

AECD - 2683

UNITED STATES ATOMIC ENERGY COMMISSION

THE ALLOY SYSTEMS URANIUM-ALUMINUM AND URANIUM-IRON

by

Paul Gordon
A. R. Kaufmann

Massachusetts Institute of Technology

Date Declassified: August 26, 1949

Issuance of this document does not constitute
authority for declassification of classified
copies of the same or similar content and title
and by the same author.

Technical Information Division, ORE, Oak Ridge, Tennessee
AEC, Oak Ridge, Tenn., 2-20-50--650-A10228

This document is
PUBLICLY RELEASABLE
Hugh Kinser
Authorizing Official
Date 1/23/06

DISCLAIMER

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

DISCLAIMER

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

THE ALLOY SYSTEMS URANIUM-ALUMINUM AND URANIUM-IRON*

By Paul Gordon† and A. R. Kaufmann‡

INTRODUCTION

The large-scale manufacture and use of uranium in conjunction with the atomic energy development during the war led to a need for knowing the equilibrium diagrams of uranium with various other metals. The alloys of uranium with aluminum and with iron were among the first that were studied for this purpose. Much of the work was done in the manner of a survey since the need was to determine the important features of the phase diagrams rather than to obtain completely detailed results. For this reason no attempt was made to locate exactly such features as liquidus lines, solid solubility limits, and compound and eutectic compositions. It is believed, however, that there are no great inaccuracies in the diagrams reported here and that no important points were overlooked.

Earlier work on alloys of uranium with aluminum and iron is almost nonexistent and in each case is considered to have been of little value by M. Hansen.¹ It is interesting to note, however, that the compound UAl_3 was first reported in 1902 by L. Guillet.

EXPERIMENTAL PROCEDURE

Materials

The uranium used for making most of the aluminum alloys was obtained from material prepared by Metal Hydrides, Incorporated, and melted in vacuum at Massachusetts Institute of Technology. Because of the lack of an adequate supply of metal, it was necessary to use material from several different batches and, hence, it is impossible to state an exact analysis. However, a few results indicated about 0.01 to 0.03 per cent iron and probably about 0.03 to 0.05 per cent carbon. Toward the end of the work a small amount of metal was obtained from Brown University and from Iowa State College and this was used in determining the transformations in pure metal and in some dilute alloys. All of the aluminum used in this investigation came from a supply of high purity metal (greater than 99.9 per cent aluminum) which was obtained through the courtesy of Dr. Mehl of the Carnegie Institute of Technology.

The uranium used for making the alloys with iron was produced by the bomb reduction process which has been described by J. Chipman.² This metal, after vacuum melting, contained about 99.9 per cent uranium by weight with carbon and iron as the chief impurities. Electrolytic iron containing about 0.012 per cent carbon, 0.020 per cent nickel, and 0.009 per cent copper was used in making the melts.

*This work was carried out at the M.I.T. Metallurgical Project during the year 1943 under the sponsorship of the Manhattan Project (Contract W7405-eng-175).

†Assistant Professor of Physical Metallurgy, Illinois Institute of Technology.

‡Associate Professor of Metallurgy, Massachusetts Institute of Technology.

patterns without any treatment. The uranium-rich powders usually gave a weak pattern of UO_2 , but this did not interfere with observation of the lines due to the metal. Several attempts were made to quench uranium-rich powders from about 1000°C by breaking the quartz capsule under water, but this always yielded nothing but UO_2 . Calibration of the x-ray film was done by means of tungsten lines.

Heat-Treatment of Specimens

Most of the alloys were examined as solidified but in certain cases it was necessary to heat-treat and quench. This was accomplished by sealing off specimens, which were about $1/8$ in. in diameter, in an evacuated quartz tube which was broken under water for the quench. The quartz tube was fastened to a block of nickel which served both to give a uniform temperature in the furnace and to act as a hammer for breaking the quartz.

It was found that the uranium-rich alloys would react with the quartz at temperatures above 1000°C and pick up enough silicon to alter the microstructure. In order to avoid this, the specimens were placed inside tiny cups of BeO and then sealed up as before. This technique was satisfactory up to about 1300°C , at which temperature the devitrification of the quartz became serious. A small amount of heat-treatment at temperatures up to 1400°C was carried out in an atmosphere of purified helium which was maintained under slight pressure inside a Zircofrax tube. This arrangement gave sufficient protection from oxidation to allow at least several hours heat-treatment. Some of the aluminum-rich alloys were heat-treated at 500 to 600°C for as long as a week in a vacuum of about 10^{-2} mm Hg without serious oxidation.

Thermal Measurements

After removing a portion of the ingot for metallographic examination, the remainder of the specimen was used for thermal analysis. A hole was drilled into the softer specimens to receive the thermocouple while the harder and more brittle alloys were crushed to a powder which was packed around the thermocouple. A bare thermocouple was used for some of the lower temperature measurements in the solid state, while a magnesia tube was used for protection against the uranium-rich alloys at higher temperatures and a quartz tube inside a magnesia tube was used for the high-aluminum alloys. This amount of protection was necessary because of the aluminum vapors which quickly attacked the platinum-platinum-rhodium thermocouple.

