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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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 a first series of the niobium-tungsten-hafnium with nominal carbon additions of 0.5, 0.25, 0.1 and 0.05 w/o were completed. Preliminary microscopic examination shows that precipitation of a second phase or phases has occurred in all the annealed alloys. A limited number of the niobium-tungsten-zirconium alloys containing nominal 0.25, 0.1 and 0.05 w/o C has been heat treated at 1600C (2912F) at this writing. Again all the alloys examined metallographically exhibit the structures with a varying degree of precipitation of a second phase. In both niobium-tungsten-hafnium and niobium-tungsten-zirconium alloy systems, an additional series of selected alloys of nominal 0.01 w/o C will be prepared. Arc-melting of the niobium-oxygen master alloys is nearly completed. Tentative selection of the oxygen additions to these two alloy systems is described herein.

I. INTRODUCTION

This report is the second 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 December 1964 to 28 February 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. RESULTS AND DISCUSSION

A. Niobium-Tungsten-Hafnium Alloys with Carbon Additions

Isothermal annealing of the niobium-tungsten-hafnium-carbon alloys has progressed very well. A first series of the ternary alloys containing nominal 0.5, 0.25 and 0.1 w/o C were annealed both at 1600 and 1300C (2912 and 2372F) while the majority of alloys with the nominal addition of 0.05 w/o C has also been treated isothermally at these two temperatures to date.

Metallographic examination of these annealed and quenched alloys revealed that the second phase, of one kind or, perhaps, of two different types, is present in all. Even an alloy of Nb-0.5 w/o W - 0.5 w/o Hf - 0.05 w/o C exhibits fine precipitates dispersed sparsely within the grains and a more preferential precipitation of the second phase along the grain boundaries at both temperatures. This finding of the extremely restricted solubility of carbon in the niobium-tungsten-hafnium alloys necessitates additional melts to be prepared.

It seems to indicate that the alloy additions of tungsten and hafnium have hardly modified the characteristic of the unalloyed niobium in relation with carbon. There are a host of publications¹⁻⁶ available in the literature pertaining to the solid solubility of carbon in niobium. In spite of inevitable discrepancies among the various investigations, a reasonable solvus curve for the terminal niobium-carbon solid solution can be constructed through these data points: 0.046 and 0.018 w/o C at 1600 and 1300C (2912 and 2372F), respectively. Therefore, carbon additions at the level of as little as 0.01 w/o are felt to be needed in the study of this niobium-tungsten-hafnium alloy system. Melting of additional alloys containing nominal 0.01 w/o C will be initiated immediately.

Microhardness (DPH) data were taken from all available specimens, both as-cast and annealed. There is a general trend that hardness increases with increasing carbon content in a given alloy addition. The trend becomes more pronounced, it is observed, among the alloys containing greater amounts both in tungsten and hafnium.

B. Niobium-Tungsten-Zirconium Alloys with Carbon Additions

Only a limited number of the niobium-tungsten-zirconium alloys with the nominal carbon additions of 0.25, 0.1 and 0.05 w/o were

melted, homogenized and subjected to isothermal annealing at 1600 and 1300C (2912 and 2372F). To date the 1600C heat treatment has partially been completed while the 1300C anneal is in progress. Preliminary metallographic examination of a first series of the niobium-tungsten-zirconium-carbon alloys annealed at 1600C reveals that a varying degree of precipitation of a second phase has occurred in all the alloys, including an alloy of Nb-0.5 w/o W-0.5 w/o Zr-0.05 w/o C. It is felt necessary that a new series of the selected compositions in this alloy system be prepared with the nominal 0.01 w/o C. Arc-melting of these alloys will be started immediately along those in the niobium-tungsten-hafnium alloy system.

C. Preparation of Niobium-Oxygen Alloys

In preparation for the oxygen addition to the niobium-tungsten-hafnium and niobium-tungsten-zirconium alloys, arc-melting of Nb-5 w/o O (nominal) was initiated some time ago using the niobium pentoxide which was purchased from Spex Industries, Inc., Metuchen, New Jersey. When the microstructure of the first master alloy was examined, it appeared to be of a three-phase rather than two-phase configuration as predicted from the niobium-oxygen phase diagram by Elliott.⁷ This aroused one's suspicion as to the purity of the oxide, reportedly 99.9 w/o plus. The second master alloy was arc-melted similarly using the same material; the alloy structure was found to be identical. Correspondence was exchanged with the supplier regarding its reported purity but it failed to produce any satisfactory results. Search for another source was prompted subsequently. This resulted in receiving a small quantity of high-purity niobium pentoxide through the courtesy of the Metal Products Division of Fansteel Metallurgical Corporation, Muskogee, Oklahoma. The furnished analysis for the oxide is tabulated below.

<u>Impurities</u>	<u>ppm</u>
B ₂ O ₃	< 2
CaO	10
CrO ₃	< 5
CuO	15
FeO	< 50
MgO	5
MnO	10
MoO ₃	< 5
NiO	< 5
SiO ₂	20
SnO ₂	< 5
Ta ₂ O ₅	< 100
TiO ₂	< 25
WO ₃	< 25
ZrO ₂	< 10
Balance, Nb ₂ O ₅	> 99.97 w/o

The newly acquired oxide was used to make the master alloy of the same composition. To one's satisfaction the alloy was of the two-phase structure envisioned. A series of the niobium-oxygen master alloys using the 99.97 w/o plus oxide have since been in preparation. Each melt weighing approximately 12 g was checked for its structure, homogeneity and microhardness. Chemical analysis for the batch of these master alloys will be conducted at Oregon Metallurgical Corporation, Albany, Oregon.

D. The Niobium-Tungsten-Hafnium and Niobium-Tungsten-Zirconium Alloys with Oxygen Additions

The oxygen levels to be introduced in the niobium-tungsten-hafnium and niobium-tungsten-zirconium alloys were decided tentatively to be 1.0, 0.5 and 0.1 w/o.

As described previously, the solid solubility of carbon in the niobium-tungsten-hafnium and niobium-tungsten-zirconium alloys does not differ appreciably from that in niobium. The case for the addition of oxygen to these refractory-metal alloys may be parallel to that for the carbon addition. Through the literature survey three published data concerning the solid solubility of oxygen in niobium were found.^{7, 8, 9} They demonstrate quite a diversity as to not only

the solid solubility limit of oxygen in niobium but also its temperature dependency. Inasmuch as the aforementioned oxygen levels to be investigated are based on the controversial data, these values will be amended as soon as a need arises.

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