showing a bright band of epsilon phase, etched with tartaric-citric-nitric-HF-H₂O solution. X-250.

Figure 3

Zirconium-uranium bond area after annealing at 1100°C and quenching showing the absence of epsilon phase, etched with tartaric-citric-nitric-HF-H₂O solution. X-250.

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b. Thermal Treatment of Bonded Specimens

Sections of castings from the first five runs listed in Table I were thermal cycled in vacuo by induction heating in a water jacketed quartz envelope to about 700°C in one minute and radiation cooling to about 150°C in ten minutes. Each sample survived ten of these cycles without evidence of bond failure.

Further cycling tests were conducted on sections from runs 3 and 7 (Table I). The sections were very rapidly induction-heated to about 700-750°C and water quenched. Sections of run 7 failed by bond separation after one cycle, while the section from run 3 survived three such cycles without separation. Additional tests of this nature are planned.

c. Capping and Corrosion Testing of Canned Slugs

A variation of the method of weld closure described in the preceding report was used to cap specimens for corrosion testing. Previous corrosion tests have shown that the zirconium weld area should be free of uranium to assure adequate corrosion resistance. In order to prevent uranium from coming in contact with the areas to be welded a graphite ring was inserted in the top of the zirconium sleeve to a depth of one-eighth of an inch and a graphite plug was inserted to a corresponding depth in the bottom of the sleeve. The graphite inserts protected the ends against contact with the molten uranium during the casting operation. Upon removal of the graphite, a uranium-free can lip was left on both ends and welded by an inert atmosphere arc.

Corrosion tests consisted of immersion in 178°C water for periods up to 200 hours. With some of the specimens, a quick test was made initially in boiling ten per cent nitric acid. The results of these tests are given in Table II. No weld failures were observed. All corrosion failures took place in the zirconium can wall.

While the corrosion tests on this series are somewhat inconclusive one apparent conclusion can be drawn. Those specimens which had been bonded at temperatures above 1200°C failed in the corrosion test whereas those prepared at lower bonding temperatures stood up well. It was noted that those specimens prepared at the lower bonding temperatures failed at the bond in the thermal cycling tests whereas those prepared at the higher bonding temperatures stood up. There would thus appear to be an upper and a lower limit in the bonding conditions, the lower limit being set by the bond strength requirements and the upper limit by the corrosion resistance of the can wall. More data are needed, however, and work is continuing.

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Two of the four-inch canned slugs (runs 7 and 8 in Table I) and an eight-inch slug (run 9) were capped and tested as described above and shipped for further evaluation.

2. Casting into Uranium Alloys Cans (O. N. Carlson)

Experimental work is continuing in the casting of uranium into tubes made of the corrosion resistant uranium-niobium alloy. There are two aspects of the problem; first, preparation and fabrication of the alloy cans and secondly, determination of proper conditions to produce complete bonding of the uranium to the alloy.

Homogeneous alloys have been prepared by induction melting or arc-melting the pure metals together. A simpler and more inexpensive co-reduction method involving the bomb process has also been used to prepare low percentage alloys of niobium in uranium.

Table II

Results of Corrosion Tests on Canned Slugs

Run Number (See Table I)	<u>Bonding Conditions</u>		Corrosive Medium	Time hours	Results
	Temp. °C	Time seconds			
7	1060	1	Boiling 10% HNO ₃	24	No apparent change
			178°C water	15	No apparent change
1	1125	120	178°C water	200	No apparent change
4	1250	15	178°C water	100	Failed along can wall, not weld area
5	1250	30	178°C water	100	Failed along can wall
8	1125	1	Boiling 10% HNO ₃	21	No apparent change
			178°C water	15	No apparent change

A series of five weight per cent niobium alloys has been prepared by the addition of either niobium metal powder, niobium tetrachloride, or niobium pentoxide to the bomb charge. Chemical analyses of alloys prepared with the above additions to the bomb charge indicated that all have very nearly the desired composition. Comparison of the alloys as prepared by co-reduction using either the niobium metal powder or the pentoxide in the bomb charge revealed no differences in the physical properties. These observations indicate that niobium-uranium alloys could probably be produced by the addition of niobium pentoxide to the present production bomb charges. The five per cent co-reduced alloys all are extremely hard (Rockwell A 76) which makes machining or drilling of the alloy almost impossible. The arc-melted or gamma quenched condition is being investigated.

