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THE URANIUM-TITANIUM ALLOY SYSTEM

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by

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Report BMI-774(draft)

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THE URANIUM-TITANIUM ALLOY SYSTEM

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ABSTRACT

A uranium-titanium constitution diagram is presented. There is complete solid solubility between titanium and gamma uranium above about 2100 F. Only one compound exists in the system. It has a hexagonal structure based on U_2Ti . It has a fairly wide range of stability, particularly on the titanium side. Beta-titanium solid solution decomposes eutectoidally into alpha titanium and compound at 1150 F. Eutectoid composition is about 72 atomic per cent titanium. Gamma-uranium solid solution decomposes eutectoidally at 1325 F into beta uranium and compound. Eutectoid composition is about 6 atomic per cent titanium. Beta uranium and compound react peritectoidally at 1233 F to give alpha uranium. Solubility of titanium in alpha and beta uranium is low as is the solubility of uranium in alpha titanium.

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INTRODUCTION

Earlier work⁽¹⁾ by the present authors, in collaboration with D. E. White and A. U. Seybolt of Knolls Atomic Power Laboratory, resulted in an incomplete phase diagram for the uranium-titanium system. More recently, Buzzard, Liss, and Fickle of The National Bureau of Standards presented a tentative diagram for the uranium-rich end of the system⁽²⁾. High-purity materials were used in the present re-examination of the whole system of uranium-titanium alloys.

PREPARATION OF THE ALLOYS

Melting stock for the alloys was high-purity uranium, containing about 0.09 per cent carbon as the only appreciable impurity, and high-purity iodide-process titanium purchased from New Jersey Zinc Company. Both metals were cold rolled to about 1/16-inch thickness, sheared to about 1/4-inch squares, and cleaned by pickling. The alloys were arc melted under a helium atmosphere in a water-cooled copper crucible. A thoriated-tungsten electrode was used. The furnace chamber was evacuated, then flushed with helium, prior to each melting. It was finally filled with stagnant helium at one atmosphere pressure.

Each alloy was remelted three times after the original melting, to insure homogeneity. The alloy button was turned bottom side up

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before each remelting operation. An attempt was made, with most of the alloys, to keep the ingot size the same. Therefore, ingot weight varied from 25 to 100 grams as the uranium content of the alloy increased. Some twenty-two alloys were examined. Their compositions were spaced at appropriate intervals between 100 per cent titanium and 100 per cent uranium. Analyses were made on chips taken after fabrication. The major contaminant was carbon, which varied from 0.03 to 0.08 per cent. It appeared in the microstructure as titanium carbide. Alloy compositions were calculated to a carbon-free basis for consideration on the diagram.

Tungsten and copper, possible contaminants from the melting operations, were generally less than 100 parts per million each.

FABRICATION OF THE ALLOYS

All alloys were forged and rolled to bars approximately 1/3 inch square. They were clad either in SAE 1020 steel or in a 5 per cent chromium, 3 per cent aluminum, titanium-base alloy, depending on the fabrication temperature. A temperature of 1800 F (980 C) was used for alloys near the compound composition. This necessitated using the titanium-base alloy, since iron reacts with titanium at this temperature, producing a low melting alloy. Other alloys were fabricated at 1450 F (790 C), using steel jackets. No iron-titanium reaction occurred at this temperature. The jackets were welded in place in an argon atmosphere.

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Those alloys sheathed in steel were declad and then re clad between rolling and forging operations. On the other hand, those clad with the titanium alloy were cut to a roughly rectangular shape prior to cladding and were then carried through both the forging and rolling operations without opening. Those alloys near the compound composition were found to be cracked when the cladding was removed. The cracked materials had been plastically deformed, however, and at least some of the cracking had occurred during cooling. The final diagram suggests that alloys near the compound composition could probably have been fabricated more easily at a temperature of about 2200 F (1205 C).

