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THE NIOBIUM-THORIUM ALLOY SYSTEM

J. M. Dickinson, O. N. Carlson, and H. A. Wilhelm

ABSTRACT

The niobium-thorium alloy system has been investigated by X-ray, thermal, metallographic, and resistance methods and a phase diagram for the alloy system proposed. Niobium forms a eutectic with beta thorium at 1435°C at 8% niobium. The extent of solid solubility is very limited at both ends of the system at all temperatures. The maximum solubility is believed to be less than 1% niobium in thorium at the eutectic temperature. The addition of niobium to thorium lowers the reported alpha-beta transformation slightly. No intermediate phases were found in the investigation of the alloys.

INTRODUCTION

Alloys of thorium, particularly those with elements of low cross sections, have been of considerable interest to the atomic energy program in recent years. Since the phase diagrams of these alloys are important to the understanding of thorium metallurgy, this investigation was undertaken to propose a phase diagram for the thorium-niobium alloy system.

A survey of the Hume-Rothery (1) rules disclosed that the niobium-thorium alloy system would be expected to have no solid solubility. Because of the large difference in electronegativity between thorium and niobium a possibility existed that intermediate phases might be present. According to a calculation based on Hildebrand's (2) rule thorium and niobium were expected to be completely miscible in the liquid state. From these factors it was concluded that the niobium-thorium alloy system was most probably a eutectic type system perhaps complicated by the formation of intermediate phases.

EXPERIMENTAL PROCEDURE

Materials

The niobium powder and niobium sheet used in this investigation were obtained from Fansteel Metallurgical Corporation. Both forms

of the niobium were reported by the manufacturer to be 99% pure. The powdered niobium contained approximately 1800 ppm of carbon while the niobium sheet contained less than 500 ppm of carbon. The niobium powder was extremely brittle after being arc-melted while the niobium sheet remained very ductile.

The thorium sponge was prepared experimentally in this laboratory and is of high purity. The major analyzed impurity in the thorium is carbon which is present in amounts varying from 200 to 400 ppm.

Preparation of Alloys

Most of the alloys were prepared by arc-melting together small pieces of thorium sponge and 1 to 10 g pellets of pressed, but not sintered, niobium powder. The alloys were melted into flat disks weighing about 70 g. Each alloy was melted four times before being removed from the furnace and the sample was turned over between each melting operation to encourage thorough mixing.

Special shapes of alloys such as bars and cylinders were prepared by arc-melting the alloy disks into water cooled copper molds of the required size and shape.

Metallography

Since the niobium-thorium alloys were very soft, special precautions were necessary in the grinding and polishing operations. The best results were obtained by grinding on silicon carbide papers lubricated with either kerosene or water. The alloys were polished alternately on a microcloth covered wheel using a soap suspension of Linde "A" as an abrasive and electrolytically in 3N nitric acid containing 1% potassium fluoride. The alloys were etched in the electrolyte employed for the polishing operation using a current density of from 20 to 300 ma per cm². Alloys containing over 90% niobium were satisfactorily etched by immersion in a bath of concentrated nitric acid containing about 5% hydrofluoric acid.

X-Ray Method

The X-ray diffraction patterns were obtained using copper K alpha radiation supplied by a North American Phillips X-ray source. A 114.7 mm diameter Debye-Scherrer type powder camera, a 120 mm diameter self-focusing back-reflection camera, and a high temperature attachment mounted on a Norelco diffractometer were used to obtain the X-ray data.

Powdered specimens for use in the Debye-Scherrer and the back-reflection cameras were prepared by filing the alloys, removing the iron contamination with a magnet, and annealing the powder for 113 hours at 600°C in quartz tubes that had been evacuated by a zirconium getter. A correction was made for both linear and non-linear film shrinkage using the method described by Dickinson and

Armstrong in an earlier paper (3). The lattice constants were determined using the extrapolation method described by Nelson and Riley (4). The high temperature studies were carried out in the high temperature camera designed by Chiotti (5) of this Laboratory. Briefly, the camera consisted of a vacuum chamber containing a tantalum sheet resistance furnace and a thorium or a carbon specimen holder. The vacuum chamber was provided with an aluminum window to allow passage of the X-ray beam. X-ray diffraction patterns could be obtained at temperatures as high as 1600°C. A pressure of 2×10^{-6} to 5×10^{-5} mm of mercury was maintained during the heating cycle. High temperature X-ray specimens measuring $1/4$ by $1/16$ by $3/4$ inches were milled from arc-melted bars and polished in accordance with standard metallographic procedures.

Melting Range Determination

Three independent methods were used to determine the solidus of the niobium-thorium alloy system. Differential cooling curves employing a neutral body were obtained on several alloys. Both niobium-tungsten and platinum-platinum, 13% rhodium thermocouples were employed. The difference in temperature between the specimen and the niobium neutral body was recorded on the X_2 scale, -1.5 to +1.5 millivolt range, of a Leeds and Northrup Speedomax Recorder, while the temperature of the specimen was recorded on the X_1 scale of the same instrument.

