225-04
11/12/64
MCW-1487

AEC Research and Development Report

CONTRACTOR FOR U.S. ATOMIC ENERGY COMMISSION

EQUILIBRIUM STRUCTURES IN THE HIGH URANIUM-IRON ALLOY SYSTEM

MASTER

November 6, 1964

WELDON SPRING PLANT

MALLINCKRODT CHEMICAL WORKS
URANIUM DIVISION

Contract No. W-14-108-Eng-8

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MCW-1487

UC-25, Metals, Ceramics,
and Materials
(TID-4500, 34th Edition)

TOPICAL REPORT

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by

J. A. Straatmann
N. F. Neumann

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Mallinckrodt Chemical Works
Uranium Division
Weldon Spring, Missouri

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ABSTRACT

The boundaries and phase fields existing in uranium alloys containing from 400 to 5000 ppm by weight iron at temperatures from 600° to 1200°C have been determined from differential thermal, metallographic, and microprobe analyses. The phase diagram and the methods used to determine it are included as well as micrographs of the studied specimens. The retention of beta-uranium at room temperature and the occurrence of a subgrain network are also discussed and micrographs of these phenomena are shown.

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INTRODUCTION

In order that the uranium-iron alloy system be completely understood, it is essential to know the relationships that exist between these two elements in their equilibrium condition. This knowledge is necessary to the development of the proper processing and heat-treatment procedures. Previous work has been done on this alloy system,^{1,2,3,4,5,6,7} but disagreement exists as to the exact location of the solubility limits of iron in the various uranium allotropes. Through the use of two established techniques (differential thermal analysis and optical metallography) and one new technique (electron microprobe analysis), we have been able to clearly define the phase fields for the uranium-iron alloy system in the range of 400 to 5000 ppm by weight iron.

TECHNIQUES AND APPARATUS

I. Materials

The uranium-iron alloys were prepared by the thermite reduction of production-grade uranium tetrafluoride with magnesium in 4-kg laboratory-scale bombs; the iron was added in elementary form. The pure uranium metal was also made by thermite reduction, but a very pure uranium tetrafluoride was used for its preparation. The analytical data for these materials are listed in Table I.

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*Present Address: Ames Laboratory, Iowa State University of Science and Technology, Ames, Iowa.

Table ICompositions of Pure Uranium and Uranium-Iron Alloys

<u>Specimen Number</u>	<u>Chemical Analysis (ppm)^a C</u>	<u>Spectrochemical Analysis (ppm)^a</u>							
		<u>B</u>	<u>Cr</u>	<u>Cu</u>	<u>Fe</u>	<u>Mg</u>	<u>Mn</u>	<u>Ni</u>	<u>Si</u>
"Pure" U	24	< 0.10	< 4	4	18	8	2	5	16
U-Fe 4		< .10	12	6	600	10	12	26	42
U-Fe 6		< .10	12	6	800	< 10	12	25	48
U-Fe 8		< .11	10	5	1000	10	7	22	44
U-Fe 9		.10	13	9	1200	16	11	30	51
U-Fe 10		.13	12	7	1550	11	12	32	62
U-Fe 11		< .30	15	4	2100	30	15	19	100
U-Fe 12		.19	11	17	2400	24	16	28	71
U-Fe 13		.14	8	13	2600	21	8	29	57
U-Fe 14		.19	8	14	3000	14	9	30	65
U-Fe 15		.22	13	17	5000	12	10	44	100

^aAll values given in parts per million by weight.

II. Sample Preparation

Samples for microexamination were annealed for 75 hours in resistance heated furnaces, the temperature being controlled with Leeds and Northrup Series 60 controllers. Previous experience has shown that most precipitates will form or dissolve in less than 15 minutes. Microprobe analysis has shown that the 75-hour annealing time is sufficient to insure equilibrium conditions throughout the sample at the annealing temperatures utilized in this study. Verification of the control temperature was made by suspending a Chromel-Alumel thermocouple just above the specimens and obtaining the temperature by use of a Leeds and Northrup potentiometer. The furnaces were kept under a vacuum of approximately 50 microns during the entire annealing time. At the end of the annealing period, the vacuum was broken with helium and the samples were immediately water quenched.

A. Optical Metallographic Samples

The annealed samples to be viewed optically were ground with decreasing grit size through 600 grit abrasive and mechanically attack polished through alumina grade B abrasive, with chromic acid as the carrier. The samples were then given an electroetch in orthophosphoric acid at a potential of 20 volts for 20 seconds, with constant agitation of the solution. The electroetching solution was composed of:

orthophosphoric acid -- 10 volumes
ethylene glycol -- 5 volumes
ethyl alcohol -- 8 volumes

This was followed by a 3- to 5-second flashing, to remove the oxide stain caused by etching at this high voltage.