HEAT TREATMENT OF THE URANIUM-TITANIUM ALLOYS

The rolled bars, after being declad and shaped to remove surface contamination*, were all given an homogenizing treatment of 160 hours at 2000 F. All were heat treated at the same time in one furnace, but each was sealed in a purified argon atmosphere in an individual Vycor glass tube. Argon pressure was such that it was approximately atmospheric at temperature. Figure 1 shows a sketch of the tube. The end of the tube containing the chips was heated to 1200 F (650 C) for 10 minutes prior to the heat treatment. This purged the atmosphere of residual reactive gases. The balance of the tube was warmed during the purge to liberate adsorbed moisture and gases, which also reacted with the hot chips. The bars were furnace cooled from the homogenization treatment.

* Samples were taken at this stage for analysis.

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Specimens of each alloy were water quenched after 2 hours heating at 1000, 1200, 1400, 1600, 1800, and 2000 F (540, 650, 760, 870, 980, and 1095 C). In addition, some were treated at intermediate temperatures of 1300, 1500, and 1700 F (705, 815, and 925 C) and at 2150 (1175 C). Specimens, about 1/8-inch cubes, were cut from the bars, sealed in individual Vycor tubes, as shown in Figure 1, and heat treated as described. All specimens heat treated at the same temperature were processed together. Samples were quenched by breaking the Vycor tube rapidly under water.

METALLOGRAPHIC EXAMINATION OF URANIUM-TITANIUM ALLOYS

Specimens were mounted in bakelite and ground wet on 180-grit paper held on a 1750-rpm disc. They were then ground wet by hand, using 240-, 400-, and 600-grit papers. The rough grinding was continued long enough to get well below the surface. Specimens were mounted separately because of the variation in the rate of etching between alloys.

The specimens were polished with rouge on a 4-inch, 1725-rpm wheel covered with Miracloth.

Alloys on the titanium side of the compound composition were etched with a solution of two per cent hydrofluoric acid in water saturated with oxalic acid. A few crystals of ferric nitrate were added as a brightener. Specimens were immersed five seconds, polished to

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FIGURE 1. VYCOR PROTECTIVE TUBES FOR HEAT TREATMENT OF URANIUM-TITANIUM ALLOYS

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remove the etch, then re-etched. With the higher titanium alloys, it was often necessary to start the etch on the polishing wheel, because of the formation of a passive film. In some instances, a plain two per cent hydrofluoric etch was satisfactory.

For the alloys on the uranium side of the compound, a distinction between the compound and the uranium phases developed after standing a short time in air. This could be hastened by the application of heat, such as obtained by placing the specimen on a radiator. A deep etch was necessary to develop details in the uranium-rich phase, such as the Widmanstätten pattern sometimes obtained by quenching gamma uranium. A two per cent hydrofluoric acid solution was used for this deep etching.

Specimens were examined at 100, 500, and sometimes 2000 magnification. In most instances, pictures were taken for record purposes. Figures 2 through 10 show typical structures.

X-RAY EXAMINATION OF URANIUM-TITANIUM ALLOYS

To aid in the interpretation of microstructure, X-ray diffraction methods were used to identify phases. The best diffraction data were obtained with an X-ray spectrometer, using filtered copper radiation. The majority of the X-ray data were obtained from the polished and etched samples used for metallographic study. Because many of the samples were very coarse-grained, it was necessary to mount the specimen on a

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500X

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FIGURE 2. 100 PER CENT TITANIUM, HOMOGENIZED 160 HOURS AT 2000 F (1095 C) AND SLOW COOLED. LARGE-GRAINED ALPHA TITANIUM.

500X

850988

FIGURE 3. 70 WEIGHT PER CENT, 92.05 ATOMIC PER CENT TITANIUM, QUENCHED AFTER TWO HOURS AT 1600 F (870 C). WIDMANSTATTEN ALPHA TITANIUM WHICH HAD BEEN BETA TITANIUM AT TEMPERATURE.