Observations were made in a resistance furnace using the inverse rate method and taking readings every 5°C , although this was sometimes reduced to 1°C . The heating or cooling rate generally was about 5 to 10°C per minute, but sometimes was as low as 1°C per minute. Several attempts were made to secure a constant rate of heating or cooling. One of these consisted of using a temperature controller and two thermocouples to maintain a constant temperature difference between the specimen and the furnace. This procedure was satisfactory in the lower ranges of temperature, but led to spurious effects above about 1200°C . A variation of the technique was to maintain the temperature difference manually instead of with a controller and this was more satisfactory since it avoided the small fluctuations due to the on-and-off cycle of the controller. Another method consisted of driving the temperature setting of the controller slowly up or down, but this again did not give a sufficiently smooth variation. The procedure which was finally adopted was simply to raise or lower the voltage applied to the furnace by increments large enough to effect a change of about 200 to 400°C in the temperature and then to conduct readings during the time that the rate of change of temperature was satisfactory. This meant a certain amount of repetition in order to get the temperature ranges to overlap but the method still was considered more satisfactory than the others.

The thermal measurements up to about 1550°C were made in the apparatus shown in Fig. 2. Most of the work was done in a vacuum of the order of 10^{-3} mm Hg, but occasionally an argon atmosphere was used. The quartz tube, which formed the vacuum chamber, was prevented from collapsing at the high temperatures by the thin graphite tube inside of it. The quartz lasted a long time at temperatures up to 1300°C , but was good for only about 10 to 20 hr at 1400°C and 2 to 4 hr at 1500°C . A few rough observations were made at temperatures above 1550°C using induction heating in the regular melting furnace and reading temperature as a function of time.

X-ray diffraction patterns of alloys with increasing aluminum content substantiate the conclusion that no additional phases exist between uranium and the compound UAl_2 . The identification of this compound as UAl_2 is based on microscopic examination of the alloys and on the crystal structure determined by x rays. Because of the difficulty with chemical analysis and inhomogeneity in the alloys the micro-examination could not fix the location to better than about ± 2 atomic per cent. The x-ray crystal structure analysis was not carried out far enough to give a unique molecular formula for the compound, but comparison of the density obtained by direct measurement with that calculated from the measured unit cell gave fairly good substantiation to the formula UAl_2 ; values of $\sin^2\theta$ using copper K-alpha radiation are given in Table 1. The lines may be indexed on a diamond cubic pattern with $a_0 = 7.74$ A. This must mean that there are 8 uranium atoms to a unit cell, since the scattering from the aluminum atoms is very small, and hence there would be 16 aluminum atoms in a unit cell if the formula UAl_2 is correct. With this number of atoms to a cell, the x-ray density is 8.38 g/cm³, while the measured density is 8.21 g/cm³. This is a fairly good check considering the experimental difficulty of getting a sound and homogeneous alloy, but the result probably is not good enough to prove the formula UAl_2 . A calculation of line intensities, which would prove this point, was not made at Massachusetts Institute of Technology.

The melting point of UAl_2 was not uniquely determined because of the difficulties encountered at high temperature. The thermal effect shown at about 1590°C is believed to be significant, but it was obtained under poor conditions using induction heating. No evidence of an appreciable solid solution range on either side of this compound was found.

The next phase on the aluminum side of UAl_2 is the compound UAl_3 , and in this case the formula has been proved to be correct by an x-ray crystal structure determination. The $\sin^2\theta$ values together with the line intensities and indices for the diffraction pattern of UAl_3 are given in Table 2. The pattern is that of a simple cube with relatively small deviation from the expected line intensities. This must mean that the uranium atoms are at the corners of a cube and, if aluminum atoms are placed at the faces of the cube, the calculated line intensities check very closely with the observed values. The lattice parameter of the cube is 4.27 A and, taking one uranium atom and three aluminum atoms to a unit cell, a calculated density of 6.8 g/cm³ is obtained. The measured density is only 6.4 g/cm³, but the disagreement with the calculated value is due to the difficulty in getting a homogeneous specimen of fairly large size.

Alloys between UAl_2 and UAl_3 show a two-phase structure with each constituent in massive form as shown in the photomicrograph, Fig. 7a. This structure, along with the clear-cut thermal data shown in Fig. 3, proves that UAl_3 forms by means of a peritectic reaction between UAl_2 and liquid. The peritectic temperature, as observed on alloys during heating, is located at about 1350°C . No attempt was made to determine the exact extent of the peritectic line into the liquid field.

A third compound, which is considered to be UAl_5 , occurs on the aluminum side of UAl_3 . The chief evidence for the existence of this compound is given by x-ray diffraction patterns and by the consistent thermal data, which indicate a peritectic reaction between UAl_3 and liquid at about 730°C (Fig. 3). The formula UAl_5 has not been definitely proved since the crystal structure has not been obtained from the x-ray diffraction pattern; the $\sin^2\theta$ values and line intensities, however, are listed in Table 3. Metallographic examination places the compound in the vicinity of UAl_5 , but again difficulties with inhomogeneity and chemical analysis precluded a more precise determination.

Cast alloys between UAl_3 and UAl_5 exhibited a rather indecisive two-phase structure which contained the two compounds in massive form in a matrix composed largely of the same two phases in a finely divided state. This microstructure persisted even after a fairly long heat treatment just below the peritectic temperature as shown in Fig. 7b. Some of this matrix probably also was aluminum due to the peritectic reaction not having gone to completion, but there was not enough of it to appear in the diffraction patterns. Thermal measurements usually gave a weak indication of the eutectic at 640°C (between UAl_5 and Al) in the alloys lying between UAl_3 and UAl_5 and this was apparently due to residual aluminum. An 80 per cent aluminum specimen which was annealed at 700°C for about a week gave only a very feeble effect at 640°C , whereas in the cast condition this thermal break had been much stronger.

begin to melt until a temperature of 975°C is reached, and it is not completely molten until 1115°C is attained.