B. Microprobe Analysis Samples

Samples for microprobe analysis were mounted in a conductive resin mixture ("Diall" 1610 from Mesa Plastics Company, Los Angeles, Calif.); then they were ground and polished through alumina grade A abrasive. They were then cathodically etched in argon gas at 4×10^{-4} mm Hg for 10 minutes at 5000 volts. The etched samples were immediately transferred to the vacuum system of the microprobe for analysis.

III. Procedures

A. Differential Thermal Analysis

The transformation temperatures of "pure" uranium and uranium-iron alloys, with 1200, 3000, and 5000 ppm iron additions, were investigated by use of a differential thermal analysis (D.T.A.) apparatus. A schematic diagram of the apparatus is shown in Figure 1. The heating rate of the D.T.A. furnace was controlled at 0.5°C per minute by means of a Minneapolis Honeywell programmer. During a run the system was kept under a vacuum of approximately 50 microns. A Leeds and Northrup, Type G, X and Y recorder was used to record the temperatures of the specimens. Periodic measurements were made with a Leeds and Northrup potentiometer so that the accuracy of the recorder could be checked. The curves obtained represent the temperature difference between the uranium specimen and a reference specimen of carbon (which has no allotropic transformations). In general, the temperature difference is zero, but when a transformation occurs on heating the uranium or the uranium-iron alloy, its temperature will become constant owing to heat absorption, while the temperature of the carbon sample continues to rise. This is reflected as a dip in the D.T.A. curve. The curves for "pure" uranium and a uranium-1200 ppm iron alloy are shown in Figure 2.

B. Microprobe Analysis

A Cambridge Mark II Microscan X-ray Analyzer was used for the microprobe analysis and its operation has been reported elsewhere.⁸

Figure 1. Schematic Diagram of the Differential Thermal Analysis Apparatus.

TEMPERATURE DIFFERENCE BETWEEN URANIUM AND CARBON SPECIMENS, °C

Figure 2. Differential Thermal Analysis Heating Curves.

C. Optical Metallographic Analysis

Microexamination of individually annealed uranium-iron alloys was performed on a Bausch and Lomb metallograph. The specimens were viewed under various illuminations and magnifications to determine if iron precipitates existed at the various temperatures and concentrations studied.

DISCUSSION

The resulting uranium-iron phase diagram is shown in Figure 3. The dotted lines indicate phase boundaries that were not definitely established in this study.

I. Thermal Arrests

The thermal arrests obtained by D.T.A. are listed in Table II. The arrests obtained on heating were averaged, and these values were taken as the transformation temperatures of uranium and uranium-iron alloys, since uranium and its alloys have a negligible superheating effect at the slow heating rate utilized in this study. From observation of the results obtained on heating of "pure" uranium, it can be seen that the alpha-to-beta and the beta-to-gamma transformations agree closely with previously reported values.⁹ The arrests for the uranium-iron alloys indicate that the addition of iron lowers the alpha-to-beta and the beta-to-gamma transformations of uranium.

Table II

Thermal Arrests of "Pure" Uranium and Uranium-Iron Alloys

<u>Material</u>	<u>Run</u>	<u>Heating, °C</u>		
		<u>$\alpha \rightarrow \beta$</u>	<u>$\beta \rightarrow \gamma$</u>	<u>$\gamma \rightarrow \gamma + L$</u>
"Pure" U	1	673	769	---
	2	668	771	---
	3	675	771	---
	Average	672	770	---
1200 ppm Fe	1	666	761	---
	2	668	764	---
	3	667	763	---
	Average	667	763	---
3000 ppm Fe	1	670	765	850
	2	668	763	852
	3	667	764	848
	Average	668	764	850
5000 ppm Fe	1	667	761	805
	2	667	763	803
	3	667	760	808
	Average	667	761	805
U-Fe Alloys	Average	667	763	---

Figure 3. The Uranium-Iron Equilibrium Phase Diagram.

II. Microprobe Analysis

Microprobe analysis was performed by comparing the Fe K α emission intensity from the uranium matrix with that of the U₆Fe inclusions found in the samples. Background corrections were made from the average of measurements taken 1/2° above and below the Fe K α peak. No correction for mass absorption or fluorescence was made because the Fe concentration of the U₆Fe was reasonably close to that of the matrix. A 25-kv electron beam was used at a sample current of 2.5×10^{-7} amp. Counting times were selected such that a precision of ± 50 ppm at the 95% confidence level was achieved.

