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Quarterly Progress Report No. 4

Contract No. AT(11-1)-1092-Task B

September 1965

STUDIES OF THE EFFECT OF INTERSTITIAL ADDITION
ON THE PHASE EQUILIBRIA OF THE NIOBIUM-RICH REGION
OF THE NIOBIUM-TUNGSTEN-HAFNIUM
AND NIOBIUM-TUNGSTEN-ZIRCONIUM ALLOY SYSTEMS

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**UNIVERSITY OF DENVER
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AND NIOBIUM-TUNGSTEN-ZIRCONIUM ALLOY SYSTEMS

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ABSTRACT

Investigation of the effect of carbon and oxygen additions on the phase relationships of the niobium-rich region of the niobium-tungsten-hafnium and niobium-tungsten-zirconium alloy systems is in progress. The niobium-rich solid solution phase boundaries for the niobium-rich region of the niobium-tungsten-hafnium and niobium-tungsten-zirconium systems with the addition of nominal 0.01 w/o C were established metallographically at 1600 and 1300 C (2912 and 2372 F). Similar data for these two alloy systems without intentional carbon addition are quoted from the previous investigation for comparison. The pronounced effect of small carbon additions in reducing the solid solution phase field is evident in the two systems. A limited number of the niobium-tungsten-hafnium and niobium-tungsten-zirconium alloys containing small quantities of oxygen is available to date and a majority of these has been heat treated.

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I. INTRODUCTION

This report is the fourth quarterly report describing the research activities at the Metallurgy Division of the Denver Research Institute of the program sponsored by the United States Atomic Energy Commission under Contract No. AT(11-1)-1092-Task B. The period covered by this report is from 1 June 1965 to 31 August 1965. The objective of this sponsored research is to study the effect of interstitial addition on the phase equilibria of the niobium-rich region of the niobium-tungsten-hafnium and niobium-tungsten-zirconium alloy systems. Specifically the interstitial elements under investigation are carbon and oxygen. This is a continuation of the program, "Determination of the Niobium-Rich Region of the Ternary Phase Diagrams, Niobium-Tungsten-Hafnium and Niobium-Tungsten-Zirconium" which was completed in August 1964.

The principal technique to be used in alloy-structure evaluation will be metallographic analysis. X-ray diffraction analysis will assist in identification of intermediate phases. Microhardness measurement will be made also. Two isothermal sections at 1600 and 1300 C (2912 and 2372 F) in the niobium-rich region of each alloy system will be studied at the interstitial levels of approximately 0.25, 0.1 and 0.05 w/o. The newly determined niobium-rich solid solution boundaries will be compared with the respective boundaries of the ternary alloy systems without addition of carbon and oxygen.

II. RESULTS AND DISCUSSION

A. Niobium-Tungsten-Hafnium Alloys with Carbon Additions

Isothermal annealing at 1600 and 1300 C (2912 and 2372 F) of the niobium-tungsten-hafnium alloys with carbon additions was completed. Table I shows the experimental alloys prepared and the annealing schedule. The nominal carbon additions ranged from 0.5 to 0.01 w/o while the contents of both tungsten and hafnium varied from 0.5 to 25 w/o. The effect of small addition of carbon on the terminal solid solution boundary in the niobium-rich region of the niobium-tungsten-hafnium alloy system is pronounced. At the level of nominal 0.01 w/o C the solid solution phase boundaries at W:Hf=1:1 are placed between Nb-0.5 w/o W-0.5 w/o Hf and Nb-1 w/o W-1 w/o Hf at 1600 C (2912 F) and less than Nb-0.5 w/o W-0.5 w/o Hf at 1300 C (2372 F). This can be compared with the solid solution phase boundaries determined for the corresponding alloy system without intentional carbon additions¹: about Nb-11 w/o W-11 w/o Hf and Nb-4.0 w/o W-4 w/o Hf at 1600 and 1300 C (2912 and 2372 F), respectively. The effect of carbon additions on the terminal solid solution phase boundaries both at the Nb-25 w/o W and Nb-25 w/o Hf extremities is also obvious. The metallographic placement of the phase boundaries is shown below:

Alloys	1600 C (2912 F) Anneal		1300 C (2372 F) Anneal	
	@ Nb-25w/o W	@ Nb-25w/o Hf	@ Nb-25w/o W	@ Nb-25w/o Hf
Nb-W-Hf alloys without carbon additions	9.7w/o Hf	4w/o W	2.6w/o Hf	3.2w/o W
Nb-W-Hf alloys with nominal 0.01 w/o C additions	~1w/o Hf	<1w/o W	<1w/o Hf	<1w/o W

Powder X-ray technique was used to identify the precipitated phases in the annealed alloys. The data are tabulated in Table II with the lattice parameters determined for the niobium-rich solid solution phase and microhardness values.

¹ Albert S. Yamamoto, "Part II. Phase Equilibria of the Niobium-Tungsten-Hafnium and Niobium-Tungsten-Zirconium Systems," Denver Research Institute, University of Denver for U. S. Atomic Energy Commission, Contract No. AT(11-1)-1092-Task B, October 1964.