Fabrication of the alloy into crucibles or cans, 1/8 inch wall thickness, 5/8 inside diameter and three inches in height has been accomplished by casting in vacuo into a graphite mold as was described in a previous report. Uranium is cast into the alloy crucibles in the same type of apparatus as was used in the zirconium and niobium can experiments.

As previously reported, castings made into 7.5 per cent niobium-uranium alloy cans which had been preheated to temperatures ranging from 900°C to 1225°C in no case gave a good bond. At 1225°C the alloy can had partially melted but still did not result in a uniform bond. The formation of an oxide film at the interface of the can during the preheat period was believed responsible for the poor bonding. To overcome this difficulty the uranium was poured into cold alloy cans (300°C) and then heated to about 1175°C, a temperature just below the solidus of the 7.5% niobium alloy. The results are shown in Table III. It thus appeared that pouring

Table III

Bonding Results of Cast Uranium to 7.5% Nb-U Alloy

Run	Alloy-Can Temp. at Pouring, °C	Bonding Temp., °C	Bonding Time, min.	Nature of Bond
1	300	1180	1/2	Irregular bonding
2	300	1190	2	Same
3	300	1200	2	Same

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into the cold cans did not offer complete protection against the oxide film formation.

The next experiment was to electrodeposit a thin protective layer of copper on the alloy which was then preheated before pouring. The results are given in Table IV. At preheat temperatures

Table IV
Bonding Results of Cast Uranium to Copper-Plated 7.5%
Nb-U Alloy Cans

Run	Alloy-Can Temp. at Pouring, °C	Bonding Temp., °C	Bonding Time, min.	Nature of Bond
1	900	1180	45 sec.	Good bond, with 5 mil diffusion layer
2	850	1180	45 sec.	Same as above
3	975	1180	1 min.	Partial bonding

of 850 and 900°C followed by a short bonding time at 1180°C, a good even bond between the uranium and the alloy surface was obtained. Above 950°C the uranium-copper eutectic melts and apparently provides less protection against oxide formation as indicated in Table IV.

Further evaluation of bonding conditions and the strength of the bond is now in progress.

Alloy Studies

1. Uranium-Niobium Alloys (B. A. Rogers)

a. Preparation of Alloys

A new series of uranium-rich alloys, 0.25, 0.5, 1, 3, 5, 7, 10, and 30 weight per cent niobium, has been prepared. As before, the component metals were biscuit uranium and scrap niobium sheet-ends. The melting was done under helium in a tungsten-electrode, copper-crucible arc furnace. These alloys are being used in a

detailed examination of the part of the constitutional diagram that is related to the transformations in uranium.

In addition to the series mentioned, alloys containing 50 and 80 per cent niobium were prepared. Between these percentages, alloys are extremely difficult to make because the molten part of the alloy tends to flow away from the arc and push the unmolten portions of the charge before it.

b. Hardness of the Arc-Melted Alloys

Hardness measurements were taken on slabs cut from the arc-melted ingots. Both Rockwell and Vickers instruments were used. The results are presented in Table V.

Table V

The Hardness of Arc-Melted Uranium-Niobium Alloys

Melt No.	Niobium %	Hardness	
		Rockwell A	Vickers
M-822	0.25	58	196
M-821	0.50	63	245
M-828	1.0	72	347
M-829	3.0	71	306
M-826	4.5	63	245
M-830	5.0	62	234
M-824	7.0	62	209
M-831	10.0	64	221
M-825	30.0	67	260

c. Fabrication

Some of the uranium-niobium alloys are difficult to fabricate. A 0.5 per cent niobium alloy could be reduced 89 per cent by rolling without intermediate annealing treatments but the slab of ingot had been heated five hours at 850°C before being rolled. Preliminary heating of the 0.5 per cent alloy appeared to be beneficial but the treatment was not helpful in most instances. A three per cent niobium alloy that had been heated at 850°C could be reduced about 40 per cent by cold rolling before cracking developed. Alloys containing 15 and 20 per cent niobium were swaged hot in steel jackets but a contamination of the specimens with iron is suspected. These two

alloys were swaged cold to smaller diameters after the swaging in jackets.

