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THE CONSTITUTION OF DELTA-PHASE ALLOYS OF
THE SYSTEM URANIUM-MOLYBDENUM-TITANIUM

by

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THE CONSTITUTION OF DELTA-PHASE ALLOYS OF THE SYSTEM URANIUM-MOLYBDENUM-TITANIUM

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An investigation of the phase relationships between the delta phases of the uranium-molybdenum and uranium-titanium systems was conducted by studying alloys ranging in composition from uranium-31.5 a/o molybdenum to uranium-34 a/o titanium. A ternary cut showing these phase relationships is presented upon the basis of thermal-analysis data obtained and upon the basis of metallographic and X-ray examination of heat-treated and quenched specimens. Isothermal ternary sections, inferred from phase relationships determined between the two delta phases, are presented for the uranium-molybdenum-titanium system.

In the compositional range investigated, a gamma-uranium solid solution exists at elevated temperatures. At about 900 C the delta U_2Ti phase, with limited molybdenum solubility, forms. Epsilon, a molybdenum-titanium-rich solid solution appears at the same temperature and appears in all phase regions that exist below this temperature except in the terminal delta-phase regions. The gamma phase is stable to approximately 660 C in titanium-rich alloys; the gamma and delta U_2Ti phases decompose at this temperature to alpha uranium in a peritectoid reaction. The gamma phase in molybdenum-rich alloys decomposes in an apparent eutectoid reaction, at about 593 C, to the delta-uranium-molybdenum and alpha-uranium phases. The epsilon phase, while present, presumably plays a negligible role in these reactions.

Titanium was found to markedly decrease the stability of retained gamma in these alloys. Age-hardening characteristics developed in titanium-containing uranium-molybdenum alloys quenched from 900 C and aged at 500 C are ascribed to decomposition of gamma to the alpha and epsilon phases.

INTRODUCTION

Alloys of uranium with molybdenum, titanium, and zirconium, respectively, are of great interest because of their potential use as reactor fuels. As a result, this interest extends to the constitution of these alloys, particularly in view of their uniqueness of constitution. In these systems, alone, among known uranium alloy systems, an intermediate phase forms by direct decomposition of the high-temperature gamma-uranium phase.

As a prelude to possible future alloy development, an investigation has been undertaken of the phase relationships that occur between the intermediate phases of these systems. These phase relationships have already been reported for the intermediate delta phases of the uranium-zirconium and uranium-titanium systems⁽¹⁾.

The results of an investigation of the phase relationships between the delta phases of the uranium-molybdenum and uranium-titanium systems are reported here. The phase relationships that occur in the binary systems pertinent to this investigation are shown in Figure 1. Phase nomenclature appearing throughout this report is as shown in these diagrams.

EXPERIMENTAL PROCEDURE

Alloys were cast and fabricated to flat plate. Specimens were heat treated and examined metallographically and by X-ray techniques. Thermal-analysis data and a limited amount of hardness data were obtained.

Alloy and Specimen Preparation

Biscuit uranium, high-purity molybdenum sheet, and iodide titanium were arc melted and then cast into 1/2-in. -diameter wire-bar forms. Nominal compositions of the alloys prepared are given in Table 1.

TABLE 1. URANIUM-MOLYBDENUM-TITANIUM
ALLOY NOMINAL COMPOSITIONS

Alloy	Composition (Balance Uranium), a/o	
	Molybdenum	Titanium
1	31.5	0
2	29.5	2.5
3	27	5
4	24	8
5	20	12.5
6	15	18
7	8.5	25
8	5	29
9	3	31
10	1	33
11	0	34

(1) References appear at end of report.

FIGURE 1. SOLID-STATE PORTIONS OF THE URANIUM-MOLYBDENUM⁽²⁾, URANIUM-TITANIUM⁽²⁾, AND TITANIUM-MOLYBDENUM⁽³⁾ CONSTITUTIONAL DIAGRAMS

A 3/4-in. section of each as-cast bar was removed for thermal analysis, while the remainder of the bar was fabricated to flat plate by being rolled out of a helium-atmosphere furnace at 1800 F. The majority of the alloys rolled satisfactorily at this temperature; Alloys 1, 2, and 11 cracked during fabrication.

The as-cast thermal-analysis specimens and the fabricated plate were given a homogenization treatment of 2 hr at 1095 C and furnace cooled before further study.