2. The solubility of iron in alpha and beta uranium, and of uranium in alpha iron is practically negligible.

3. The gamma iron field is quite limited. Its actual extent has not been determined, but is known to be less than 0.5 atomic per cent of uranium.

4. At the uranium-rich end, there is a peritectic reaction which occurs at 815°C involving the phases gamma uranium, liquid, and U_6Fe .

5. At 770°C, a eutectoid reaction takes place between the phases gamma uranium, beta uranium, and U_6Fe . The eutectoid composition has been placed somewhat below 1 atomic per cent iron in view of the fact that specimens of the 1.0 atomic per cent iron alloy quenched from above the eutectoid temperature still show the presence of some U_6Fe in the form of globules quite a bit larger than the eutectoid particles in Figs. 10a and 10b.

6. A phase change between alpha and beta uranium appears at 675°C in the composition range between almost pure uranium and the compound U_6Fe .

7. Between the two compounds U_6Fe and UFe_2 a eutectic transformation occurs at the surprisingly low temperature of 725°C.

8. The compound UFe_2 melts at 1235°C creating an open maximum in the diagram.

9. At 1080°C another eutectic transformation appears, involving UFe_2 , gamma iron, and liquid.

10. The alpha to gamma transformation in iron occurs at about 910°C. In this case, the thermal data were somewhat inconsistent. The thermal holds obtained on the alloys containing 91.8 atomic per cent iron and above were all somewhat high. The 80.5 atomic per cent iron alloy showed the alpha to gamma break only after complete homogenizing, and even then a large spread between the thermal holds of cooling and heating appeared as indicated in Fig. 9. The microscopic evidence of this transformation was quite definite, however. Specimens of the 80.5, 91.8, and 99.0 atomic per cent iron alloys were quenched from just below and just above 910°C. The resulting microstructures for the 91.8 atomic per cent iron alloy are illustrated in Fig. 16. The Widmanstätten structure appearing in the iron phase of the specimens quenched from just above 910°C is good proof that the iron has undergone a phase change. There is some sign of very finely dispersed precipitated particles in the iron phase, which is probably a result of the alpha to gamma transformation (see Fig. 14d, 15b, and 15d).

11. The details of the diagram in the vicinity of the delta iron transformation and the melting point of iron are somewhat doubtful. It is believed that the calibration of the thermocouple used was inconsistently low in this high temperature range. The melting point of iron, the temperature of the gamma-delta transformation, and the melting point of nickel in a check run were all from 15 to 25°C lower than the standard values given for these points. The thermal points plotted in Fig. 9 for the high iron alloys at and above the gamma transformation have, therefore, been plotted higher than the experimentally determined values by an amount (25°C) sufficient to bring the melting point of iron up to the accepted value of 1535°C. In all the alloys exhibiting the gamma-delta transformation, the temperature of this reaction remains the same as in pure iron, thus signifying negligible solid solubility of uranium in delta iron.

PROPERTIES OF URANIUM-ALUMINUM AND URANIUM-IRON ALLOYS

No systematic attempt was made to determine the physical properties of the uranium-aluminum alloys, but a few observations made in the course of the phase diagram study are worthy of mention. With regard to the three intermetallic compounds it may be said that all of them are brittle enough to be readily crushed with a hammer, but that none of them is hard enough to scratch glass. The densities of UAl_2 and UAl_3 are about 8.3 and 6.8 g/cm³, respectively, while that of UAl_5 was not determined.

Table 1 — X-ray Diffraction Results for UAl_2 — Diamond Cubic Lattice: $a_0 = 7.74 \text{ \AA}$

$\sin^2\theta^*$	hkl	Line Intensity†
0.0314	111	W to M
0.0816	220	S
0.1126	311	S
0.1615	400	W
0.1922	331	M
0.2425	422	S
0.2714	511,333	S
0.3208	440	M
0.3505	531	M
0.3994	620	M
0.4305	533	M to W
0.4790	444	W
0.5088	711,551	W to M
0.5574	642	S
0.5868	731,553	S
0.6362	800	VW
0.6660	733	VW
0.7113‡	822	M to S
0.7408‡	555	M to S
0.7882‡	840	M
0.8174‡	911	M
0.8645‡	664	M
0.8940‡	931	M

* Values obtained with Cu-K alpha radiation.

† VW — Very Weak; W — Weak; M — Medium; S — Strong.

‡ Last six values obtained with Cu-K alpha₁ radiation.