The method of Pirani and Alterthum (6), which consists of heating a bar of the alloy by passing a high electrical current through it while observing the melting temperature with an optical pyrometer focused on a small hole that had been drilled in the bar, was also used to determine the eutectic temperature. Further evidence of the eutectic temperature was obtained by high temperature resistance measurements using the method and equipment described by Chiotti (7).

The thorium-rich liquidus curve was determined primarily by high temperature solubility studies. Crucibles of thorium metal were prepared by arc-melting and filled with an alloy of the eutectic composition. The crucible was then heated in a tantalum tube resistance furnace at the desired temperature until equilibrium was obtained and the portion of the sample that had been liquid was sampled for chemical analysis. To insure that the region that had been liquid was homogeneous three samples were taken by drilling successively larger holes. The analytical results gave the composition of the liquid at the specified temperature that had been in equilibrium with solid thorium.

Chemical Analysis

The separation of niobium from thorium was based on the insolubility of niobium in concentrated nitric acid containing sodium fluosilicate. The residue was collected on a filter paper,

ignited to the pentoxide and weighed. Thorium was determined in the standard way by precipitating thorium oxalate from the filtrate at a pH of 1, filtering, igniting to the oxide and weighing.

EXPERIMENTAL RESULTS

The phase diagram shown in Figure 1 has been constructed on the basis of data obtained by thermal analysis, X-ray diffraction, resistance measurements, and metallographic examination.

Eutectic Composition

The composition of the eutectic was located by microscopic examination. A 1.4% niobium alloy, Figure 2, contains a very fine eutectic structure in the grain boundaries plus primary grains of alpha thorium. Figure 3 shows a 3.9% niobium alloy that has been annealed below the eutectic temperature and rapidly cooled. This alloy also shows primary grains of thorium in a matrix of eutectic. An 8.0% niobium alloy (Figure 4) contains essentially all eutectic and is considered to be the eutectic composition. Figure 5 shows the structure of an annealed 9.0% niobium alloy containing primary niobium dendrites plus eutectic. The photomicrographs shown in Figures 6 and 7 are of a 25.5% and a 59.8% niobium alloy and show niobium dendrites plus eutectic. A small amount of fine eutectic structure is still visible in the 95% niobium alloy (Figure 8).

The phases present in the niobium-thorium alloys were identified by X-ray diffraction studies. Alpha thorium, $a_0 = 5.089 \text{ \AA}$, and niobium, $a_0 = 3.301 \text{ \AA}$, were present in a 52.2% niobium alloy. On the basis of the X-ray phase identification and the microstructures of the niobium-thorium alloys it is apparent that the alloy system is a eutectic type system with little if any solid solubility.

Solid Solubility

The extent of solid solution at room temperature has been estimated by X-ray diffraction studies. No change in the lattice constant of niobium was found upon the addition of thorium so that the extent of solid solubility of thorium in niobium is considered negligible. Figure 9 is a curve of the lattice constant of thorium against weight per cent niobium. There is a discontinuity in the curve occurring at a niobium concentration of less than 0.1% indicating that the extent of solid solubility of niobium in alpha thorium is less than 0.1%. However, carbon has been shown to increase the lattice constant of thorium so that there is a possibility that the lowering of the lattice constant may be due to the "getting" action of niobium on the carbon that had been in solid solution in the thorium. The extent of the lowering is such that the addition of only 0.1% niobium does not account for all of

Fig. 1 - Niobium-thorium phase diagram.

Fig. 2 - 1.4% Niobium. As arc-melted. Eutectic in grain boundaries. Electrolytic etch. X250.

Fig. 3 - 3.9% Niobium. Partially spheroidized eutectic plus thorium. Electrolytic etch. X250.

Fig. 4 - 8.0% Niobium. Annealed 8 hours, 1100°C. Eutectic. Electrolytic etch. X500.

Fig. 5 - 9.0% Niobium. Annealed. Niobium (white needles) plus spheroidized eutectic. Electrolytic etch. X250.

Fig. 6 - 25.5 Niobium. As arc-melted. Niobium dendrites plus eutectic. Electrolytic etch. X250.

Fig. 7 - 59.8 Niobium. As arc-melted. Niobium dendrites plus eutectic. Electrolytic etch. X250.

Fig. 8 - 95% Niobium. As arc-melted. Niobium crystals plus eutectic in grain boundaries. Aqua regia +5% HF etch. X250.

Fig. 9 - Change in lattice constant of thorium upon the addition of niobium.

the lowering of the lattice constant that was observed; therefore, there is undoubtedly some solubility of niobium in alpha thorium, although probably much less than 0.1% niobium.

The extent of solid solubility of niobium in beta thorium is less than 1% at the eutectic temperature. Eutectic structure could be identified microscopically in 1% niobium alloys quenched from the eutectic temperature. High temperature X-ray measurements indicate that the extent of solid solubility near the eutectic temperature is negligible. These X-ray data are based on only a few lines in the front reflection region which, of course, limits the accuracy of the measurements.

