PHASE EQUILIBRIA OF THE TANTALUM-RICH REGION
OF THE TANTALUM-TUNGSTEN-HAFNIUM
AND TANTALUM-TUNGSTEN-ZIRCONIUM SYSTEMS

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ABSTRACT

The solid-state phase equilibria at 1600C (2912F) and 1100C (2012F) are being determined for the tantalum-rich regions of the Ta-W-Hf and Ta-W-Zr alloy systems. Alloys for the investigation are prepared by arc melting charges consisting of a 60 Ta-40 w/o W master alloy with appropriate additions of tantalum and hafnium or tantalum and zirconium. The as-cast alloys are homogenized by means of a high-temperature vacuum heat treatment prior to the vacuum annealing treatments at the two isothermal levels. Metallographic examination of the annealed structures and X-ray diffraction studies of the alloys are the principal techniques employed in the investigation to determine the phase equilibria.

The extent of the single-phase terminal solid-solution region in each system has been determined for the two isothermal levels and data are presented in the form of schematic diagrams of the observed microstructures.

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	ii
I. INTRODUCTION	1
II. EXPERIMENTAL PROCEDURES	2
A. Isothermal Annealing	2
B. Metallographic Examination	2
III. FUTURE WORK	10
REFERENCES	11
DISTRIBUTION LIST	12

I. INTRODUCTION

This report is the fourth quarterly report describing the progress achieved on the research program, "Phase Equilibria of the Tantalum-Tungsten-Hafnium and Tantalum-Tungsten-Zirconium Systems." The research program is sponsored by the United States Atomic Energy Commission, Contract No. AT(11-1)-1092-Task F.

The objective of the research program is to establish the phase relationships in the tantalum-tungsten-hafnium and tantalum-tungsten-zirconium systems at the 1600C (2912F) and 1100C (2012F) isothermal levels. The accurate determination of the solid-solution boundary for the tantalum-rich region in each system is the primary goal of the investigation. Other phase regions which may be located within the compositional area of interest will also be delineated and all phases in equilibrium with the tantalum-rich solid solution will be identified. Alloys included in the investigation are in the compositional range from 100 percent tantalum up to a maximum of 25 weight percent each of tungsten and hafnium or tungsten and zirconium.

Alloys are prepared by arc melting weighed charges of a master alloy (60 w/o Ta-40 w/o W) with additions of tantalum and hafnium or tantalum and zirconium in a non-consumable electrode arc furnace under an inert atmosphere. The as-cast alloys are homogenized in a tantalum-element, high temperature vacuum furnace prior to the isothermal anneals. Isothermal annealing treatments at 1600C (2912F) are conducted in this same furnace, whereas a nichrome-wire-wound resistance tube furnace is utilized for the 1100C (2012F) temperature level anneals. Interpretations of the microstructures of the heat treated alloys are made employing standard metallographic and X-ray diffraction techniques.

II. EXPERIMENTAL PROCEDURES

A. Isothermal Annealing

Forty-five alloys of the tantalum-tungsten-zirconium system have been isothermally annealed at 1600C (2912F) and thirty alloys of this system have been isothermally annealed at 1100C (2012F). Similarly, twenty-eight alloys of the tantalum-tungsten-hafnium system have been annealed at 1600C (2912F) and fifteen alloys of this system have been annealed at 1100C (2012F). Table I lists the alloy compositions which have been annealed. The 1600C anneals were conducted in a tantalum-tube, resistant element vacuum furnace for seven days. Each alloy was individually wrapped in tantalum foil to prevent physical contact between specimens. Anneals at 1100C were conducted in a resistance-wire-wound tube furnace and the tantalum wrapped specimens were sealed in double capsules of quartz which had been evacuated and then purged and backfilled with argon prior to sealing. The duration of the 1100C anneals was 60 days. Homogenization treatments prior to the isothermal anneals were conducted at 1800C (3272F) or 1900C (3452F) for the alloys containing zirconium and at 2200C (3992F) for the hafnium-containing alloys.

B. Metallographic Examination

The as-cast and isothermally annealed alloys were prepared for metallographic examination by standard techniques. After being ground on 80, 120, 400, and 600-grit abrasive papers, the alloy specimens were polished on rotating laps using 6-micron diamond paste as the abrasive for the first stage polishing operation.

Alloys containing greater than five percent zirconium were given a final polish on a rotating lap with No. 3 alumina in saturated solution of potassium ferricyanide. Final polishing of alloys containing less than 5 percent zirconium and all hafnium-containing alloys was done on a vibratory polisher with No. 3 alumina in a water suspension as the abrasive.

Etching of the alloy samples to develop the microstructure was accomplished with the following etchants for the composition ranges indicated.