Thermal Analysis

The complete series of alloys were subjected to conventional differential thermal analysis at heating and cooling rates of 3 C per minute. For this purpose, 1/2-in. -deep holes were drilled in the cast homogenized wire-bar specimens for insertion of temperature measuring and differential thermocouples. Thermal data were recorded on a Brown Elektronik X-Y recorder.

Heat Treatment

On the basis of thermal data obtained, specimens were cut from the fabricated plates and given the following heat treatments:

- (1) 20 hr at 850 C and water quench
- (2) 40 hr at 800 C and water quench
- (3) 120 hr at 700 C and water quench
- (4) 3 weeks at 625 C and water quench
- (5) 4 weeks at 550 C and water quench
- (6) 4 weeks at 500 C and water quench.

In addition, selected specimens, annealed previously at 700 C, were reannealed for 24 hr at 680 C and water quenched for further examination.

A series of molybdenum-rich specimens were heat treated also for the purpose of obtaining some indication of the effect of titanium on the stability of the gamma phase of the uranium-molybdenum base alloy. These specimens were annealed for 2 hr at 900 C, water quenched, and were then transformed at 500 C for 1, 22, 100, and 500 hr. In addition to examining these specimens metallographically, Vickers hardness measurements were obtained.

Heat treatment of specimens at 800 C and above was performed in a vacuum furnace under a pressure of 10^{-4} mm of mercury or less. All other specimens were sealed in evacuated Vycor tubes for heat treatment.

Metallographic Examination

Specimens for metallographic examination were mounted in bakelite, ground wet through 600-grit paper, and polished on Forstmann's cloth with Linde B abrasive and a dilute chromic acid solution. A number of specimens were given an additional electropolish at 40 d-c volts in a solution consisting of 4 parts chromic acid (100 g CrO_3 in 118 cm^3 H_2O) and 1 part glacial acetic acid.

A number of etching techniques were investigated. The best results were obtained by electropolishing in solutions of chromic acid and glacial acetic acid in the ratios of 4:1 and 18:1 at 6 and 20 d-c volts, respectively. The chromic acid base solutions were prepared by mixing 100 g CrO_3 in 118 cm^3 H_2O and 100 g CrO_3 in 100 cm^3 H_2O , respectively.

X-Ray Diffraction Techniques

Samples for X-ray diffraction examination were prepared by sawing a section out of the heat-treated metallographic specimens, wet grinding one end of the section to a slender point, and then electropolishing this end in a solution consisting of 1 part chromic acid (100 g CrO_3 in 118 cm^3 H_2O) and 4 parts acetic acid.

All samples were examined in a 57.3-mm Debye camera with filtered iron radiation. Only the tip of the sample was exposed to the X-ray beam.

EXPERIMENTAL RESULTS AND DISCUSSION

The ternary cut shown in Figure 2 is based upon the results of this investigation and shows the relationships occurring between the uranium-31.5 a/o molybdenum and uranium-34 a/o titanium delta-phase compositions. It is idealized in some respects, since small departures from the composition line assumed may be expected to introduce additional phase regions, particularly in the vicinity of the delta phases. Also, the upper temperature limit of the gamma-plus-epsilon region is extremely sensitive to small variations in molybdenum content and may be expected to increase or decrease rapidly in temperature with small increases or decreases in molybdenum content.

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FIGURE 2. PROPOSED TERNARY SECTION BETWEEN URANIUM-31.5 a/o MOLYBDENUM AND URANIUM-34 a/o TITANIUM

Thermal-Analysis Data

Data obtained by thermal analysis are shown in Table 2. No data are shown for Alloys 1, 2, and 3 because no evidence of transformation was obtained on either heating or cooling. The metastable gamma phase is apparently retained in these alloys on cooling to room temperature and on subsequent heating to the temperature of transformation, thereby accounting for the absence of a thermal arrest. This stability of the gamma phase is also evident in the temperatures of transformation recorded on cooling in the remaining alloys, the gamma phase decomposing only after being super-cooled about 50 C.