Table 3—X-ray Diffraction Results for UAl_5 —Structure Not Determined

$\text{Sin}^2\theta^*$	Line Intensity†	$\text{Sin}^2\theta^*$	Line Intensity†
0.0166	W	0.3689	W to M
0.0345	W	0.3893	W
0.0454	W	0.4012	VW
0.0529	VW to W	0.4081	VW
0.0602	M to S	0.4184	W to M
0.0965	M	0.4269	W to M
0.1126	M	0.4408	VW
0.1243	VW to W	0.4948	VW
0.1255	VW to W	0.5035	VW
0.1427	VW to W	0.5245	M
0.1477	VW	0.5349	M to S
0.1615	W	0.5679	VW
0.1693	W	0.5834	W
0.1720	W	0.5954	W to M
0.1746	W	0.6039	W
0.1827	W	0.6260	W
0.1853	VW	0.6429	W
0.2033	VW	0.6595	M
0.2189	VW	0.6693	W
0.2380	S	0.6824	W
0.2500	VW	0.7254	W
0.2652	M	0.7486	W
0.2824	W to M	0.7737	W
0.2903	W to M	0.7854	W to M
0.2951	W to M	0.8078	W to M
0.3078	W to M	0.8306	W
0.3192	VW	0.8460	W
0.3290	VW	0.8692	M
0.3439	W to M	0.8864	W
0.3488	W to M	0.8983	W
0.3605	M to S		

*Values obtained with Cu-K alpha radiation.

†VW—Very Weak; W—Weak; M—Medium; S—Strong.

Table 5—X-ray Diffraction Results for U_6Fe —Lattice Structure Undetermined

$\text{Sin}^2\theta^*$	Line Intensity†
0.0807	W to M
0.0975	VW
0.1065	VW
0.1175	VW
0.1278	M
0.1949	W
0.2139	W
0.2707	VW
0.2934	W to M
0.3102	VW
0.3605	W to M
0.3765	W
0.3875	W
0.4277	W
0.4948	VW
0.5061	VW
0.5383	VW
0.5799	M
0.6961	W
0.7215	W
0.7401	W
0.7522	W
0.8125	W to M
0.8294	W to M
0.8460	W to M
0.8692	W to M
0.8830	W to M

*Values obtained with Cu-K alpha radiation.

†VW—Very Weak; W—Weak; M—Medium; S—Strong.

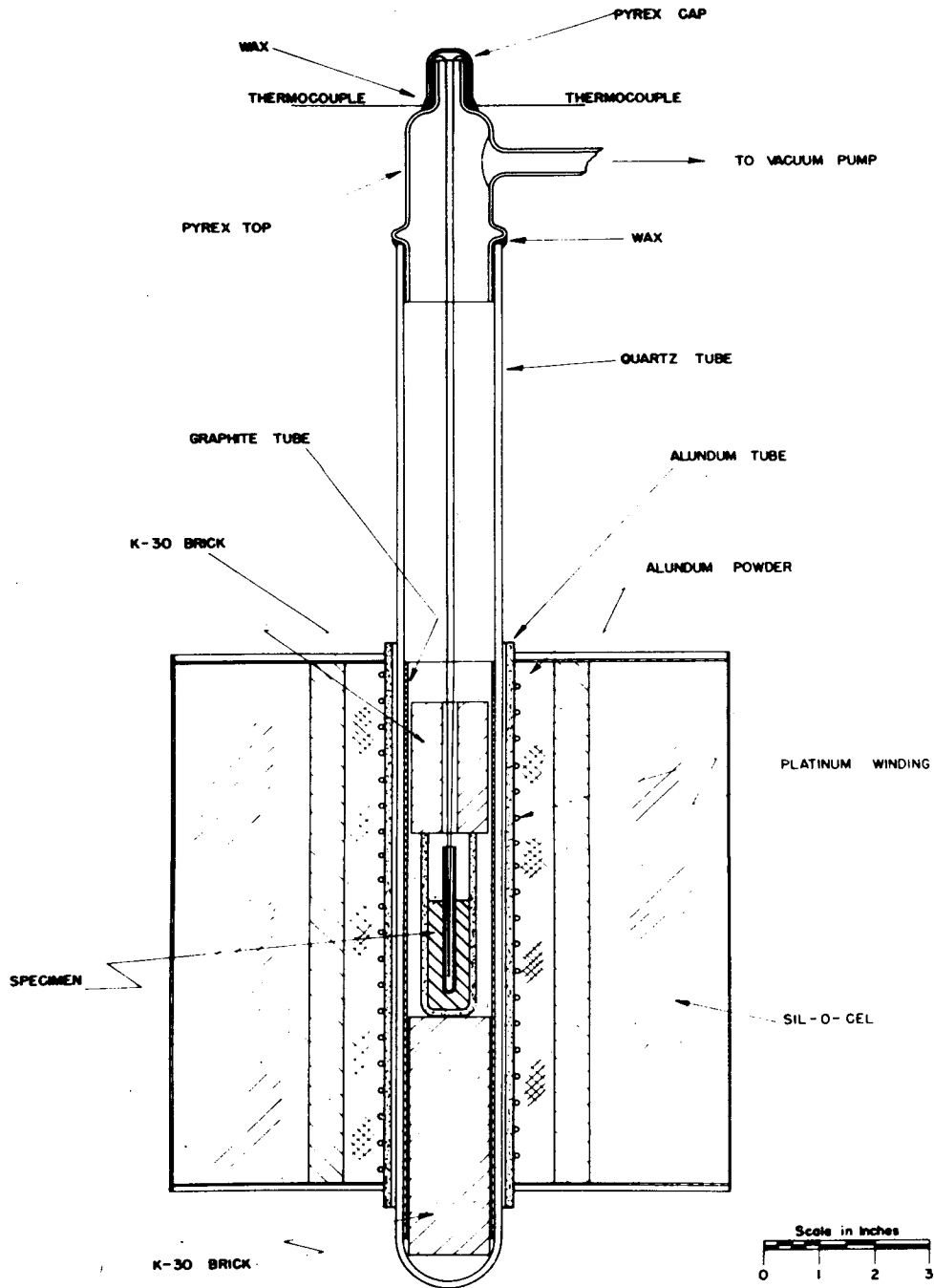
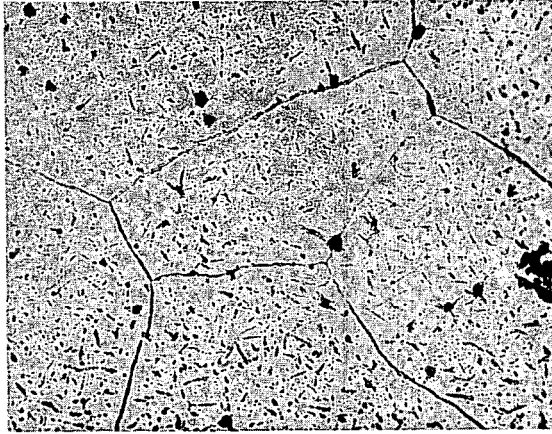


