Quarterly Progress Report No. 3
Contract AT(11-1)-1092-Task B

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

- Submitted to -

U. S. Atomic Energy Commission
Chicago Operations Office
9800 South Cass Avenue
Argonne, Illinois 60439

Attention: Mr. Fred C. Mattmueller
Director, Research Contracts Division

- Submitted by -

University of Denver
(Colorado Seminary)
Denver Research Institute
Denver, Colorado 80210

June 1965

APPROVED FOR THE DIRECTOR:

PREPARED BY:

William M. Mueller
Head, Metallurgy Division

Albert S. Yamamoto
Research Metallurgist

APPROVED BY:

Charles E. Lundin
Technical Assistant to
the Division Head
Metallurgy Division

DRI #2231

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

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. Isothermal annealing at 1600 and 1300C (2912 and 2372F) of the niobium-tungsten-hafnium with nominal carbon additions of 0.5, 0.25, 0.1, 0.05 and 0.01 w/o were completed. Microscopic examination of the annealed alloy structure shows a second phase or phases present in all the alloys investigated at both temperatures except a Nb-0.5 w/o W-0.5 w/o Hf-0.01 w/o C which showed nearly a single-phase structure at 1600C (2912F). A limited number of the niobium-tungsten-zirconium alloys containing nominal 0.25, 0.1, 0.05 and 0.01 w/o C was heat treated isothermally at both 1600 and 1300C (2912 and 2372F). All the annealed and quenched alloys examined metallographically exhibit the structures with precipitates, varying in the amounts and mode of precipitation. X-ray diffraction studies of the carbon-bearing alloys in the two systems are in progress. Arc-melting of the niobium-tungsten-hafnium and niobium-tungsten-zirconium alloys with oxygen additions will be carried out throughout the next period.

I. INTRODUCTION

This report is the third quarterly report describing the research activities of the program sponsored by the United States Atomic Energy Commission under Contract AT(11-1)-1092-Task B. The period covered by this report is from 1 March 1965 to 31 May 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 and micro-hardness measurement will complement the metallographic interpretation. Two isothermal sections at 1600 and 1300C (2912 and 2372F) in the niobium-rich region of each alloy system will be investigated at the interstitial levels of approximately 0.25, 0.1 and 0.05 weight percent. The intermediate phases will be identified and 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. EXPERIMENTAL PROCEDURES

X-Ray Diffraction Analysis

For identification of a second phase or phases found in the annealed niobium-tungsten-hafnium and niobium-tungsten-zirconium alloys with carbon additions, X-ray diffraction techniques will be employed. Powder specimens will be prepared by filing annealed alloy samples. Iron contamination will be removed by the use of a magnet. The powder will then be sealed in an evacuated Vycor capsule and stress-relief annealed at 900C (1652F). The specimen will be exposed to nickel-filtered copper K α radiation in a 114.6 mm Debye-Scherrer camera.

III. RESULTS AND DISCUSSION

A. Niobium-Tungsten-Hafnium Alloys with Carbon Additions

Isothermal annealing at 1600 and 1300C (2912 and 2372F) of the first series of the niobium-tungsten-hafnium-carbon alloys containing nominal 0.5, 0.25, 0.1, 0.05 and 0.01 w/o C has been virtually completed. The alloys prepared to date in this study are tabulated in Table I. In addition to these alloys, a minimum number of niobium-carbon, niobium-tungsten-carbon and niobium-hafnium-carbon alloys were melted.

Examination of the annealed microstructure of these alloys reveals that the solid solubility of carbon in the niobium-tungsten-hafnium solid solution is restricted. A Nb-0.5 w/o W-0.5 w/o Hf-0.01 w/o C alloy, annealed at 1600C (2912F) for one week, exhibits a microstructure of nearly single-phase solid solution. In the same alloy, heat treated isothermally at 1300C (2372F), the minute precipitates are dotted along the grain boundaries and delineate the subgrain structure. Even a binary Nb-0.01 w/o (nominal) C alloy annealed both at 1600 and 1300C shows the microstructure which is at the threshold of the solid solubility limit of carbon in niobium. This finding indicates that the solid solubility of carbon in niobium is less than the literature values which were summarized and reported in the last Quarterly Progress Report; approximately 0.05 and 0.02 w/o C at 1600 and 1300C, respectively. Either tungsten, or hafnium or the combination of the two additives to niobium does not seem to alter the solid solubility of carbon in niobium.

A few representative niobium-tungsten-hafnium-carbon alloys were selected for analysis. For this study, the emphasis was placed on finding the actual carbon contents. Table II shows the chemical analysis results reported for the first series of the alloys. The reported carbon contents are generally in agreement with the nominal.

X-ray diffraction analysis of selected annealed alloys has been initiated for identification of the precipitated phase or phases. No data have been obtained as yet for this report. This phase will be the major activity for the remainder of the contractual period.