TABLE 2. DIFFERENTIAL-THERMAL-ANALYSIS DATA

Alloy	Composition (Balance Uranium), a/o		Transformation Temperatures, C	
	Molybdenum	Titanium	Heating	Cooling
4	24	8	593	-
5	20	12.5	652	607
6	15	18	660	627
7	8.5	25	654, 821	596, 790
8	5	29	657, 855	586, 834
9	3	31	652, 863	590, 848
10	1	33	877	-
11	-	34	920	882

The only alloy that gave any evidence of the transformation of delta uranium-molybdenum to gamma was Alloy 4, a slight thermal arrest being noted at 593 C. This temperature is intermediate to the temperature of the isotherms on either side of the uranium-molybdenum delta phase. It is suggested that a slight decrease in temperature, after delta uranium-molybdenum formation, is sufficient to increase the stability of the delta phase to the point that equilibrium is reached between it and the alpha phase, thereby restricting the gamma phase and related regions.

In the titanium-rich alloys, only a single thermal arrest indicative of an isotherm was detected. The absence of a second isotherm indicates only one isothermal reaction, the alpha-to-gamma transformation, occurs in these alloys, the transformation taking place at 660 C, the beta-uranium eutectoid temperature in uranium-molybdenum alloys. The absence of a reaction involving beta uranium indicates that beta-phase regions must be restricted to high-uranium alloys.

The second thermal break noted in titanium-rich alloys occurred over a temperature range, the temperature noted being taken as the end of transformation. This thermal break varied with composition and was evidently associated with the appearance and disappearance of the delta U_2Ti phase.

Metallographic Results

Typical microstructures of heat-treated alloys are shown in Figure 3. Metallographic identification of phases present in specimens annealed at the lower temperatures was difficult because of the fineness of precipitate; thus, it was necessary to rely upon X-ray data. However, when correlated with X-ray data the microstructures were extremely useful in determining the presence of small amounts of phases that were undetectable by X-ray.

Figures 3a and 3b show the two- and three-phase structures stable at 850 C.

At 700 C, Figure 3c, three phases are found in the alloy that was two phase at 850 C. The darker etching areas contain three phases, the lighter areas two phases.

The structures, at 700 C, of the terminal-binary alloys are shown in Figures 3d and 3e. It is seen that the uranium-molybdenum binary alloy consists of two phases, gamma and epsilon, indicating that the solubility of molybdenum in gamma uranium is less than the nominal molybdenum content of 31.5 a/o.

Structures obtained at 500 C are shown in Figures 3f, 3g, 3h, and 3i. The delta uranium-molybdenum structure is shown in Figure 3f. The addition of 2.5 a/o molybdenum results in the formation of alpha and epsilon, Figure 3g. Figures 3h and 3i show the two-phase structure, alpha plus epsilon, and the three-phase structure, alpha plus epsilon plus delta U_2Ti . Fairly large epsilon particles, which precipitated during the initial homogenization treatment, appear in these last two structures.

X-Ray Diffraction Results

The results of X-ray diffraction examination of samples are given in Table 3 and in Figure 4. These show the relative intensities of the phases identified and the lattice-parameter variations in alloys quenched from 700 C.

Phase-identification data are also shown plotted in Figure 2. It must be realized that identification of phases by X-ray is limited to the major phases appearing in the specimens and that minor-phase constituents may not be detected.

500X N33787
a. Uranium-15 a/o Molybdenum-18 a/o Titanium, 20 Hr 850 C, Water Quench, Gamma + Epsilon

500X 0 N33788
b. Uranium-5 a/o Molybdenum-29 a/o Titanium, 20 Hr 850 C, Water Quench, Gamma + Epsilon + Delta U_2Ti

250X N33789
c. Uranium-15 a/o Molybdenum-18 a/o Titanium, 120 Hr 700 C, Water Quench, Gamma + Epsilon + Delta U_2Ti

250X N33790
d. Uranium-34 a/o Titanium, 120 Hr 700 C, Water Quench, Delta U_2Ti

250X N33791
e. Uranium-31.5 a/o Molybdenum, 3 weeks 625 C, Water Quench, Gamma + Epsilon (Trace)

500X N33792
f. Uranium-31.5 a/o Molybdenum, 4 weeks 500 C, Water Quench, Delta U-Mo

500X N33793
g. Uranium-29.5 a/o Molybdenum-2.5 a/o Titanium, 4 weeks 500 C, Water Quench, Delta U-Mo + Epsilon + Alpha

500X N33794
h. Uranium-20 a/o Molybdenum-12.5 a/o Titanium, 4 weeks 500 C, Water Quench, Alpha + Epsilon

500X N33795
i. Uranium-15 a/o Molybdenum-18 a/o Titanium, 4 weeks 500 C, Water Quench, Alpha + Epsilon + Delta U_2Ti

