Report No. BMI-1002
Metallurgy and Ceramics
(M-3679, 15th Ed.)

Contract No. W-7405-eng-92

LOW-MELTING ALLOYS FOR CAST FUEL ELEMENTS

by

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Price $ 0.25

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

May 19, 1955

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An investigation has been conducted to determine the composition of uranium-rich ternary eutectic alloys most suitable for reactor application in the as-cast condition. These determinations have been based upon metallographic examination and thermal analysis of as-cast alloys.

Of the systems studied, ternary eutectic alloys have been identified in a number of systems, at or near the following compositions: uranium-22.5 a/o chromium-2.5 a/o thorium, uranium-12 a/o silicon-3 a/o aluminum, uranium-14 a/o chromium-4 a/o aluminum, uranium-10 a/o silicon-10 a/o chromium, uranium-10 a/o silicon-2.5 a/o thorium, uranium-11 a/o silicon-4 a/o vanadium, and uranium-9 a/o silicon-6 a/o nickel.

The absence of a ternary eutectic in the uranium-rich portion of the following systems has also been established: uranium-silicon-iron, uranium-vanadium-iron, uranium-chromium-vanadium, and uranium-vanadium-thorium.

A brief investigation of uranium binary systems has established the uranium-silicon eutectic composition as 8.6 a/o silicon. Data have also been obtained on the uranium-aluminum, uranium-copper, uranium-iron and uranium-tin systems.

INTRODUCTION

The possibility of casting fuel elements for use in a power reactor has long been considered. In addition to ease of fabrication, there is considerable interest in the adaptability of such fuel alloys to pyrometallurgical processing methods.

Because of the materials problems involved in processing alloys of high melting point, eutectic alloys of lower melting point than the elemental constituents offer promise for such application. However, although the uranium-chromium eutectic alloy has been studied intensively for such use, few other alloys of high-uranium composition have been investigated.

A program was therefore adopted to develop and examine uranium-rich eutectic alloys, both binary and ternary. Previous work(1)* had shown that a ternary eutectic exists in the uranium-chromium-iron system.

* References are at end of report.

The investigation was restricted to alloys of high uranium content. Eutectic compositions of a number of alloys were determined. While these compositions are not precise for every alloy, the values are sufficiently exact for preliminary studies of castability and physical properties. Selected alloys will eventually be evaluated by irradiation.

EXPERIMENTAL PROCEDURE

The determination of ternary eutectic alloys was based upon metallographic examination and thermal analysis of arc-melted alloys. Binary alloy systems were briefly investigated by these methods, also.

The ternary systems investigated were: uranium-chromium-thorium, uranium-silicon-aluminum, uranium-silicon-iron, uranium-aluminum-chromium, uranium-silicon-chromium, uranium-thorium-silicon, uranium-vanadium-silicon, uranium-vanadium-iron, uranium-nickel-silicon, uranium-chromium-vanadium, and uranium-vanadium-thorium.

The binary systems of uranium with the following metals were also studied: silicon, aluminum, copper, iron, and tin.

Alloy Selection and Preparation

Ternary alloy systems for study were selected after a brief survey of the binary systems involved. The presence of a eutectic in all three binary systems dictates a ternary eutectic of lower melting point than in the binary systems.

Selection of alloy compositions for initial study was based on phase relationships and melting temperatures in the binary systems. Where compounds appear in the binary systems, the possibility of a quasi-binary section between these compounds must be considered, particularly between compounds in the uranium binary systems. Compositions which were uranium rich with respect to such possible sections were selected. As the probability exists that a ternary eutectic will be closer in composition to the lower rather than higher melting binary eutectic, compositions were selected with this in mind, although, in general, compositions of the initial alloys prepared were varied to bracket the surfaces of primary crystallization.

On the basis of examination of these initial alloys, additional alloys were prepared to locate the ternary eutectic composition more precisely.

A few binary alloys were also selected for study. Constitutional diagrams of most of these alloys showed a eutectic at low alloy content.

Alloys were prepared from biscuit uranium, sponge thorium, and commercial-grade high-purity metals. The alloys were arc melted from five to seven times under a helium atmosphere into button form. All buttons appeared homogeneous except for those containing thorium. When these were sectioned, pieces of unreacted thorium were visible to the eye. As a result, alloys containing thorium were melted from seven to ten times to insure homogeneity.