Fig. 2—Apparatus for thermal measurements.

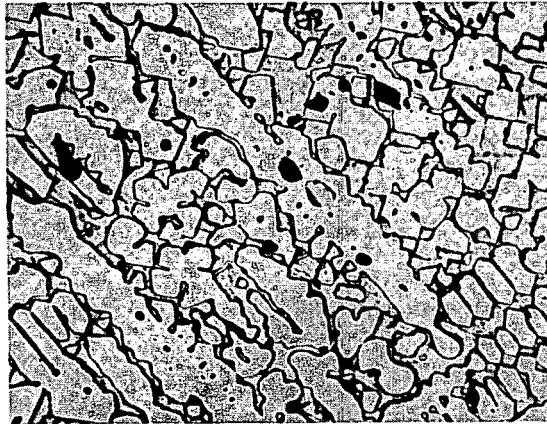


(a) 100X

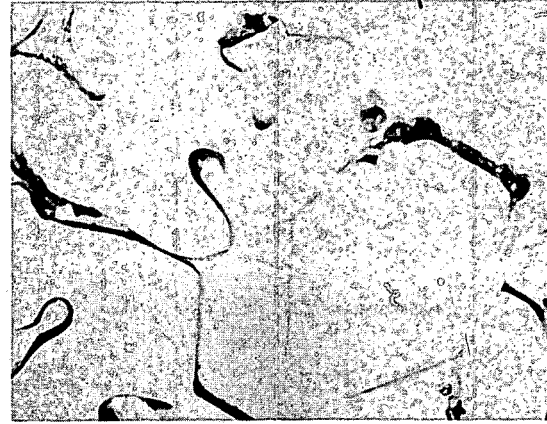


(b) 100X

Fig. 4—Microstructures of cast uranium-aluminum alloys (electrolytic etch). (a) 5 atomic per cent Al; UA_{12} at grain boundaries and within grains of uranium-rich eutectic. (b) 20 atomic per cent Al; dendritic and grain boundary UA_{12} in uranium-rich eutectic.