FIGURE 3. MICROSTRUCTURES OF ANNEALED AND QUENCHED URANIUM-MOLYBDENUM-TITANIUM ALLOYS

TABLE 3. RESULTS OF X-RAY DIFFRACTION EXAMINATION
OF URANIUM-MOLYBDENUM-TITANIUM ALLOYS

Alloy	Composition (Balance Uranium), a/o		Annealing Temperature, C	Relative Phase Intensities (a)				
	Molybdenum	Titanium		δ_{U-Ti}	ϵ_{Mo-Ti}	γ_U	δ_{U-Mo}	α_U
6	15	18	850	0	S	VS	0	0
8	5	29	850	MS	MF	VS	0	0
4	24	8	800	0	S	VS	0	0
6	15	18	800	0	S	S+	0	0
9	3	31	800	M	M	S	0	0
1	31.5	0	700	0	0	VS	0	0
2	29.5	2.5	700	0	M	VS	0	0
3	27	5	700	0	MS	VS	0	0
4	24	8	700	0	S	VS	0	0
5	20	12.5	700	0	S	MFd	0	VF+
6	15	18	700	MF	S	Md	0	VF
7	8.5	25	700	S	M	Fd	0	0
8	5	29	700	VS	0	0	0	0
9	3	31	700	VS	VVF+d	VFd	0	0
10	1	33	700	VS	0	0	0	0
11	0	34	700	VS	0	0	0	0
7	8.5	25	680	VS	F	VFd	0	VVF
2	29.5	2.5	625	0	M	VS	0	0
3	27	5	625	0	S	VS	0	0
4	24	8	625	0	VS	MF+	0	F
6	15	18	625	M	MSd	0	0	VS
8	5	29	625	VS	Fd	0	0	VVF
10	1	33	-	VS	0	0	0	0
2	29.5	2.5	550	0	MF+	VS	VS	0
4	24	8	550	0	VS	0	0	MS
6	15	18	550	M	MS	0	0	S
8	5	29	550	VS	0	0	0	F
10	1	33	550	VS	0	0	0	0
1	31.5	0	500	0	0	0	VS	0
2	29.5	2.5	500	0	MS	F	MS+	VF+
3	27	5	500	0	S	0	M+	M
4	24	8	500	0	VS	0	Fd	M
5	20	12.5	500	0	VS	0	0	MF

(a) V = very
M = medium
S = strong
F = faint
d = diffuse.

FIGURE 4. LATTICE-PARAMETER VARIATIONS OF PHASES IN URANIUM-MOLYBDENUM-TITANIUM SPECIMENS QUENCHED FROM 700 C

The lattice parameter variations at 700 C indicate the limits of the two- and three-phase regions. The epsilon phase varies in lattice constant from 3.147 Å to 3.206 Å, which corresponds to a variation from essentially pure molybdenum to a molybdenum-60 w/o titanium binary alloy. The actual composition of the epsilon solid solution in this three-phase region probably contains less than 60 w/o titanium because the uranium in solution would expand the unit cell of this phase by an unknown amount.

The lattice constant of the gamma phase increased from 3.20 Å in the binary uranium-molybdenum alloy to 3.44 Å in Alloy 4. This indicates an increase in uranium content of the gamma phase with increasing titanium addition. The X-ray pattern of the gamma phase in Alloys 5, 6, and 7, which contained still more titanium, was diffuse, and only approximate lattice constants could be estimated. These ranged from 3.46 Å to 3.50 Å and showed no consistent variation. Apparently, at this temperature the equilibrium gamma phase is no longer stable, and some transformation occurs on quenching, the expanded lattice constants indicating a uranium-enriched gamma phase. The presence of faint alpha patterns in two of these alloy specimens shows that a partial decomposition of gamma to alpha uranium has occurred.

Measurements of lattice spacings of the delta U_2Ti phase indicate a fairly large solubility of molybdenum, the spacing showing a regular increase in Alloys 8, 9, 10, and 11. However, metallographic and thermal data do not agree with this large solubility range. Metallographically, Alloys 8, 9, and 10 were at least two-phase alloys at 700 C. A thermal arrest noted in Alloys 8 and 9 indicates that at a minimum these alloys were two phase at the isotherm temperature. In addition, three phases were identified by X-ray diffraction in Alloy 9. This observation does not necessarily limit this alloy to a three-phase region, however, since precipitation from the delta phase could have occurred on quenching from 700 C. At any rate, the data are not consistent on the ternary solubility of this phase. It is possible that maximum solubility occurs at a compositional section higher in titanium than was investigated, placing Alloys 8, 9, and 10 in a two-phase region where lattice parameter variations may be expected. However, it is suspected that the time of heat treatment, 120 hr at 700 C, may have been insufficient to produce equilibrium in the delta phase, thereby accounting for the apparently wide solubility range.