Metallographic Examination

A quarter section of each alloy button was mounted in Bakelite, ground wet through 600-grit paper, and was polished with diamond abrasive on a wheel covered with Forstmann's cloth.

The alloys were etched with a mixture of 4 parts acetic acid and 1 part of base solution. The base solution consisted of 128 g chromic oxide dissolved in 100 cm^3 water. It was used electrolytically at 20 to 45 v.

Thermal Analysis

Heating curves were obtained by means of a 36-gage Chromel-Alumel thermocouple spot welded between two slivers of specimens. The resulting "sandwich" was wrapped in platinum foil and was heated in an electrical coil under a vacuum for transformations below 850 C, and in a furnace for transformations at higher temperatures.

As an example, a heating curve obtained on a uranium-3 a/o thorium-5 a/o silicon alloy is shown in Figure 1. This is not a precise method of determining melting points, but quickly gives data of sufficient accuracy for a study of the type reported.

RESULTS AND DISCUSSION

Upon the basis of metallographic and thermal data obtained, the existence or absence of a ternary eutectic in each of the ternary systems investigated has been established.

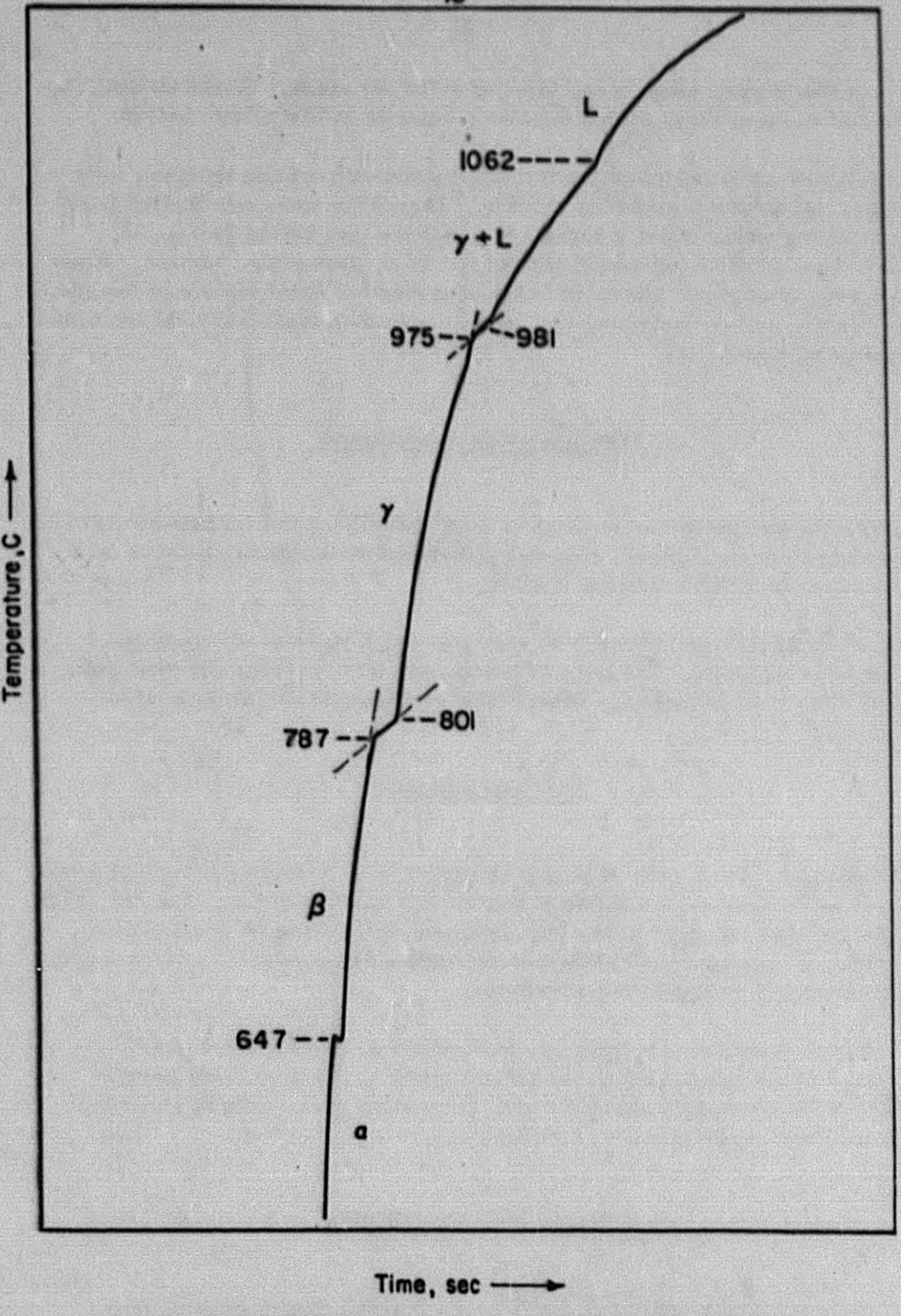


FIGURE 1. TYPICAL HEATING CURVE WITH TEMPERATURES OF TRANSFORMATION

A-14849

Metallographic and thermal data have also been obtained on uranium-rich binary alloys.

Ternary Alloys

For most of the alloy systems investigated, the exact composition of the ternary eutectic was not determined. The structures of ternary alloys which were closest in composition to a ternary eutectic, from among the alloys prepared, are shown in Figure 2. Examination of these structures will reveal that departures from the precise ternary eutectic compositions are slight, in most cases.