An attempt was made to swage the 30 per cent alloy hot in a steel jacket. As alloying takes place between the alloy and the jacket at about 775°C , the specimen was electroplated with silver before it was jacketed. The swaging operation was conducted at 750°C . The silver coating was helpful in preventing reaction between the alloy and the jacket but the specimen was found to have cracked during the operation.

d. Determination of Melting Points

Construction of a melting point apparatus to operate in a vacuum was completed during the current quarter. It consisted of two water-cooled copper electrodes to which heavy copper clamps were attached. The specimen was then fastened between the clamps leaving a length of about 0.8 centimeter of specimen available for observation. At the center of this short length, which was narrowed locally, a small hole was drilled almost through the specimen. A pyrometer was sighted through a window on this hole and a record made of the temperature at which the hole began to fill with molten metal. The method appears to give reasonably accurate results as judged from experiments on metals of known melting point but probably is less accurate for alloys because the ease with which the metal begins to run into the hole may depend on the character of the specimen. Melting temperatures observed during heating of two alloys in a high frequency furnace tend to confirm the melting points determined by this procedure.

Results of melting point determinations on the new series of alloys are given in Table VI.

e. Dilatometric Measurements

Dilatometric measurements were made with the specimens under argon. All test pieces were one inch long cylinders cut from the cast alloys. The apparatus was constructed so that a plot of length versus temperature was obtained directly by means of an X-Y recorder. The plots show changes in slope corresponding to the alpha to beta and beta to gamma transitions and, also, changes that have not been accounted for. The data are given in Table VII with no attempt at interpretation.

f. Measurements of Electrical Resistivity

Measurements of electrical resistivity at elevated temperature have been made on 1 per cent niobium and 15 per cent niobium alloys. The specimens were maintained in a vacuum corresponding to about 2×10^{-6} or 3×10^{-6} mm. Hg. Chromel P wires were used for both

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Table VI

The Melting Points of Some Uranium-Niobium Alloys

Melt No.	Niobium %	Corrected Melting Point, °C
Biscuit	0.0	1134
M-688 (arc-melted)	0.0	1129
M-822	0.25	1140
M-821	0.50	1141
M-706	1	1154
M-829	3	1225
M-830	5	1256
M-824	7	1306
M-831	10	1337
M-825	30	1545
M-827	50	1828
M-799	80	2485

Table VII

Temperatures at which Pronounced Changes in Slope or Discontinuities Occur in Dilatometric Curves of U-Nb Alloys

Melt No.	Niobium %	Change on Heating Temperature, °C	Change on Cooling Temperature, °C
M-795	0.0	--- 661 --- 768	--- 639 --- 744
M-821	0.5	--- --- 658 ---	--- 610 --- 704
M-707	1	--- 633 657 704	633 663 768
M-708	2	--- 639 666 722	622 673 721
M-767	4.5	--- 638 663 ---	646
M-824	7	(513)* --- --- ---	574 --- --- ---
M-831	10	530 636 --- ---	545 --- --- ---
M-709	20	518 642 --- ---	614 (679)*

* Regarded with skepticism.

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current and potential leads and an Alumel lead was brought out for measurement of temperature. The leads to the 1 per cent alloy were spot welded onto the specimen. Leads to the 15 per cent alloy were fastened to tantalum sleeves that were swaged onto the ends of the specimen. Because of the danger of alloying between the leads and the alloy, measurements on the 1 per cent specimen were not made above 750°C.

The resistance-temperature curve of the 1 per cent alloy showed a definite discontinuity at about 642°C on heating and 632°C on cooling. A break appeared also in the curve of the 15 per cent alloy at 635°C on heating and a less sharp change took place at about the same or a slightly higher temperature on cooling, but the data were not as consistent as they should be.

The 1 per cent niobium alloy had a temperature coefficient of resistance of about 16.9×10^{-4} ohm/ohm deg. C in the range from 0° to 200°C.

g. The Constitutional Diagram

Figure 4 shows the outlines of a tentative diagram of the uranium-niobium alloy system as well as it can be estimated now. It does not include some results obtained in metallographic and X-ray work which need confirmation.