Recent data relevant to this investigation have been found in the literature. A. Taylor¹ reports preliminary observations made in the niobium alloys containing approximately 0.1 w/o carbon and varying

TABLE I.
 NIOBIUM-TUNGSTEN-HAFNIUM-CARBON ALLOYS
 PREPARED TO DATE IN THIS INVESTIGATION

Alloy Base	Nominal Carbon Additions				
	0.5 w/o	0.25 w/o	0.1 w/o	0.05 w/o	0.01 w/o
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				X
Nb-25W-0.5Hf	X			X	
Nb-25W-1Hf	X			X	X
Nb-25W-5Hf	X	X	X		
Nb-25W-25Hf	X			X	X

TABLE II.
CARBON ANALYSIS RESULTS FOR SELECTED
NIOBIUM-TUNGSTEN-HAFNIUM-CARBON AND
NIOBIUM-TUNGSTEN-ZIRCONIUM-CARBON ALLOYS

Nominal Alloy Composition	Melt No.	Analyzed Carbon Content, w/o
Nb-0.5W-0.5Hf-0.01C	629	0.016
Nb-1W-25Hf-0.01C	631	0.023
Nb-1W-1Hf-0.05C	562	0.052
Nb-25W-1Hf-0.05C	608	0.056
Nb-5W-5Hf-0.1C	551	0.093
Nb-10W-10Hf-0.1C	543	0.054
Nb-0.5W-0.5Zr-0.01C	642	0.029
Nb-1W-1Zr-0.05C	571	0.062

amounts of hafnium (9.3 w/o, 17.7 w/o, 25.5 w/o and 32.7 w/o). All the alloys, after quenching from the homogenization temperature of 2000C (3632F) indicate the presence of a second phase which "is, in all probability, the carbide Nb_2C ." The solid solubility limit of carbon in Nb-Hf alloys is estimated to be less than approximately 0.1 w/o at 2000C (3632F). The 1800C (3272F) isotherm for the niobium-hafnium-carbon system presented by Stechner and his colleagues² contains the phase fields in the niobium-rich corner as follows: (Nb-Hf-C) solid solution, $(\text{Nb-Hf-C})_{\text{ss}} + \text{Nb}_2\text{C}$, $(\text{Nb-Hf-C})_{\text{ss}} + (\text{Nb, Hf})_2\text{C} + (\text{Nb, Hf})\text{C}_{1-x}$, and $(\text{Nb-Hf-C})_{\text{ss}} + (\text{Nb, Hf})\text{C}_{1-x}$.

B. Niobium-Tungsten-Zirconium Alloys with Carbon Additions

A limited number of the niobium-tungsten-zirconium alloys with the nominal carbon additions of 0.25, 0.1, 0.05 and 0.01 w/o were prepared. The heat treatments at 1600 and 1300C (2912 and 2372F) for the first series of the alloys have been completed. The alloys being used in this study are shown in Table III. Some niobium-zirconium-carbon alloys were melted and heat treated in conjunction with the study of the complex alloys. Currently additional alloys are being melted to complete the investigation.

Metallographic examination of these alloys indicates that the solubility of carbon in the niobium-tungsten-zirconium solid solution is restricted as in the case for the niobium-tungsten-hafnium alloys. Only the 1600C (2912F) anneal microstructure of a Nb-0.5 w/o W-0.5 w/o Zr-0.01 w/o C shows virtually a single-phase structure.

A couple of the niobium-tungsten-zirconium-carbon alloys were sent for analysis. The reported results for Nb-0.5 w/o W-0.5 w/o Zr-0.01 w/o C and Nb-1 w/o W-1 w/o Zr-0.05 w/o C alloys are included in Table II with the data for the niobium-tungsten-hafnium-carbon alloys. The reported carbon contents are higher than the intended.

Identification of the second phase or phases in the annealed niobium-tungsten-zirconium-carbon alloys will be made by X-ray diffraction study. X-ray powder specimens are being prepared at this writing.

Some pertinent information in conjunction with this investigation is available. Recently Barber and Morton³ report that they observed Nb_2C and ZrC coexisting in the niobium-zirconium-carbon alloys which

TABLE III.
 NIOBIUM-TUNGSTEN-ZIRCONIUM-CARBON ALLOYS
 PREPARED TO DATE IN THIS INVESTIGATION

Alloy Base	Nominal Carbon Additions			
	0.25 w/o	0.1 w/o	0.05 w/o	0.01 w/o
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-0.5Z	X	X		
Nb-25W-1Zr	X		X	X
Nb-25W-25Zr	X			X

were annealed at 1300C (2372F). No other details as to alloy composition are available at the moment. According to Stechmer et al. who investigated the niobium-zirconium-carbon system², they observed the following phase-fields in the niobium-rich region at 1700C (3092F): (Nb-Zr-C) solid solution, (Nb-Zr-C)_{ss} + Nb₂C, (Nb-Zr-C)_{ss} + (Nb, Zr)₂C + (Nb, Zr)C_{1-x}, and (Nb-Zr-C)_{ss} + (Nb, Zr)C_{1-x}.