Uranium-Chromium-Thorium

The ternary eutectic composition in this system has been determined as uranium-22.5 a/o chromium-2.5 a/o thorium. The corresponding eutectic structure is shown in Figure 2a.

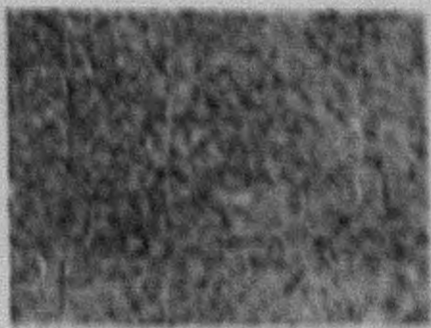
Apparently, the melting point of the uranium-chromium eutectic alloy, 860 C, is little affected by the thorium addition, the maximum amount it is lowered probably being about 10 C. All the alloys close to the ternary eutectic composition showed approximately the same melting point, all within the experimental error. As a result, the ternary eutectic composition is based primarily upon the observed metallographic structure.

Uranium-Silicon-Aluminum

A ternary eutectic exists in this system close to the composition uranium-12 a/o silicon-3 a/o aluminum. Since this alloy contains primary silicon in its structure (Figure 2b), a reduction in the amount of silicon to produce the ternary eutectic alloy is indicated. The melting point of the eutectic alloy will be about 950 C.

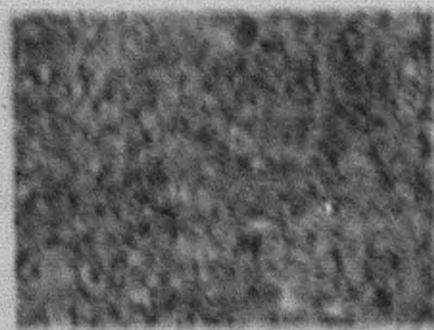
Uranium-Silicon-Iron

The presence of primary compound, U_6Fe, in all the alloys investigated in this system indicates that a ternary eutectic does not occur at the uranium-rich end of the system. Instead, a quasi-binary between U_6Fe and one of the silicon compounds probably intervenes between the uranium-rich portion of the diagram and a ternary eutectic. The structure shown in Figure 2c is that of an alloy whose composition places it on the ternary eutectic side of