500X

83764

FIGURE 4. 51.4 WEIGHT PER CENT, 84 ATOMIC PER CENT TITANIUM, HOMOGENIZED 160 HOURS AT 2000 F (1095 C) AND SLOW COOLED. LARGE-GRAINED ALPHA TITANIUM.

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500X

83779

FIGURE 5. 51.4 WEIGHT PER CENT, 84 ATOMIC PER CENT TITANIUM, QUENCHED AFTER TWO HOURS AT 2000 F (1095 C). BETA TITANIUM DEEP ETCHED TO SHOW GRAIN BOUNDARIES.

100X

83837

FIGURE 6. 31.5 WEIGHT PER CENT, 69.4 ATOMIC PER CENT TITANIUM, QUENCHED AFTER TWO HOURS AT 1400 F (760 C). BETA TITANIUM WITH RESIDUAL COMPOUND IN GRAIN BOUNDARIES AND FOUND IN THE REMNANTS OF THE EUTECTOID. THIS IS CLOSE TO THE EUTECTOID COMPOSITION.

500X

83756

FIGURE 7. 21.3 WEIGHT PER CENT, 57.4 ATOMIC PER CENT TITANIUM, HOMOGENIZED 160 HOURS AT 2000 F (1095 C) AND SLOW COOLED. COMPOUND PLUS COMPOUND-ALPHA-TITANIUM EUTECTOID.

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100X

86102

FIGURE 8. 10.8 WEIGHT PER CENT, 37.6 ATOMIC PER CENT TITANIUM, QUENCHED AFTER TWO HOURS AT 1200 F. ESSENTIALLY ALL COMPOUND.

500X

83745

FIGURE 9. 7.5 WEIGHT PER CENT, 28.7 ATOMIC PER CENT TITANIUM, HOMOGENIZED AT 2000 F (1095 C) AND SLOW COOLED. COMPOUND AND ALPHA URANIUM.

500X

86105

FIGURE 10. 2.0 WEIGHT PER CENT, 9.2 ATOMIC PER CENT TITANIUM, QUENCHED AFTER TWO HOURS AT 1400 F (760 C). WIDMANSTATTEN ALPHA URANIUM AND COMPOUND.

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goniometer and adjust the angle of incidence of the X-ray beam upon the sample in order to obtain all the reflections possible from the various phases.

The following phases were identified in the system:

1. Alpha titanium - low-temperature hexagonal phase
2. Beta titanium - high-temperature body-centered phase
3. Compound based on U_2Ti - hexagonal phase,
 $a_0 = 4.817 \text{ \AA}$, $c_0 = 2.844 \text{ \AA}$
4. Alpha uranium - low-temperature phase
5. Gamma uranium - high-temperature phase

In no case was beta-uranium identified.

DETERMINATION OF LIQUIDUS TEMPERATURES

Liquidus temperatures, for twelve of the alloys, were determined optically by observing the temperature at which the center of a $1/8 \times 1/8 \times 1/2$ -inch specimen melted. The specimens were supported on the edge of a strip of thin tantalum sheet bent to triangular shape. The determinations were conducted in an induction-heated, argon-atmosphere furnace. The readings were corrected by observing the melting temperatures of substances of known melting point. Results are given in Table 1.

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TABLE 1. LIQUIDUS TEMPERATURES OF URANIUM-TITANIUM ALLOYS

Specimen	Uranium, %		Liquidus, C(corrected)
	Wt.	At.	
Uranium	100	100	1132 $\pm$ 10
11	98	90.8	1210 $\pm$ 20
22	96.4	84.3	1230 $\pm$ 20
21	94.8	78.4	1350 $\pm$ 20
3	92.5	71.3	1370 $\pm$ 20
9	89.2	62.4	1435 $\pm$ 20
1	86.4	56.1	1465 $\pm$ 20
6	78.7	42.6	1535 $\pm$ 20
20	68.5	30.6	1555 $\pm$ 20
23	60.6	23.7	1615 $\pm$ 20
19	48.6	16.0	1625 $\pm$ 20
18	30.0	7.95	1645 $\pm$ 20
16	0.9	0.2	1685 $\pm$ 25
Iodide Ti	0	0	1725 $\pm$ 25

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URANIUM-TITANIUM DIAGRAM

Figure 11 is the phase diagram of the uranium-titanium system, based principally on the present work. The points indicate the phases believed to exist at temperatures based on the metallographic and X-ray examinations.