Melting Range

The data obtained from the three methods used to determine the eutectic and liquidus temperatures have been plotted in Figure 10. Seven heating and cooling curves obtained with a Pt-Pt, 13% Rh thermocouple on an 8% niobium alloy gave a thermal arrest at $1435 \pm 7^\circ\text{C}$. The cooling curves obtained with Nb-W thermocouples were, for the most part, quite erratic, and the results were not weighed heavily in constructing the phase diagram. Melting temperatures obtained by the melting bar method were in good agreement with those obtained from the cooling curves, but have a tendency to be slightly higher. This is as expected since the method depends upon the observation of the first formation of the liquid in a small hole in a bar of the alloy. A break was recorded in the resistance curves at $1435 \pm 5^\circ\text{C}$. Since all three methods are in good agreement in the eutectic region the eutectic temperature has been set at 1435°C .

The thorium liquidus data were primarily obtained from solubility measurements at high temperatures. These data when plotted fall on a straight line between the thorium melting point and the eutectic point. Several observations were made concerning the liquidus curves incidental to the determination of the eutectic temperature by the melting bar and resistance methods. In those cases when it was possible to get an accurate temperature measurement after the first sign of liquid had appeared, the sample was heated until it melted in two. This temperature was taken as an indication of the liquidus temperature.

Effect of Niobium on the α - β Transformation of Thorium

Chiotti (5) has recently identified an allotropic form of thorium that exists above $1400 \pm 25^\circ\text{C}$. The high temperature form is body centered cubic and has a lattice constant of about $4.12 \text{ \AA}$ at 1400°C . The effects of impurities on the transformation are only partially known; however, carbon has been shown to raise the transformation temperature drastically. Since the actual temperature at which the transformation occurs in high purity thorium is not accurately known, it is very difficult to establish with any degree of certainty the effects of niobium on the transformation.

Fig. 10 - Thermal, resistivity, and X-ray data for the niobium-thorium alloy system.

Resistivity versus temperature curves were obtained upon several thorium-rich alloys and in every case a break that was due to the transformation of thorium was detected. The temperatures at which this transformation occurred were badly scattered between 1335 and 1386°C (Figure 10). This rather large variation in the transformation temperature was not unexpected since the break starts over a rather large temperature range in thorium. However, the resistivity break observed in the niobium-thorium alloys came at a somewhat lower temperature than that observed for thorium.

High temperature X-ray data were also obtained on several thorium-rich alloys. These data are listed in Table 1. Again there is a large scattering in the values observed for the transformation temperature. Such a scattering has also been observed for the transformation in thorium that contains no niobium; in fact, the transformation temperature has been observed from about 1375 to over 1550°C in thorium with varying minor impurities.

Table 1

High Temperature X-Ray Results

Alloy Composition	Transformation Temperatures			
	Heating		Cooling	
	Started	Finished	Started	Finished
0.1	1370	1415	1355	1335
1	1390	1415	1385	1335
1	1345			
1	1325	1390	1345	1320
1	1370	1375		
3	1385	1405	1370	1355
5 ^a	1325	1325		

^aThe furnace shorted out and destroyed the sample during the experiment.

The evidence obtained from both the resistance data and the X-ray data indicate that the addition of niobium to thorium lowers the transformation temperature of thorium slightly.

SUMMARY

The niobium-thorium alloy system has been shown to be of the eutectic type with no intermediate phases present. The eutectic composition at about 8 weight per cent niobium has been determined from metallographic evidence and chemical analysis. On the basis of melting bar studies, cooling curves and resistivity measurements the eutectic temperature has been found to be $1435^{\circ} \pm 10^{\circ}\text{C}$. The thorium-rich liquidus has been determined experimentally. This curve extends almost linearly from the eutectic point to the melting point of thorium at 1690°C .

The solubility of thorium in solid niobium is considered to be negligible. On the basis of precision X-ray data the solid solubility of niobium in alpha thorium is less than 0.1 weight per cent. As estimated from metallographic examination the maximum solid solubility of niobium in beta thorium is less than 1 per cent.

The alpha-beta transformation of thorium reportedly at 1400°C is lowered slightly by the addition of niobium. No microscopic evidence could be found for the existence of a eutectoid suggesting that this lowering could be due to a scavenging action of niobium on thorium metal.

LITERATURE CITED

1. Hume-Rothery, W. The Structure of Metals and Alloys, London, England, Institute of Metals. 1936.
2. Hildebrand, J. H. and Scott, R. L. Solubility of Non-Electrolytes, p. 333, 3rd ed., New York, Reinhold Publishing Corporation. 1950.
3. Dickinson, J. M. and Armstrong, P. E. "A Method of Correcting for Film Shrinkage". To be submitted for publication.
4. Nelson, J. M. and Riley, D. P., Proc. Phys. Soc. (London) 57, 160 (1945).
5. Chiotti, P. ISC, Classified Report, Atomic Energy Commission (Jan., Feb., and Mar., 1953).
6. Pirani, M. and Alterthum, H., Z. Elektrochem. 29, 5 (1923).
7. Chiotti, P. Unpublished Ph.D. Thesis, Ames, Iowa, Ames Laboratory of Atomic Energy Commission (1952).