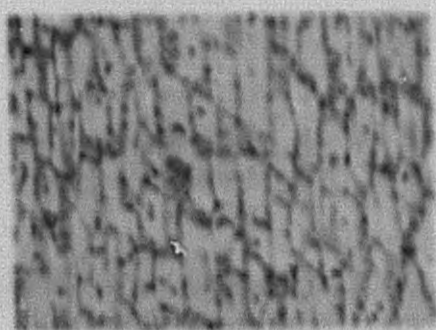
250X RM790

a. Uranium-[illegible] a/o Chromium-
2.5 a/o Thorium
Ternary Eutectic



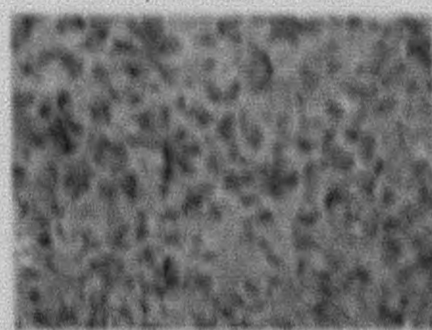
250X RM788

b. Uranium-12 a/o Silicon-
5 a/o Aluminum
Eutectic-Plus-Silicon Compound



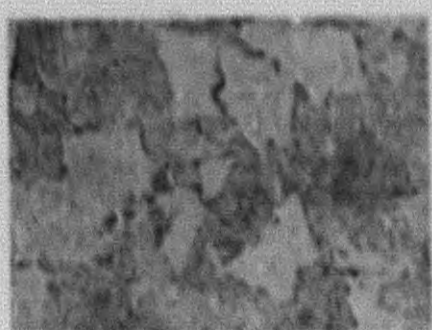
250X N17618

c. Uranium-4 a/o Silicon-
17 a/o Iron
Iron Compound-Plus-Eutectic



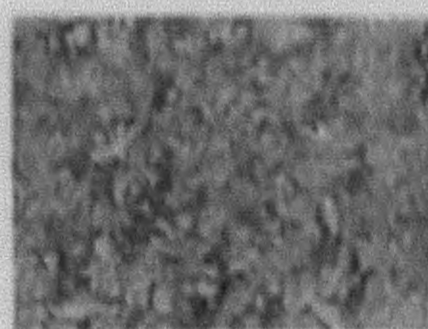
250X N18190

d. Uranium-4 a/o Aluminum-
14 a/o Chromium
Binary-Plus-Ternary Eutectic



250X N18193

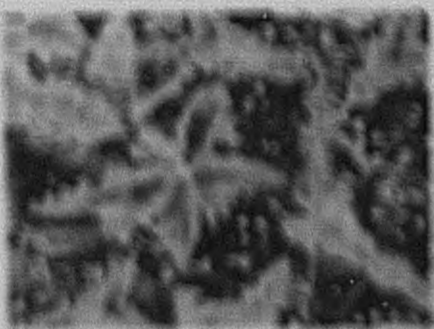
e. Uranium-10 a/o Silicon-
10 a/o Chromium
Binary-Plus-Ternary Eutectic



250X RM516

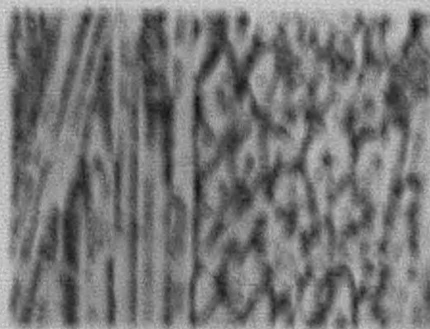
f. Uranium-2.5 a/o Thorium-
10 a/o Silicon
Uranium-Plus-Thorium-Plus Eutectic

FIGURE 2. AS-CAST MICRO-



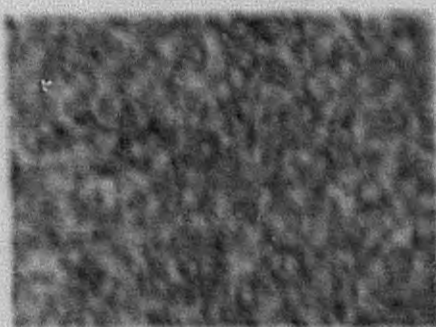
[illegible] [illegible]

g. Uranium-8 a/o Silicon-
11 a/o Vanadium
Binary-Plus-Ternary



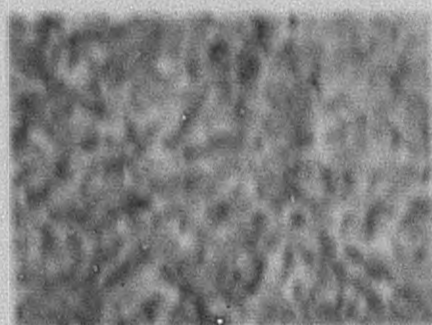
[illegible] [illegible]

h. Uranium-5 a/o Vanadium-
10 a/o Iron
Iron Compound-Plus-Eutectic



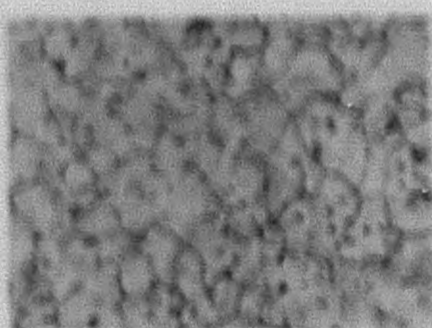
[illegible] [illegible]