An indication of the changing composition of the epsilon phase present in the three-phase region of the ternary cut was obtained by measurement of lattice parameters in three-phase alloys quenched from 850, 800, and 700 C. The epsilon-lattice constants were 3.268, 3.221, and 3.206 Å, respectively. This change corresponds to an increase of over 40 w/o molybdenum in molybdenum-titanium binary alloys. If it is assumed that the uranium content of this phase decreases with decreasing temperature, then the molybdenum content increase in the ternary solid solution should be somewhat less over this temperature range.

Hardness Changes During Transformation
of Molybdenum-Rich Alloys

The effect of titanium on transformation of the gamma phase in molybdenum-rich alloys is shown by the hardness changes given in Table 4.

TABLE 4. HARDNESS CHANGES IN URANIUM-MOLYBDENUM-TITANIUM ALLOYS QUENCHED FROM 900 C AND TRANSFORMED AT 500 C

Alloy	Composition (Balance Uranium), a/o		VHN, 10-Kg Load for Given Time, hr, at 500 C				
	Molybdenum	Titanium	0	1	22	100	500
1	31.5	0	376	370	342	312	322
2	29.5	2.5	322	327	363	370	442
3	27	5	314	325	455	488	488
4	24	8	309	325	530	525	493
5	20	12.5	314	585	530	459	464

The gamma phase is retained on quenching these alloys from 900 C, the hardness of the retained gamma phase decreasing with the first small titanium addition. The character of the hardness change accompanying transformation at 500 C also changes with this addition. In the binary alloy, Alloy 1, the gamma to delta uranium-molybdenum transformation is accompanied by a decrease in hardness, while all of the titanium-containing alloys show age-hardening characteristics. The speed with which maximum hardness is reached increases with titanium content indicating decreased stability of the gamma phase.

The age-hardening reaction is evidently associated with precipitation of the alpha and epsilon phases, maximum hardness of the transformation products being seen to increase with the amount of these phases formed. Alloy 5, in which the gamma phase decomposes to alpha and epsilon only, reaches maximum hardness after approximately 1 hr, overaging with additional transformation time.

SUMMARY AND CONCLUSIONS

Upon the basis of thermal analysis, metallographic, and X-ray data, a ternary cut showing the phase relationships, which occur between the delta phases of the uranium-molybdenum and uranium-titanium systems, has been constructed.

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FIGURE 5. INDICATED ISOTHERMAL TERNARY SECTIONS OF URANIUM-MOLYBDENUM-TITANIUM SYSTEM

A single-phase gamma solid solution exists at temperatures above that at which the delta U_2Ti phase forms. Below this temperature, a molybdenum-titanium-rich solid solution was found in all but the terminal delta-phase alloys.

Evidence for two isothermal reactions was found, one occurring at about 593 C in molybdenum-rich alloys, the other occurring at about 660 C in titanium-rich alloys. Both reactions are evidently associated with gamma-phase decomposition, to delta uranium-molybdenum and alpha uranium, respectively.

No evidence for the appearance of beta uranium in phase regions of the ternary cut was obtained, indicating that this phase must be restricted to uranium-rich alloys.

Solubility of titanium in the delta uranium-molybdenum phase is very limited. Solubility of molybdenum in the delta U_2Ti phase may be quite extensive, as indicated by X-ray diffraction lattice-parameter studies, although based on metallographic and thermal-analysis data the solubility is much more limited. If the solubilities indicated by X-ray are correct, it seems reasonable to assume that maximum solubility occurs in compositions richer in titanium than those investigated.

Upon the basis of the experimental data, a series of isothermal ternary sections have been constructed, Figure 5, as an aid in interpretation of the ternary cut. The phase relationships shown in these sections are seen to be consistent with the ternary cut of Figure 2 and are believed to offer a reliable description of phase relationships in the uranium-molybdenum-titanium system. It is apparent that compositional limits of the various phase regions cannot be selected from these sections. However, they should provide a firm basis for any future, more detailed studies of the system.

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