The iron content found in the uranium matrix of samples containing iron precipitates defines a point on the boundary line of the gamma-uranium and gamma-uranium + U₆Fe fields or the beta-uranium and beta-uranium + U₆Fe fields depending on the temperature of the heat treatment. By analysis of two specimens in both the gamma- and beta-uranium temperature ranges, the boundary lines between the one- and two-phase regions existing in each range can be located. The values obtained in both the gamma and beta temperature ranges are listed in Table III.

Table III

Microprobe Analysis of the Iron Content in the
Gamma- and Beta-Uranium Matrixes

<u>Material</u>	<u>Annealing Temp. °C</u>	<u>Annealing Time hr</u>	<u>Iron Content in "U" Matrix ppm</u>
U-Fe 14	797	75	2950 $\pm$ 50
U-Fe 14	780	75	2500 $\pm$ 50
U-Fe 14	774	75	2270 $\pm$ 50
U-Fe 14	750	75	845 $\pm$ 50
U-Fe 14	693	75	560 $\pm$ 50
U-Fe 14	690	75	550 $\pm$ 50

III. Optical Metallography

The disappearing-phase technique was employed for locating the boundaries between the one- and two-phase fields. All the microstructures contain small amounts of nonmetallic inclusions [UC, UN, U(C,N), U(C,N,O)], which appear even in very pure uranium metal.¹⁰ These inclusions can be recognized^{11,12} and their presence was not considered an additional phase during the microexamination.

A. Structural Shape of U₆Fe Precipitates

Figures 4, 5, 6, 7, and 8 show the changes that occur in the shape of the U₆Fe precipitates or in the liquid phase with changing temperature and iron content. These figures contain various iron alloys individually annealed at selected temperatures and then examined by optical metallography.

The photographs in Figures 4 and 5 show a uranium-5000 ppm iron alloy at temperatures ranging from the gamma-uranium + liquid field to the alpha-uranium + U₆Fe field. Figure 4a shows grains of gamma-uranium enclosed in a liquid network, the liquid region being very high in iron probably having an iron content close to that of the peritectic U₆Fe phase. Figure 4b shows a specimen heat treated at 780°C in the gamma-uranium + U₆Fe field. It contains very large globular precipitates of U₆Fe. This should be expected since the iron and uranium atoms have high diffusion rates at high temperatures. Heat treatment at a lower temperature, in the beta- or alpha-uranium + U₆Fe field, yields a network of U₆Fe precipitate throughout the uranium matrix. The U₆Fe also occurs in small rounded particles, the number of these increasing as the temperature is lowered (Figures 5a and 5b).

Figures 6, 7, and 8 contain photographs of various uranium-iron alloys in the beta-uranium + U₆Fe field at 740°C and the alpha-uranium + U₆Fe field at 660°C. From observation of the microstructures of these alloys, it can be seen that the U₆Fe precipitate in the high iron alloys occurs in the form of a network distributed throughout the uranium matrix (Figures 6a and 8a). Alloys of a lower iron content (3000 ppm Fe) reveal a pattern of elongated U₆Fe particles occurring along with small rounded U₆Fe particles (Figures 6b and 8b). Figures 6c and 8c show a uranium-2400 ppm iron alloy. The elongated U₆Fe precipitates have disappeared and all the U₆Fe occurs in small rounded particles. Below this iron content, the number of U₆Fe precipitates decreases until they finally disappear from the microstructure in alloys in the beta-phase field (Figures 7a and 7b).

B. Subgrain Boundaries Network

Examination of the iron alloys under dark field illumination revealed a subgrain boundary network in alloys quenched from the gamma-uranium temperature range. This network probably results from the rejection of iron on quenching into the beta-uranium temperature range. This

a. 5000 ppm Fe - 75 hr @ 850°C. 250X.

b. 5000 ppm Fe - 75 hr @ 780°C. 250X.

Figure 4. Gamma-Uranium + Liquid and Gamma-Uranium + U_6Fe Phase Fields.

a. 5000 ppm Fe - 75 hr @ 690°C. 250X.

b. 5000 ppm Fe - 75 hr @ 660°C. 250X.

Figure 5. U_6Fe Precipitates in Beta- and Alpha-Uranium Matrixes.

a. 5000 ppm Fe - 75 hr @ 740°C.
250X.

b. 3000 ppm Fe - 75 hr @ 740°C.
250X.

c. 2400 ppm Fe - 75 hr @ 740°C.
250X.