i. Uranium-6 a/o Nickel-
8 a/o Silicon
Eutectic-Plus-Compound-Plus
Uranium



[illegible] [illegible]

j. Uranium-10 a/o Chromium-
9 a/o Vanadium
Eutectic-Plus-Uranium



[illegible] [illegible]

k. Uranium-13 a/o Vanadium-
1.4 a/o Thorium
Uranium-Plus-Eutectic

STRUCTURES OF TERNARY ALLOYS

this quasi-binary section. The structure consists mainly of U_6 Fe along with small amounts of eutectic. Alloys uranium-rich with respect to this section contained uranium and U_6Fe.

Uranium-Aluminum-Chromium

A ternary eutectic occurs in this system close to the composition uranium-14 a/o chromium-4 a/o aluminum. The microstructure of this alloy appears in Figure 2d. A slight increase in chromium content should result in the ternary eutectic alloy.

The uranium-chromium eutectic melting point is lowered, about 10 C, to 850 C by the aluminum addition.

Uranium-Silicon-Chromium

Examination of the structure shown in Figure 2e indicates that a ternary eutectic is located very close to the composition uranium-10 a/o silicon-10 a/o chromium. Since the melting point of this alloy was found to be higher than that of the uranium-chromium eutectic alloy, the melting point at the ternary eutectic may be expected to be about 855 C, the binary eutectic temperature of 860 C being little affected by silicon addition.

Uranium-Thorium-Silicon

The microstructures and thermal data obtained give evidence of a ternary eutectic composition in this system. The structure of the alloy closest to this composition, shown in Figure 2f, consists of uranium-2.5 a/o thorium-10 a/o silicon with a melting point of 965 C, about 25 C lower than the melting point of the uranium-silicon eutectic alloy.

The presence of both primary uranium and primary thorium in this alloy points up the difficulties encountered in insuring complete solution of thorium in the melt. Thorium has a much higher melting point than the other constituents of this alloy. In addition, uranium and thorium show a great range of liquid immiscibility, which tends to promote segregation in the melt.

Uranium-Vanadium-Silicon

A ternary eutectic occurs in this system close to a composition of uranium-4 a/o vanadium-11 a/o silicon. An alloy of this composition is shown in Figure 2g. The structure consists of duplex eutectic surrounded by ternary eutectic. The ternary eutectic melts at about 955 C, 35 C below the melting point of the uranium-silicon eutectic.

Uranium-Vanadium-Iron

The structures obtained in this system are similar to those found in the uranium-silicon-iron system. One of the structures is shown in Figure 2h. Primary U_6Fe was found in all the structures examined. A ternary eutectic probably exists in this system, but at an intermediate- or low-uranium composition.

Uranium-Nickel-Silicon

A ternary eutectic appears to exist at the high-uranium end of this system. The structure shown in Figure 2i, containing uranium-9 a/o silicon-6 a/o nickel, is that of a fairly homogeneous eutectic with a small amount of primary phases present. Since this alloy has a much higher melting point than that of the uranium-nickel eutectic, 920 compared to 740 C, a quasi-binary between uranium and some intermediate compound in the nickel-silicon, or in the ternary system itself, must exist. This would permit a ternary eutectic in the silicon-rich portion of the system. Metallographic and thermal data obtained on specimens of other alloy compositions appear to support this possibility.

Uranium-Chromium-Vanadium

No evidence for the existence of a ternary eutectic in this system was obtained. Instead the data indicate a eutectic trough, sloping gently from the vanadium to the chromium binary eutectic. The composition of the alloy whose structure is shown in Figure 2j, falls close to the eutectic trough. It melts over the range 875 to 970 C.

Uranium-Vanadium-Thorium

A ternary eutectic can be expected in this system but the data obtained do not indicate that one will be found near the uranium-rich end of the system. It appears that the eutectics of the uranium binary systems slope down toward the vanadium-thorium rich portion of the system.

Binary Alloys

The uranium-silicon eutectic occurs at a composition of 8.6 a/o silicon and at a temperature of 990 C. The eutectic structure is shown in Figure 3a.