Since no specimens were examined in the region where alpha and beta uranium should be stable, the results of Buzzard, Liss, and Fickle⁽²⁾ are used for the beta-uranium/compound-eutectoid composition and the alpha-uranium/compound-peritectoid composition. No solid-solution phase, such as labeled "delta" by Buzzard, Liss, and Fickle,⁽²⁾ was identified metallographically or by X-ray. Instead, complete solid solubility between beta titanium and gamma uranium is indicated. At about 2100 F (1150 C), the compound U_2Ti decomposes into beta-titanium / gamma-uranium solid solution.

The higher melting points observed in the uranium-rich end of the system in the previous study⁽¹⁾ and in the work by Buzzard, et al⁽²⁾ were not verified. It is believed that the high values observed earlier on samples melted in beryllia may have resulted from the same type of film that obscured the true melting point of uranium for so long.

On the titanium side of the diagram, liquidus and solidus determinations of the previous work⁽¹⁾ with less pure material are in good agreement with present observations. They are shown in Figure 11 as triangles.

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The alpha-titanium / compound-eutectoid temperature, the alpha-uranium / compound-peritectoid temperature, and the beta-uranium - compound-eutectoid temperature are those determined in the earlier work by dilatometric and thermal means⁽¹⁾. The structure of the compound confirms that determined by X-ray in the earlier work by W. J. Tucker of Knolls Atomic Power Laboratory⁽¹⁾.

One unexpected feature of the diagram is the wide stability range for the compound, especially on the titanium side.

The complete solid solubility between gamma uranium and beta titanium is not unique. A similar condition exists in the titanium-chromium, titanium-molybdenum, and titanium-columbium systems. In the case of uranium, fifty weight per cent or eighteen atomic per cent is needed to stabilize beta-titanium on quenching. Otherwise, a Widmanstätten alpha-titanium structure is obtained. On the uranium side, three weight per cent titanium, or fourteen atomic per cent is needed to stabilize gamma uranium on quenching. Otherwise, a Widmanstätten alpha-uranium structure is obtained.

An apparent anomaly occurs in samples quenched from the gamma uranium plus compound field. All these samples gave a Widmanstätten alpha-uranium structure rather than stabilized gamma uranium. This transformation may be caused by the stress induced in the gamma-uranium phase by the compound. High-temperature X-ray studies would be desirable in this range.

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The intermediate, beta-uranium, phase was not observed in any of the structures. This seems to indicate that titanium does not stabilize this structure. However, no concentrated effort was made to study this region of the diagram. One specimen quenched from the supposed beta titanium plus compound field showed a Widmanstätten alpha-uranium structure.

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M. W. Mallett

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BIOGRAPHICAL NOTES

Murray C. Udy is Assistant Supervising Metallurgist at Battelle Memorial Institute. He received his B.S. degree in Chemical Engineering in 1938 and his M.S. degree in Metallurgical Engineering from Lehigh University. In 1939, he was awarded a Battelle fellowship at The Ohio State University. In 1941, after receiving his Ph.D. degree, majoring in Metallurgy, he joined Battelle's metallurgical staff. He has been associated with Battelle's atomic energy program since 1946.

Francis W. Boulger is Supervising Metallurgist at Battelle Memorial Institute. He was graduated from The University of Minnesota with a degree in Metallurgical Engineering. In 1936, he was awarded a Battelle fellowship at The Ohio State University, and the following year, after receiving his M.S. degree in Metallurgy, joined Battelle's staff. He has worked on many aspects of steel production and more recently has been engaged in research on titanium and zirconium.

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