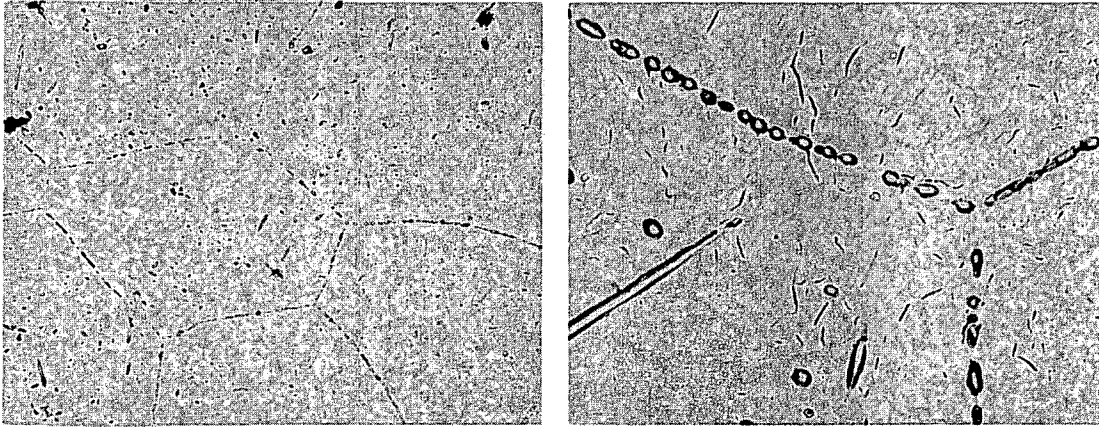


(c) 100X



(d) 500X

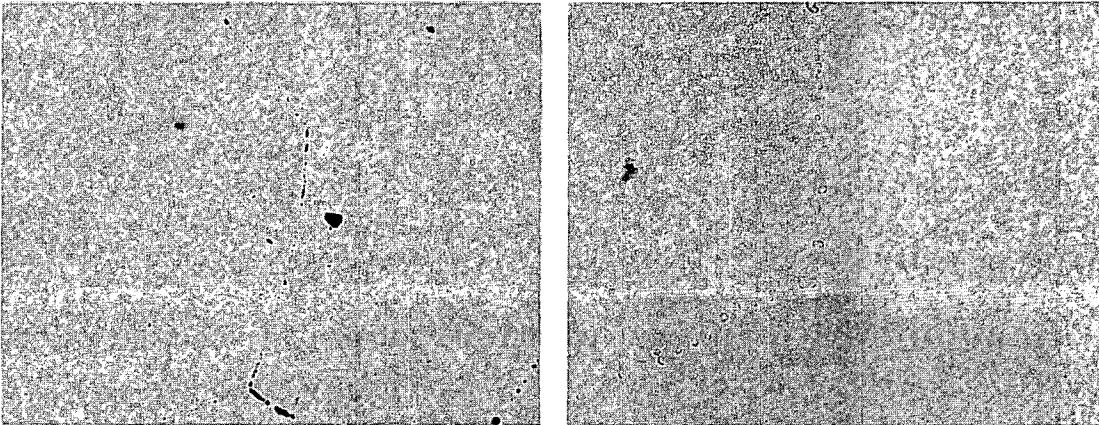
Fig. 4—Microstructures of cast uranium-aluminum alloys (electrolytic etch). (c), (d) 49 atomic per cent Al; massive UA_{12} in uranium-rich eutectic.



(a) 100X

(b) 500X

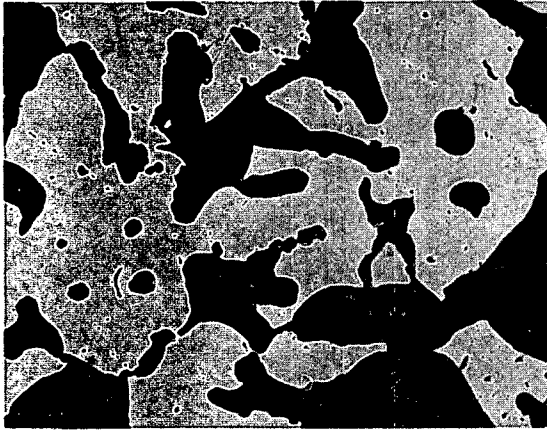
Fig. 6— Microstructures of quenched 5 atomic per cent aluminum alloy (electrolytic etch). (a), (b) Quenched from 1000°C; UAl_2 in uranium-rich matrix.



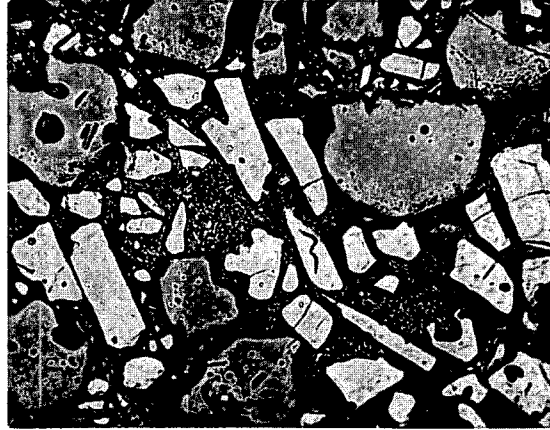
(c) 100X

(d) 500X

Fig. 6— Microstructures of quenched 5 atomic per cent aluminum alloy (electrolytic etch). (c), (d) Quenched from 1090°C; UAl_2 in uranium-rich matrix.



(a) 100X



(b) 100X

Fig. 7—Microstructures of cast uranium-aluminum alloys (1% HF acid etch). (a) 70 atomic per cent Al; massive UAl_2 and UAl_3 . (b) 80 atomic per cent Al, heated to $710^\circ C$ for 40 hr; massive UAl_3 (dark) and massive UAl_5 (light). Matrix is one or both of the two compounds finely divided.

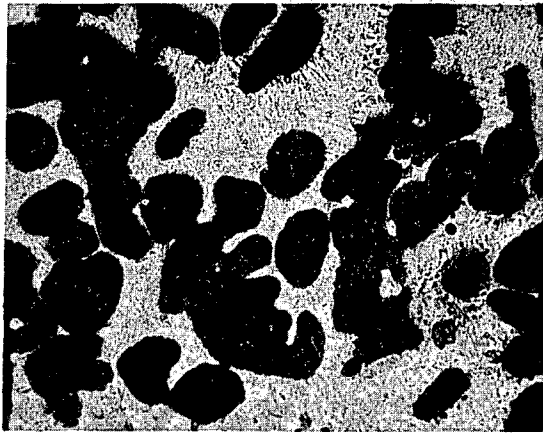


(c) 100X



(d) 500X

Fig. 7—Microstructures of cast uranium-aluminum alloys (1% HF acid etch). (c), (d) 92.5 atomic per cent Al; massive UAl_5 and coarse eutectic of UAl_5 and Al.



(a) 100X



(b) 1000X

Fig. 8—Microstructures of quenched 92.5 atomic per cent aluminum alloy (1% HF acid etch).
 (a), (b) Quenched from 750°C; massive UAl_3 in dendritic matrix of UAl_3 and Al.