TABLE I

Nb-W-Hf-C Alloys Annealed at 1600 and 1300 C (2912 and 2372 F)

Alloy Base, w/o	Nominal Carbon Additions, w/o				
	<u>0.5</u>	<u>0.25</u>	<u>0.1</u>	<u>0.05</u>	<u>0.01</u>
Nb-0.5W-0.5Hf				X	X
Nb-0.5W-25Hf	X			X	
Nb-1W-1Hf	X			X	X
Nb-1W-25Hf	X			X	X
Nb-2W-2Hf	X				
Nb-3W-3Hf	X			X	
Nb-4W-4Hf	X				
Nb-5W-5Hf	X	X	X	X	X
Nb-5W-25Hf	X	X	X		
Nb-6W-6Hf	X				
Nb-7W-7Hf	X				
Nb-10W-5Hf				X	
Nb-10W-6Hf				X	
Nb-10W-7Hf				X	
Nb-10W-8Hf				X	
Nb-10W-10Hf	X	X	X	X	X
Nb-15W-1Hf				X	
Nb-15W-2Hf				X	
Nb-15W-3Hf				X	
Nb-15W-15Hf	X				
Nb-25W-0.5Hf	X			X	
Nb-25W-1Hf	X			X	X
Nb-25W-5Hf	X	X	X		
Nb-25W-25Hf	X				

B. Niobium-Tungsten-Zirconium Alloys with Carbon Additions

The alloy compositions prepared for the study of the effect of carbon additions on phase equilibria in the niobium-tungsten-zirconium alloy system are listed in Table III along with the annealing schedule. The range of nominal carbon additions is from 0.01 to 0.25 w/o. Both tungsten and zirconium contents vary from 0.5 to 25 w/o. The effect of small additions of carbon on the niobium-rich solid solution phase field is again similar as described in the niobium-tungsten-hafnium alloy containing carbon. As follows is the summary of the metallographically determined phase boundaries for the terminal solid solution at 1600 and 1300 C (2912 and 2372 F). The data for the niobium-tungsten-zirconium alloys without intentional carbon additions are included for comparison.¹

Nb-W-Zr System	1600 C (2912 F) Anneal		1300 C (2372 F) Anneal	
	Without Carbon Additions	With 0.01w/o C Additions	Without Carbon Additions	With 0.01w/o C Additions
@ W:Zr=1:1	5.5w/o W-5.5w/o Zr	$\leq 0.5w/o W-0.5w/o Zr$	3.2w/o W-3.2w/o Zr	$< 0.5w/o W-0.5w/o Zr$
@Nb-25w/o W	2w/o Zr	$\approx 1w/o Zr$	2w/o Zr	$< 1w/o Zr$
@Nb-25w/o Zr	1.2w/o W	$< 1w/o W$	1w/o W	$< 1w/o W$

X-ray diffraction analysis of selected alloys with various carbon additions is still underway at this writing.

C. Niobium-Tungsten-Hafnium and Niobium-Tungsten-Zirconium Alloys with Oxygen Additions

A limited number of experimental alloys containing oxygen was prepared for the two alloy systems. The alloys currently available are tabulated in Table IV. The oxygen contents for the niobium-tungsten-hafnium alloys are varied from 0.5 to 0.01 w/o. While no information is found with respect to the effect of hafnium addition on the solubility of oxygen in niobium, there are a few publications available dealing with the effect of zirconium addition. The published data are extracted in the last Quarterly Progress Report, No. 3, June 1965. Consequently the level of the oxygen additions to the niobium-tungsten-zirconium alloys was lowered from that for the niobium-tungsten-hafnium-oxygen series, ranging from 0.1 to 0.01 w/o.

Annealing treatments for the first series of oxygen-bearing alloys for these two alloy systems are in progress. Table V shows those alloys whose heat treatments have been completed both at 1600 and 1300 C (2912 and 2372 F). Metallographic analysis of the annealed structure is underway.