Figure 6. U_6Fe Precipitates at Various Concentrations
in the Beta-Uranium Temperature Range.

a. 1550 ppm Fe - 75 hr @ 740°C. 250X.

b. 600 ppm Fe - 75 hr @ 740°C. 250X.

Figure 7. The Beta-Uranium + U_6Fe and the Beta-Uranium Phase Fields.

a. 5000 ppm Fe - 75 hr @ 660°C.
250X.

b. 3000 ppm Fe - 75 hr @ 660°C.
250X.

c. 2400 ppm Fe - 75 hr @ 660°C.
250X.

Figure 8. U_6Fe Precipitates at Various Concentrations
in the Alpha-Uranium Temperature Range.

rejection of iron by the beta-uranium is due to the large difference in the solubility of iron in the two allotropes. The composition of this network should be close to the composition of the beta-uranium + U_6Fe eutectoid (1950 ppm Fe). The photographs in Figure 9 show this network in a uranium-3000 ppm iron alloy quenched from the gamma-uranium + liquid, gamma-uranium, and gamma-uranium + U_6Fe temperature ranges. Since the network is very fine, it was not possible to analyze it with the microprobe. It was not found in the iron alloys heat treated and quenched from the beta- and alpha-uranium temperature ranges.

C. Retention of Beta-Uranium

An interesting phenomenon was noted during the metallographic examination of iron alloys quenched from the gamma- and beta-uranium temperature ranges. After being ground through 600 grit abrasive, the samples were left in this condition for approximately 12 hours. The surfaces of the samples exhibited a relief structure when examined after this delay. Upon examination with polarized light, a shear-type structure of alpha-uranium needles in grains of retained beta-uranium was observed. The sample surface had undergone a transformation from retained beta-uranium to alpha-uranium. This phenomenon in iron alloys has been previously reported by a number of investigators.^{3,13,14,15} Various forms of these alpha needles can be seen in the photographs in Figures 10 and 11. These needles of alpha-uranium were observed at the edges of all the iron samples, and in certain cases could be seen throughout the entire specimen after the above mentioned heat treatment. According to J. Delaplace,¹³ the critical cooling rate for the retention of beta-uranium is 100°C per second through the beta-to-alpha transformation. It is believed that the water quench given to all the metallographic samples was faster than this critical rate, although it was not measured.

CONCLUSIONS

The following solubility limits of iron in uranium and its effect on the transformations of uranium have been established:

1. The addition of iron in high uranium alloys slightly lowers both the alpha-to-beta and the beta-to-gamma transformation temperatures of uranium.
2. At the alpha-to-beta transformation temperature (667°C), the eutectoid decomposition of beta-uranium into alpha-uranium + U_6Fe occurs at 410 ppm iron.
3. At the beta-to-gamma transformation temperature (763°C), the eutectoid decomposition of gamma-uranium into beta-uranium + U_6Fe occurs at 1950 ppm iron. The beta-uranium formed by this eutectoid reaction contains 900 ppm iron.

a. 3000 ppm Fe - 75 hr @ 960°C.
Gamma + Liquid. 250X.

b. 3000 ppm Fe - 75 hr @ 830°C.
Gamma-Uranium. 250X.

c. 3000 ppm Fe - 75 hr @ 797°C.
Gamma-Uranium + U₆Fe. 250X.

Figure 9. Subgrain Boundary Networks in Samples Quenched from Above 763°C.

a. 1200 ppm Fe - 75 hr @ 940°C.
250X.

b. 2600 ppm Fe - 75 hr @ 830°C.
250X.

c. 2400 ppm Fe - 75 hr @ 780°C.
250X.

d. 3000 ppm Fe - 75 hr @ 797°C.
250X.

Figure 10. Martensitic Alpha-Uranium Needles, Specimens Water Quenched from the Gamma-Uranium Temperature Range.

a. 2400 ppm Fe - 75 hr @ 760°C.
250X.

b. 5000 ppm Fe - 75 hr @ 760°C.
250X.

c. 600 ppm Fe - 75 hr @ 721°C.
250X.

Figure 11. Martensitic Alpha-Uranium Needles, Specimens Water Quenched from the Beta-Uranium Temperature Range.

4. The maximum solubility of iron in solid uranium is 3200 ppm iron and it occurs at 805°C, the U_8Fe -peritectic transformation temperature. Above this temperature in the gamma-uranium + liquid field, the iron content of the two phases decreases with increasing temperature.

ACKNOWLEDGMENT

The authors wish to express their appreciation to L. A. Fergason and D. L. Parker for their valuable work with the electron microprobe.

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