TABLE I

Tabulation of Alloy Compositions
Annealed Isothermally at 1600C and 1100C

Ta-W-Zr System

Composition

<u>% Ta</u>	<u>-% W</u>	<u>-% Zr</u>	<u>1600C</u>	<u>1100C</u>
95	5	--	X	X
90	5	5	X	X
90	10	--	X	X
85	5	10	X	X
85	10	5	X	X
85	15	--	X	X
80	15	5	X	X
80	10	10	X	
80	5	15	X	X
80	20	--	X	X
75	5	20	X	X
75	15	10	X	X
75	20	5	X	X
75	10	15	X	X
75	25	--	X	
70	5	25	X	X
70	20	10	X	
70	10	20	X	X
70	15	15	X	X
70	25	5	X	
65	25	10	X	X
65	10	25	X	X

TABLE I (Continued)

Composition				
<u>% Ta</u>	<u>- % W</u>	<u>- % Zr</u>	<u>1600C</u>	<u>1100C</u>
65	20	15	X	X
65	15	20	X	X
60	15	25	X	X
60	25	15	X	X
60	20	20	X	X
55	25	20	X	X
55	20	25	X	X
50	25	25	X	X
91.5	2.5	6.0	X	
86.5	7.5	6.0	X	
76.5	17.5	6.0	X	
87.5	5.0	7.5	X	
82.5	10.0	7.5	X	
77.5	15.0	7.5	X	
72.5	20.0	7.5	X	
89	10	1.0	X	
88	10	2.0	X	
87	10	3.0	X	
86	10	4.0	X	
89	1.0	10.0	X	
88	2.0	10.0	X	
87	3.0	10.0	X	
86	4.0	10.0	X	

TABLE I (Continued)

Composition				
<u>% Ta</u>	<u>- % W</u>	<u>- % Zr</u>	<u>1600C</u>	<u>1100C</u>
70	5	25	X	
60	15	25	X	
50	25	25	X	
55	25	20	X	
<u>Ta - W - Hf System</u>				
80	5	15	X	X
85	5	10	X	X
90	5	5	X	X
75	10	15	X	X
80	10	10	X	X
85	10	5	X	X
70	15	15	X	X
75	15	10	X	X
80	15	5	X	X
65	20	15	X	X
70	20	10	X	X
75	20	5	X	X
60	25	15	X	X
65	25	10	X	X
70	25	5	X	X
70	5	25	X	
75	5	20	X	
95	5	--	X	
65	10	25	X	
70	10	20	X	

TABLE I (Continued)

Composition				
<u>% Ta</u>	<u>-% W</u>	<u>-% Zr</u>	<u>1600C</u>	<u>1100C</u>
60	15	25	X	
65	15	20	X	
55	20	25	X	
60	20	20	X	

<u>Etchant</u>	<u>Alloy Compositional Range</u>
<div> 10 ml HNO₃ 15 ml dist. H₂O 5 drops H₂SiF₆ </div>	> 5% Zr alloys
<div> 25 ml HNO₃ 5 ml dist. H₂O 12.5 ml HF 5 drops H₂O₂ </div>	< 5% Zr alloys
<div> 2 ml HNO₃ 2 ml H₂O₂ 5 ml HF 6 ml dist. H₂O </div>	HF alloys

The observed microstructures for the isothermal levels are presented schematically in Figures 1 through 3. At 1600C (2912F) the solubility of zirconium in the tantalum-tungsten solid solution is restricted to less than five weight percent with low tungsten contents, and less than two weight percent with a tungsten content of ten weight percent. The restricted solubility is a consequence of the solid state miscibility gap in the tantalum-zirconium binary system. Pease and Brophy¹ and Williams, Jackson, and Larsen² have determined the phase diagram for the tantalum-zirconium system. In the former case, the miscibility gap boundary between β' Ta and (β' Ta + β) is at approximately five weight percent zirconium at 1600C (2912F); whereas, in the latter case, this boundary is indicated to be at approximately twelve weight percent zirconium.

Complete solubility of hafnium in the tantalum-rich solid solution is observed at 1600C (2912F) for alloy compositions of up to five weight percent tungsten. Restricted solubility of hafnium in the tantalum-tungsten solid solution occurs in alloys containing greater than ten weight percent tungsten. Although the binary tantalum-hafnium alloy system has a miscibility gap in the solid state, the maximum is at 1265C (2309F)³. Consequently, at 1600C (2912F) the system exhibits complete solid solubility in the tantalum-rich portion of the diagram.

Figure 1. Schematic Representation of Observed Microstructures of As-Cast Alloys in the Ta-W-Zr System

Figure 2. Schematic Representation of Observed Microstructures of Alloys Isothermally Annealed at 1600C. Ta-W-Zr System

Figure 3. Schematic Representation of Observed Microstructures of Alloys Isothermally Annealed at 1600C. Ta-W-Hf System

III. FUTURE WORK

The major effort during the remainder of the contract period will be on X-ray diffraction studies of isothermally annealed alloys to determine the identity of the phases coexisting in the multi-phase alloys. Also, several additional alloy compositions will be prepared for isothermal annealing treatments to delineate the solid solution boundary in the tantalum-rich regions more accurately.

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