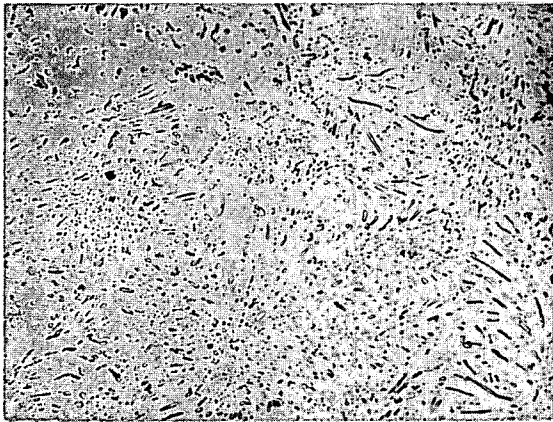


(c) 100X



(d) 500X

Fig. 8—Microstructures of quenched 92.5 atomic per cent aluminum alloy (1% HF acid etch).
 (c), (d) Quenched from 675°C; massive UAl_5 in eutectic matrix of UAl_5 and Al.

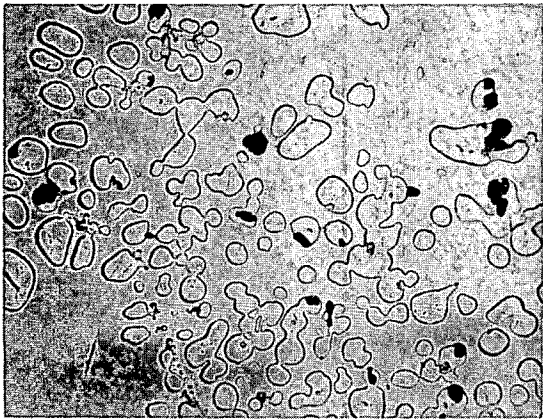


(a) 500X

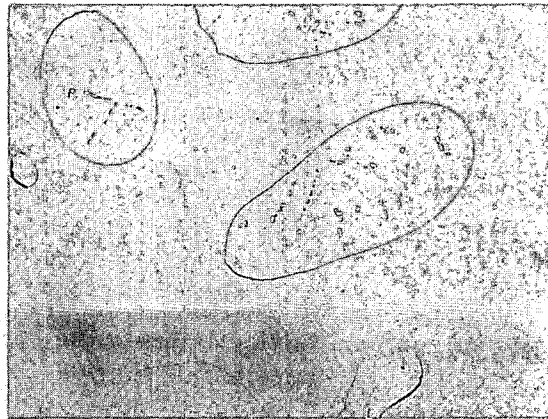


(b) 1000X

Fig. 10—Microstructures of uranium-iron alloys in the as-cast condition (electrolytic etch).
(a), (b) 1.0 atomic per cent iron; largely eutectoid of U_6Fe and U. Matrix is uranium phase.



(c) 100X

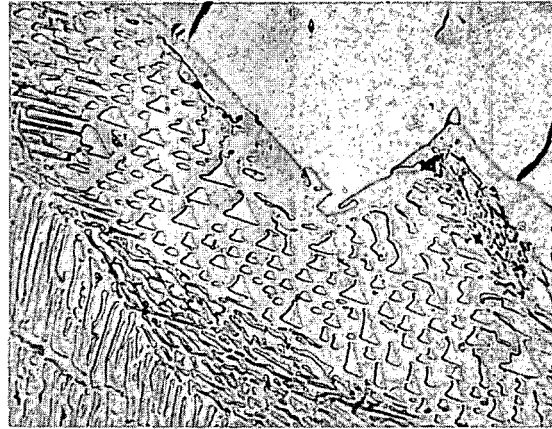


(d) 500X

Fig. 10—Microstructures of uranium-iron alloys in the as-cast condition (electrolytic etch).
(c), (d) 9.65 atomic per cent iron; peritectic structure; large globules of U in U_6Fe matrix; precipitated U_6Fe particles in U globules.



(a) 100X



(b) 500X

Fig. 12 — Microstructures of uranium-iron alloys in the as-cast condition (electrolytic etch).
 (a), (b) 39.8 atomic per cent iron; massive UFe_2 plus eutectic of UFe_2 in U_6Fe .



(c) 100X

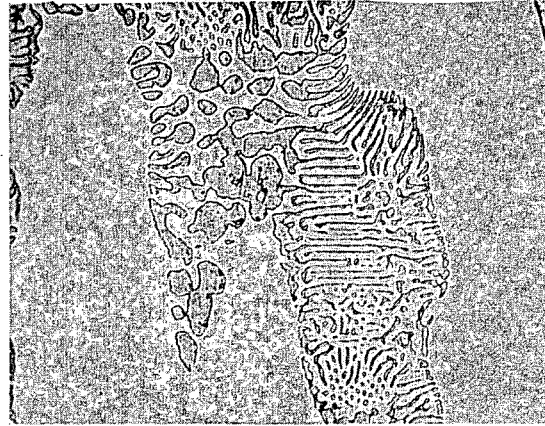


(d) 500X

Fig. 12 — Microstructures of uranium-iron alloys in the as-cast condition (electrolytic etch).
 (c), (d) 54.7 atomic per cent iron; massive UFe_2 plus eutectic UFe_2 in U_6Fe .