TABLE II
X-Ray Data for Nb-W-Hf with Various Carbon Additions

Alloys, w/o	Heat Treatment		Powder X-Ray Data		Microhardness Data, DPH(10Kg Load)
	1. 1600C Anneal	2. 1300C Anneal	2nd Phase Identified	Lattice Parameter a_0 for Nb _{ss} Phase, Å	
Nb-0.5W-25Hf-0.5C	1		HfC	3.320±0.001	232
	2		-	-	182
Nb-1W-25Hf-0.5C	1		HfC+?	3.327±0.001	238
	2		-	-	198
Nb-5W-25Hf-0.5C	1		HfC+?	3.313±0.007	268
	2		HfC	3.323±0.001	222
Nb-7W-7Hf-0.5C	1		-	-	203
	2		HfC	3.299±0.007	188
Nb-10W-10Hf-0.5C	1		-	-	228
	2		HfC	3.293±0.002	215
Nb-25W-5Hf-0.5C	1		-	-	314
	2		HfN?	3.277±0.004	327
Nb-25W-25Hf-0.5C	1		-	-	363
	2		HfC+?	3.289±0.005	376
Nb-25W-0.5C	1		-	-	306
	2		Nb ₂ C	3.273±0.006	297
Nb-1Hf-0.5C	1		Nb ₂ C+HfC	3.302±0.002	105
	2		-	-	99
Nb-0.5C	1		Nb ₂ C	3.305±0.000	99
	2		Nb ₂ C+NbC	3.304±0.011	97
Nb-5W-5Hf-0.25C	1		?	3.297±0.001	187
	2		-	-	146
Nb-5W-25Hf-0.25C	1		-	-	258
	2		Nb ₂ C+HfC+?	3.324±0.001	238
Nb-10W-10Hf-0.25C	1		HfC	-	249
	2		-	3.298±0.002	194
Nb-1Hf-0.25C	1		Nb ₂ C+HfC	3.301±0.002	109
	2		-	-	108
Nb-10W-10Hf-0.1C	1		-	-	202
	2		HfC+?	3.300±0.001	189
Nb-25W-5Hf-0.1C	1		-	-	314
	2		HfC+?	3.279±0.001	276
Nb-25Hf-0.1C	1		-	-	205
	2		HfC+?	3.312±0.012	181
Nb-0.1C	1		-	-	98
	2		None	3.305±0.001	92
Nb-10W-10Hf-0.05C	1		-	-	213
	2		None	3.301±0.001	194
Nb-1Hf-0.05C	1		-	-	114
	2		HfC	3.301±0.001	104

TABLE III

Nb-W-Zr-C Alloys Annealed at 1600 and 1300 C (2912 and 2372 F)

<u>Alloy Base, w/o</u>	<u>Nominal Carbon Additions, w/o</u>			
	<u>0.25</u>	<u>0.1</u>	<u>0.05</u>	<u>0.01</u>
Nb-0.5W-0.5Zr	X	X	X	X
Nb-0.5W-25Zr	X	X		
Nb-1W-1Zr	X	X	X	X
Nb-1W-25Zr			X	X
Nb-2W-2Zr	X	X	X	
Nb-5W-5Zr	X	X	X	X
Nb-10W-10Zr	X			X
Nb-15W-15Zr	X			X
Nb-25W-0.5Zr	X	X		
Nb-25W-1Zr			X	X
Nb-25W-25Zr	X			X

TABLE IV

Compositions of Oxygen Containing Alloys Arc-Melted to Date
for the Nb-W-Hf and Nb-W-Zr Systems

Alloy Base, w/o	Nominal Oxygen Additions, w/o				
	<u>0.5</u>	<u>0.25</u>	<u>0.1</u>	<u>0.05</u>	<u>0.01</u>
Nb-0.5W-25Hf			X	X	X
Nb-1W-1Hf		X	X		
Nb-1W-25Hf			X	X	
Nb-5W-5Hf	X	X	X	X	
Nb-10W-10Hf	X	X	X		
Nb-10W-25Hf			X	X	
Nb-15W-15Hf		X	X	X	
Nb-25W-1Hf	X	X	X	X	
Nb-25W-25Hf			X	X	
Nb-0.5W-0.5Zr				X	X
Nb-0.5W-25Zr				X	X
Nb-1W-1Zr			X	X	X
Nb-1W-25Zr				X	X
Nb-5W-5Zr				X	X
Nb-10W-10Zr			X	X	X
Nb-15W-15Zr			X	X	X
Nb-25W-0.5Zr				X	X
Nb-25W-1Zr				X	X
Nb-25W-25Zr			X	X	X

TABLE V
Nb-W-Hf-O and Nb-W-Zr-O Alloys
Annealed to Date at 1600 and 1300 C (2912 and 2372 F)

<u>Alloy Base, w/o</u>	<u>Nominal Oxygen Additions, w/o</u>				
	<u>0.5</u>	<u>0.25</u>	<u>0.1</u>	<u>0.05</u>	<u>0.01</u>
Nb-0.5W-25Hf			X	X	X
Nb-1W-1Hf		X	X		
Nb-1W-25Hf			X	X	
Nb-5W-5Hf	X	X	X	X	
Nb-10W-10Hf	X	X	X		
Nb-10W-25Hf			X	X	
Nb-15W-15Hf		X	X	X	
Nb-25W-1Hf	X	X	X	X	
Nb-25W-25Hf			X	X	
N-1W-25Zr			X	X	
N-5W-5Zr			X	X	
N-25W-1Zr			X	X	

III. FUTURE

1. Additional alloys, especially the niobium-tungsten-zirconium alloys containing carbon, will be subjected to X-ray analysis.
2. When collective analysis of the data is completed, the effect of small carbon addition on the phase equilibria of the niobium-tungsten-hafnium and niobium-tungsten-zirconium alloys in the niobium-rich region will be submitted.
3. Preparation of additional oxygen-bearing alloys for the niobium-tungsten-zirconium system will be required. The anticipated oxygen level for a limited number of alloys will be 0.005 w/o.
4. Isothermal annealing of the niobium-tungsten-hafnium and niobium-tungsten-zirconium alloys containing oxygen will continue.

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