2. Uranium-Molybdenum Alloys (B. A. Rogers)

Resistance-temperature runs have been made on a uranium-molybdenum specimen with an intended composition of 10 per cent molybdenum-90 per cent uranium (21.6 atomic per cent molybdenum). The results indicate that the resistance of a specimen in equilibrium at low temperature increases with an increase in temperature to about 570°C and then decreases to 750°C. The decrease in resistance is gradual from 570°C to about 600°C when a rapid fall at constant temperature takes place. From 600°C to 750°C, the decrease in resistance is again gradual. A higher temperature was not used in this run because the leads alloy with the specimen at the point of attachment shortly above 750°C. The trend of the curve suggests that the specimen is still passing through a two-phase region at 750°C.

Rapid cooling of the 10 per cent molybdenum specimen does suppress the transformation from the high temperature form to a considerable degree. Reversion takes place in a matter of hours at about 450°C and presumably would proceed slowly at a much lower temperature.

3. Uranium-Zirconium-Niobium Alloys (O. N. Carlson)

An investigation of uranium-rich alloys of the uranium-zirconium-niobium system was continued with particular emphasis upon the

Figure 4

Tentative phase diagram of the uranium-rich end of the uranium-niobium system.

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effects of alloy composition and heat treatment upon the corrosion, microstructure and grain size. The series of ternary alloys containing additions of 1 to 5% niobium was gamma quenched from 850°C and then alpha annealed at 425°C for 24 hours. The anneal destroyed the gamma quenched corrosion resistance of the alloys and only the 4-4, 5-5 and 3-5% Nb-Zr alloys were intact after 91 hours in 178°C water. All other alloys of the series disintegrated completely in the test.

Data previously reported show that the quenched U-Zr-Nb ternary alloys have excellent corrosion resistance properties in 178°C water. To investigate the relative corrosion resistance of these alloys further, tests were made in 232°C and 360°C water. The results of the tests are shown in Table VIII. The corrosion rates themselves have no quantitative significance but do give some comparison of the corrosion behavior.

Microscopic examination of heat treated alloys has not revealed much concerning the nature of the ternary phase system other than indicating complex solid precipitation phenomena.

One other property which was determined was the grain size of the various alloys following different heat treatments. Photomicrographs of the alloys were compared with A.S.T.M. non-ferrous grain size charts and the grain size was estimated. From this study the average diameter of the grain for alloys containing up to 5% Nb and 5% Zr appear to be unaffected by either composition or by heat treatment. The estimated grain diameters were between 0.025 and 0.035 mm for all specimens whether alpha annealed, gamma quenched from 850°C or beta quenched from 700°C.

4. Other Uranium Ternary Alloys (O. N. Carlson)

Among the elements which have proved of interest in the preparation of corrosion resistant uranium binary alloys are zirconium, niobium, chromium, vanadium, molybdenum and nickel. Various ternary combinations of these metals were prepared by arc-melting and the results of the corrosion behavior of these alloys in boiling distilled water are shown in Table IX.

From this rather limited study it is difficult to draw definite conclusions. However, it appears that none of these combinations show particularly good corrosion resistance to boiling water.

5. Uranium-Magnesium Alloys (P. Chiotti)

Work on the uranium-magnesium system was concluded during this period. A final report, ISC-377, will be available in the near future.

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Table VIII

Corrosion of Gamma Quenched U-Zr-Nb Alloys in Water at High Temperatures

Composition, wt.%		232°C Water Test		360°C Water Test	
Zr	Nb	Time hours	Wt. Change in mg/cm ²	Time hours	Wt. Change in mg/cm ²
16.7	5	50	+114	67	disintegrated
16.7	7	50	0.000	67	-68.7
16.7	10	50	+93	67	disintegrated
9.1	7	--	----	67	-48.6
5	5	--	----	67	-55.3
5	7	--	----	67	disintegrated
5	10	--	----	67	disintegrated
10	10	--	----	67	disintegrated

The chief difficulty encountered in the study of this system was the contamination of the alloys by impurities from various crucible materials used during their preparation. This resulted in the appearance of extraneous phases in the microstructures. The use of high purity magnesia to which 10 weight per cent MgF_2 was added proved to be a satisfactory crucible material. These crucibles were non-porous to magnesium-rich melts over the temperature range studied.