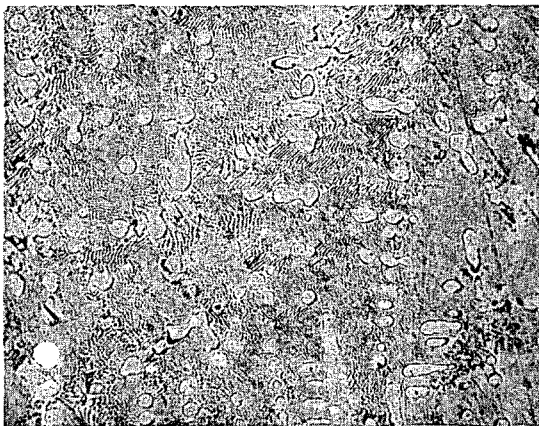


(a) 100X

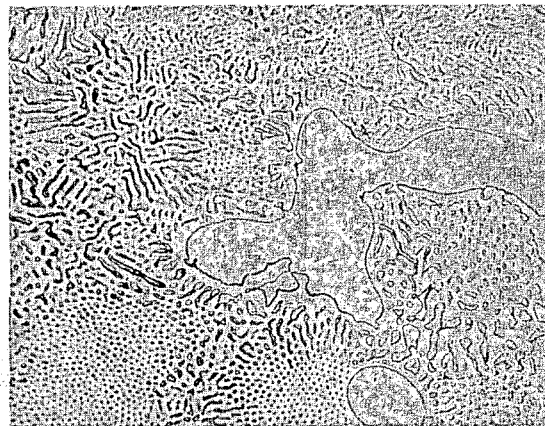


(b) 500X

Fig. 14—Microstructures of uranium-iron alloys in the as-cast condition (nital etch). (a), (b) 80.5 atomic per cent iron; massive UFe_2 plus eutectic of Fe in UFe_2 .

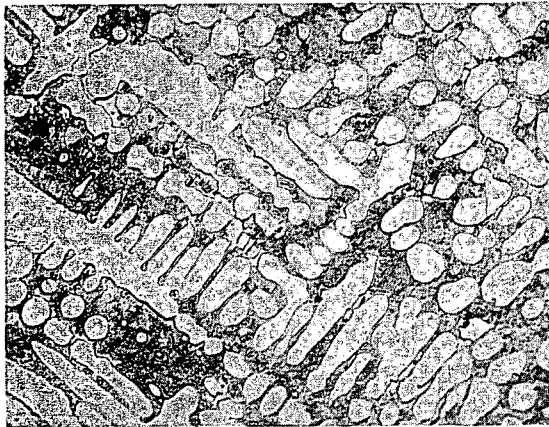


(c) 100X

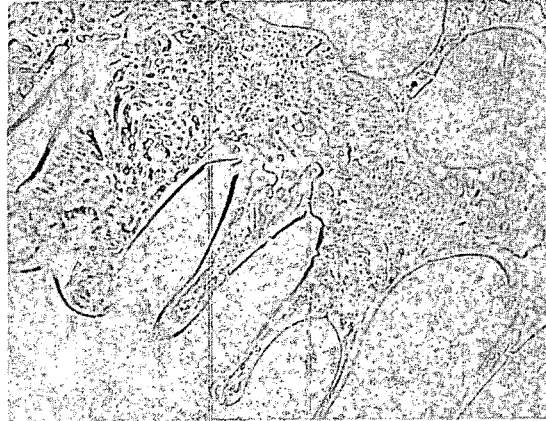


(d) 500X

Fig. 14—Microstructures of uranium-iron alloys in the as-cast condition (nital etch). (c), (d) 85.7 atomic per cent iron; massive Fe plus eutectic of Fe in UFe_2 .

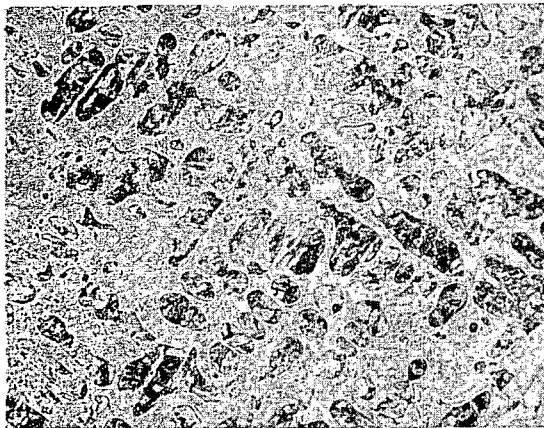


(a) 100X

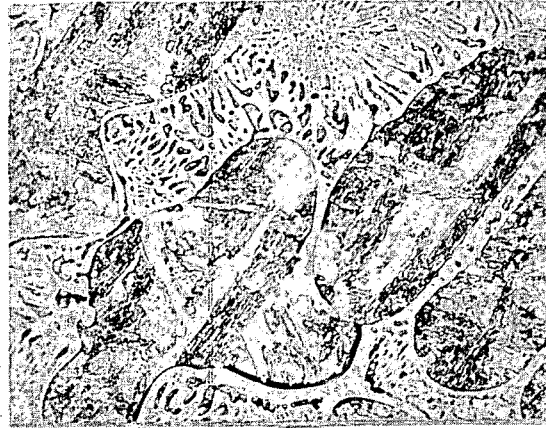


(b) 500X

Fig. 16— Microstructures of uranium-iron alloy containing 91.8 atomic per cent iron—after quenching from just below and just above the transformation temperature (910°C) for alpha to gamma iron (nital etch). (a), (b) Alloy quenched from 904°C .



(c) 100X



(d) 500X

Fig. 16— Microstructures of uranium-iron alloy containing 91.8 atomic per cent iron—after quenching from just below and just above the transformation temperature (910°C) for alpha to gamma iron (nital etch). (c), (d) Alloy quenched from 917°C . Widmanstätten structures in iron phase indicate steel has passed through the alpha to gamma transformation.