C. Oxygen Additions to the Niobium-Tungsten-Hafnium and Niobium-Tungsten-Zirconium Alloys

Experimental alloys prepared for the two alloy systems are limited as yet. These alloys were homogenized at elevated temperatures. One alloy from each alloy system was selected and sent in for analysis of the oxygen contents in the as-arc-melted and as-homogenized conditions. No report has been received as yet. Another batch of the niobium-oxygen master alloys was submitted for its oxygen content. Preparation of the niobium-tungsten-hafnium and niobium-tungsten-zirconium alloys with various amounts of oxygen will be initiated after reviewing the analysis reports of the aforementioned alloys.

There are some publications found pertaining to the alloying effect on the solubility of oxygen in niobium. The alloying element of interest is zirconium. Pollock⁴ found that the addition of a small amount of zirconium drastically reduces the solubility of oxygen in niobium. At 1600C (2912F) the solubility decreases from 6,500 ppm in pure niobium to less than 200 ppm in a Nb-1% Zr Alloy. Bryant⁵ prepared niobium alloys containing 10 w/o zirconium and from 0.1 to 1.0 w/o oxygen, equilibrated them at 1000C (1832F) and quenched. Metallographic examination revealed that an oxide phase, which was identified as ZrO₂ by X-ray methods, was present in all samples. Addition of zirconium therefore reduces oxygen solubility markedly, less than 0.1 w/o oxygen at this temperature with 10 w/o zirconium addition. According to Marcotte, Larsen and Williams⁶, the oxygen-solubility limit in the Nb-20 w/o Zr and Nb-25 w/o Zr alloys is less than 100 ppm over the temperature range 1000 ~ 1200C (1832 ~ 2192F).

IV. FUTURE

1) The major activity for the remainder of the contractual period is to obtain the X-ray diffraction data as to the identity of second phases present in the niobium-tungsten-hafnium and niobium-tungsten-zirconium alloys containing various amounts of carbon.

2) Additional carbon-bearing alloys will be melted, especially in the niobium-tungsten-zirconium system.

3) Arc-melting of the niobium-tungsten-hafnium and niobium-tungsten-zirconium alloys with oxygen additions will continue.

4) Isothermal annealing of a series of the oxygen-bearing alloys will be conducted at 1600 and 1300C (2912 and 2372F) when a sufficient number of specimens becomes available.

REFERENCES

1. A. Taylor, "Research for Solubility of Interstitials in Columbium," Quarterly Report for Period 1 March 1965 - 1 May 1965, 10 May 1965, under Contract No. AF33(657)-11157.
2. P. Stechner, F. Benesovsky, A. Neckel and H. Nowotny, "Investigation of the Systems, Titanium (Zirconium, Hafnium)-Niobium-Carbon," Monatsh. Chem., 95 (1964) 1630-1645.
3. A. C. Barber and P. H. Morton, "A Study of the Niobium-Zirconium-Carbon and the Niobium-Zirconium-Oxygen Systems," Reported at AIME Annual Meeting, New York, February 1964.
4. W. I. Pollock, "Recent Developments in Columbium Physical Metallurgy," Metals Eng. Quart., 2 (1962), 58-68.
5. R. T. Bryant, "The Solubility of Oxygen in Transition Metal Alloys," J. Less-Common Metals, 4 (1962) 62-68.
6. V. C. Marcotte, W. L. Larsen and D. E. Williams, "Phase Relationships of the Oxygen-Containing 20 and 25 Percent Zirconium-Niobium Alloys," J. Less-Common Metals, 7 (1964), 373-382.

DISTRIBUTION LIST

<u>Recipient</u>	<u>Copies</u>
U. S. Atomic Energy Commission Chicago Operations Office ATTN: F. C. Mattmueller 9800 South Cass Avenue Argonne, Illinois 60439	8
Department of the Navy Office of Naval Research Code 422 For: W. C. Thurber Washington, D.C. 20525	1
Pratt and Whitney Aircraft Division Connecticut Operations CANEL For: L. M. Raring P.O. Box 611 Middletown, Connecticut 06458	1
Westinghouse Electric Corporation Astronuclear Laboratory P.O. Box 10864 For: R. Begely Pittsburgh, Pennsylvania 15236	1
National Aeronautics and Space Administration Lewis Research Center Plum Brook Station For: T. Moss Sandusky, Ohio 44871	1
General Electric Company Nuclear Materials and Propulsion Operation For: J. McGurty P.O. Box 15132 Cincinnati, Ohio 45215	1
Aeronautical Systems Division (RTD) For: K. Elbaum Wright-Patterson Air Force Base Ohio 45433	1

DISTRIBUTION LIST (cont.)

<u>Recipient</u>	<u>Copies</u>
Wah Chang Corporation For: S. Worchester P.O. Box 366 Albany, Oregon 97321	1