No intermetallic compounds are formed in this system. The two metals are practically immiscible in the temperature range between room temperature and 1255°C. The solubility of uranium in magnesium was determined by heating the two metals in contact with each other in magnesia crucibles to the desired temperature, quenching, and then analysing the magnesium-rich portion for uranium content. Heating was done under three atmospheres of helium pressure. Magnesium was also sealed inside small uranium bombs for solubility determinations at temperatures below the melting point of uranium.

The compositions of the two liquids that co-exist under a pressure of three atmospheres at 1150°C are approximately 0.16

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Table IX

Corrosion of Miscellaneous Uranium Ternary Alloys

Composition Wt. %	Heat Treatment	Test Conditions	Wt. Change mg/cm ²
5% Zr-1% Cr	Alpha annealed 20 hours at 400°C	Boiling Dist. H ₂ O for 48 hrs.	-28.2
5% Zr-2% Cr	Alpha annealed 20 hours at 400°C	Boiling Dist. H ₂ O for 48 hrs.	-46.4
10% Zr-2% Cr	Alpha annealed 20 hours at 400°C	Boiling Dist. H ₂ O for 48 hrs.	+ 0.53
5% Mo	Alpha annealed 20 hours at 400°C	Boiling Dist. H ₂ O for 48 hrs.	-47.3
5% Mo-1% Nb	Alpha annealed 20 hours at 400°C	Boiling Dist. H ₂ O for 48 hrs.	+ 0.2
3% Mo-2% Nb	Alpha annealed 20 hours at 400°C	Boiling Dist. H ₂ O for 48 hrs.	- 2.6
1% Nb-1% Cr	Alpha annealed 20 hours at 400°C	Boiling Dist. H ₂ O for 48 hrs.	- 0.39
5% Nb-2% Cr	Alpha annealed 20 hours at 400°C	Boiling Dist. H ₂ O for 48 hrs.	-12.7
2% V-0.25% Ni	Alpha annealed 20 hours at 400°C	Boiling Dist. H ₂ O for 48 hrs.	- 1.51
1% V-0.5% Ni	Alpha annealed 20 hours at 400°C	Boiling Dist. H ₂ O for 48 hrs.	- 1.51
5% Zr-1% Cr	Quenched from 850°C	178°C H ₂ O for 89 hours	-423

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Table IX (Continued)

Composition Wt. %	Heat Treatment	Test Conditions	Wt. Change mg/cm ²
5% Zr-2% Cr	Quenched from 850°C	178°C H ₂ O for 89 hours	-495.4
10% Zr-2% Cr	Quenched from 850°C	178°C H ₂ O for 89 hours	- 5.3
5% Mo	Quenched from 850°C	178°C H ₂ O for 89 hours	disintegrated
5% Mo-1% Nb	Quenched from 850°C	178°C H ₂ O for 89 hours	- 2.3
3% Mo-2% Nb	Quenched from 850°C	178°C H ₂ O for 89 hours	- 95.7
1% Cr-1% Nb	Quenched from 850°C	178°C H ₂ O for 89 hours	disintegrated
2% Cr-5% Nb	Quenched from 850°C	178°C H ₂ O for 89 hours	- 0.719
2% V-.25% Ni	Quenched from 850°C	178°C H ₂ O for 89 hours	disintegrated
1% V-0.5% Ni	Quenched from 850°C	178°C H ₂ O for 89 hours	disintegrated

weight per cent uranium in magnesium and 0.004 weight per cent magnesium in uranium. The solubility of uranium in magnesium decreases to nearly 0.05 per cent at 675°C and to about 0.0005 per cent at 650°C. Uranium has little or no effect on the melting point of magnesium, and magnesium likewise has little effect on the melting point or transformations of uranium.

The final liquidus line of the magnesium-rich end of the system at three atmospheres pressure was obtained by a statistical treatment of the solubility data obtained. The analytical results of all samples known to be contaminated were discarded. The final results are given in Table X.