The exact composition of the uranium-copper and uranium-aluminum eutectic alloys could not be determined metallographically because small amounts of second phase appeared in the alloys. Structures are shown in Figures 3b and 3c. However, since the melting points of these alloys are little affected by small variations in composition, it is not essential to know the exact compositions for casting studies. The eutectic temperatures were found to be 1105 and 1080 C for the aluminum and copper alloys, respectively.

Both the iron and tin alloys, Figures 3d and 3e, show structures in which uranium is outlined by an intermetallic compound. This type of structure does not suggest desirable mechanical properties for use in the as-cast condition. The melting point of uranium is little affected by small amounts of these additions.

CONCLUSIONS

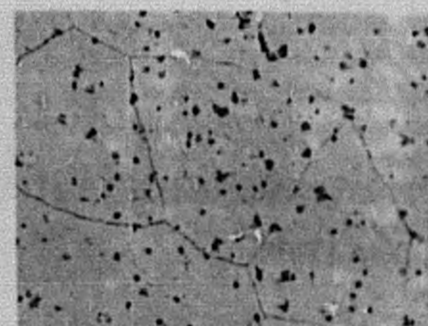
Upon the basis of metallographic and thermal data, the existence of a ternary eutectic in the uranium-rich portion of the following systems, at or near the following compositions, has been established: uranium-22.5 a/o chromium-2.5 a/o thorium, uranium-12 a/o silicon-3 a/o aluminum, uranium-14 a/o chromium-4 a/o aluminum, uranium-10 a/o silicon-10 a/o chromium, uranium-10 a/o silicon-2.5 a/o thorium, uranium-11 a/o silicon-4 a/o vanadium, and uranium-9 a/o silicon-6 a/o nickel. All of these alloys are considered as potentially useful as fuel alloys in the as-cast condition.

The absence of a ternary eutectic in the uranium-rich portion of the following systems has also been established: uranium-silicon-iron, uranium-vanadium-iron, uranium-chromium-vanadium, and uranium-vanadium-thorium. The problems encountered in casting alloys which melt over a temperature range rather than at a single temperature do not indicate that uranium-rich alloys in these systems can be considered for as-cast applications.

An investigation of uranium binary systems rules uranium alloys of low tin and iron content out of consideration for use in the as-cast condition on the basis of microstructure. Alloys of uranium with silicon, aluminum or copper are potentially useful in the as-cast condition. The uranium-silicon eutectic composition has been located at 8.6 a/o silicon.

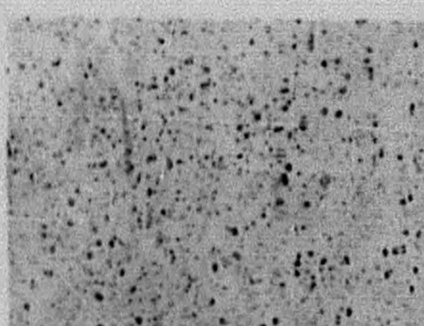
250X N15011

a. Uranium-8.6 a/o Silicon



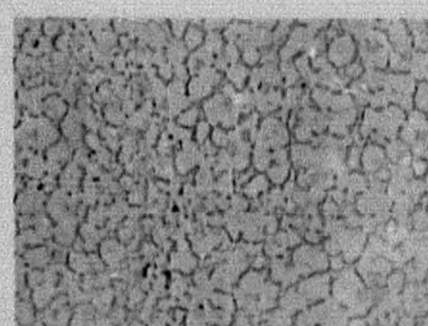
250X N13439

b. Uranium-5 a/o Aluminum



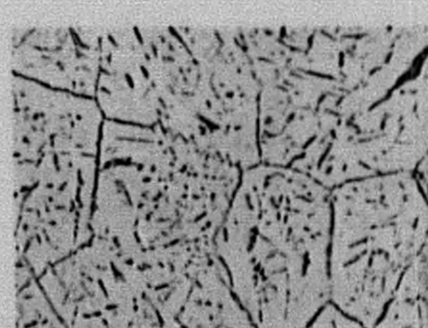
250X N13458

c. Uranium-6 a/o Copper



250X N13441

d. Uranium-2.5 a/o Iron



250X N13443

e. Uranium-2.5 a/o Tin

FIGURE 3. AS-CAST MICROSTRUCTURES OF BINARY ALLOYS

REFERENCES

(1) Saller, H. A., Rough, F. A., and Bauer, A. A., "Ternaries of the Eutectic Uranium-Chromium Alloy", BMI-868 (September 21, 1953).

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