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Table X

Solubility of Uranium in Magnesium at Various Temperatures

Temperature °C	Weight Per Cent Uranium
650	0.0005
660 ± 5	0.008 ± 0.006
695 ± 15	0.055 ± 0.028
775 ± 10	0.061 ± 0.024
845 ± 10	0.069 ± 0.024
920 ± 10	0.074 ± 0.026
980 ± 5	0.101 ± 0.036
1030 ± 5	0.098 ± 0.028
1090 ± 15	0.112 ± 0.065
1135 ± 5	0.124 ± 0.051
1225 ± 20	0.190 ± 0.040

6. Zirconium-Zinc System (P. Chiodi)

Effort during this period has been confined principally to the preparation and interpretation of alloys in the composition range of 6 to 50 weight per cent zirconium. The high vapor pressure of zinc at the melting temperature of these alloys has presented some difficulties. Two methods have been used in preparing the alloys, namely, the bomb reduction method using zirconium tetrafluoride with calcium as the reductant, and by heating the constituent metals in magnesia crucibles sealed in stainless steel bombs to near 1100°C. Alloys prepared by the bomb reduction method show evidence of liquid immiscibility in the composition range of 20 to 40 weight per cent zirconium. Alloys prepared by heating zirconium and zinc in magnesia crucibles have not thus far confirmed the existence of two liquid phases. The alloys prepared by bomb reduction are being analysed for calcium on the supposition that it may be responsible for the conflicting results observed.

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X-ray diffraction data indicate that the compound $ZrZn$ has the cesium chloride type structure. The other two compounds have not been obtained in pure form and their composition is uncertain. Powder diffraction data show that they have rather complex structures.

Physical Properties of Metals

1. Thermal Conductivity of Metals by a Steady State Method (G. C. Danielson)

The apparatus for the measurement of the thermal conductivity of metals by a steady state method has been completed and some preliminary measurements have been made on nickel.

Some modifications in the power supply were necessary to prevent arcing of relays which control the d.c. power to the furnace winding. It was also deemed advisable to replace all 120 vacuum seals with a more rugged type to eliminate leaks which frequently developed.

Pressures of 2×10^{-6} – 10×10^{-6} mm. Hg have been obtained regularly at all temperatures up to 800°C . It has been decided that Armco iron would serve better as a primary standard for making measurements than the high purity lead originally proposed because of the higher melting point of iron and the smaller spread in the reported values of conductivity.

2. Thermal Conductivity of Uranium from Diffusivity Measurements (G. C. Danielson)

The thermal diffusivity of uranium in the temperature range from room temperature to 570°C is shown in Figure 5. These measurements were made on two samples prepared from the same Hanford slug which were cooled to room temperature between successive runs. Each point in Figure 5 represents the average of three independent measurements made in succession at that temperature. The ranges of values obtained at three representative points on the curve are indicated by arrows in Figure 5. It is evident that the scatter of the points in Figure 5 is greater than would be expected from the measurement error. This indicates that the thermal diffusivity of uranium is to some extent determined by the previous thermal history of the sample.

The electrical resistivity of uranium was measured in conjunction with the thermal diffusivity measurements. These results, shown in Figure 6, are in good agreement with recent measurements by Bennett.¹

¹W. D. Bennett, "The Electrical Conductivity of Uranium", NP-3714 April, 1952.

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Figure 5

Thermal diffusivity of uranium.

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Figure 6

Electrical resistivity of uranium.

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The thermal conductivity (K) can be calculated from the thermal diffusivity (k), specific heat (c) and density (d) using the relation $K = kcd$. If one assumes free electron theory the thermal conductivity can also be calculated from the Wiedemann-Franz ratio and the electrical resistivity using the relation $K = 2.45 \times 10^{-8} T/\rho$ where T is the absolute temperature and ρ is the electrical resistivity. The results of these two calculations for uranium are shown in Figure 7.

According to Hume-Rothery¹ and others the thermal and electrical conductivities of a metal are related according to the equation $K = 2.45 \times 10^{-8} \sigma T + \beta$ where K is the thermal conductivity in watts/cm °C, σ is the electrical conductivity in ohm⁻¹ cm⁻¹, T is the absolute temperature and β is the lattice contribution to the thermal conductivity. Figure 7 indicates that below 400°C uranium exhibits little or no lattice conductivity. Above 400°C, Figure 7 shows a very large lattice conductivity.

The data shown in Figures 5 and 7 are considered to be reliable from room temperature to 400°C. Above 400°C there is a possibility that the abnormally large values of thermal diffusivity are caused by a temperature gradient in the furnace used to provide the ambient temperature for the measurements. However, as indicated in Figure 5 essentially the same results were obtained when the sample was inverted. Since the temperature gradients for the inverted sample were not the same as for the previous runs it does not seem likely that this caused the large values of thermal diffusivity.

Measurements of the thermal conductivity of uranium by Babbitt et al.² also indicate a large lattice conductivity in the temperature range above 400°C. The increase in thermal diffusivity in this temperature range was very similar to the increase in thermal conductivity reported by Babbitt. Thermal diffusivity values, like the thermal conductivity values reported by Babbitt, were not reproducible but tended to become slightly greater with successive measurements.

Additional thermal diffusivity measurements will be made in the temperature range above 400°C in a gradient-free furnace to determine if the gradient present in the furnace now being used could possibly be responsible for the large increase in the thermal diffusivity. These measurements will be extended above the transformation temperature in order to determine whether the high thermal diffusivity persists in the β phase.

No significant experimental progress has been made in the investigation to determine whether thermal diffusivity measurements

¹W. Hume-Rothery, The Metallic State. Oxford Univ. Press, London, 1931.

²J. D. Babbitt, T. M. Dauphinee, L. D. Armstrong, and W. Peria. Thermal Conductivity of Metals at High Temperatures. II. Thermal Conductivity of Uranium: A Preliminary Study. CRR-438. December 16, 1949.

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Figure 7

Thermal conductivity of uranium.

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can be used to measure the heat transfer characteristics of metal-metal junctions. A theoretical analysis of this problem is under way.

3. Thermal Conductivity and Tensile Properties of Slug Materials (G. Murphy)

Values of the thermal conductivity of uranium obtained from specimens cut from slugs indicate an average value of about 0.055 cal/cm-sec-deg. C at room temperature and an increase of about 0.016 per 100°C temperature differential in the 0-500°C range. The room temperature value agrees with values given in the literature but the rate of increase with increasing temperature is markedly higher than other data reported in the literature.

Tensile properties of the material in slugs have been evaluated at temperatures up to 500°C and room temperature fatigue tests are being run.

Preparation of Niobium Metal (H. A. Wilhelm)

The use of a mixture of calcium and aluminum for the bomb reduction of Nb_2O_5 yields biscuits of niobium-aluminum alloy. Difficulty has been encountered in removing the aluminum from the biscuit by distillation at high temperature. Biscuits have been heated at 1800 and 1900°C under vacuum for periods up to 90 minutes with apparently only partial removal of the aluminum. Chemical analyses are being made to determine the extent to which aluminum is being removed by this method. The possibility of substituting some lower boiling point metal for aluminum is being investigated.

Some progress has been made in determining the extent to which the reduction of Nb_2O_5 with carbon proceeds at various temperatures under reduced pressure. Attempts to produce niobium metal of high purity in one step by this method have been unsuccessful. This is believed to be due to the variability in the amount of CO_2 given off in the interval between room temperature and 1000°C during heating of the charge. Variation of the amount of carbon used in the charge usually results in a product containing an excess of carbon or an excess of oxygen. A two step process in which the pentoxide is reduced to a lower oxide, then analysed and then the necessary amount of carbon added to bring about final reduction to the metal is being investigated.

Production of Cast Uranium Rods (H. A. Wilhelm)

The casting of an experimental lot of uranium rods has been completed. Seven castings were made

These rods are approximately 1.45 inches in diameter and can be machined to slug size

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without further fabrication. These rods were cast by the procedure given in Report A-4045, August, 1945. The principal change in procedure was the cooling of the smoked molds under vacuum to eliminate the possibility of gases being absorbed by the mold dressing. This reduced the evolution of gas when the molten uranium was poured into the molds. Samples were taken from these castings for chemical analysis, density determination, metallographic examination, and hardness measurements.

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