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THORIUM-MOLYBDENUM PHASE DIAGRAM

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Abstract

The phase diagram of the thorium-molybdenum alloy system has been determined to be of the eutectic type with a eutectoid reaction associated with the thorium alpha-beta transformation. X-ray, thermal, electrical resistance and metallographic methods have established the eutectic point at 1380 ± 10°C and 7.0 ± 0.5 wt % molybdenum. A eutectoid reaction is proposed at 1358 ± 5°C and less than 0.1 wt % molybdenum. No solubility of thorium in molybdenum was detected at 1325°C.

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DISCLAIMER

1. Introduction

The constitutional diagram of the thorium-molybdenum system was sought in order to increase the fund of basic information concerning these materials which are of interest in both refractory and nuclear applications. Preliminary reports of this investigation have appeared in the Ames Laboratory annual research reports[1, 2]. Some of these data have also been included in a compilation by Rough and Bauer[3]. However, through the use of higher purity materials and improved experimental techniques as compared to the earlier work, the results reported here are more reliable and more complete.

2. Apparatus and Procedures

2.1 PREPARATION OF ALLOYS

The high purity molybdenum sheet used to prepare the alloys was supplied by the North American Philips Company. Table 1 gives the impurity content of this metal and the thorium used in this investigation. The crystal-bar thorium was purified in the Ames Laboratory by the iodide process.

Charges of intended compositions were arc-melted under a purified helium atmosphere in a non-consumable tungsten electrode furnace. Fairly homogeneous button- and rod-shaped samples weighing 50 to 60 g each were obtained by melting the charges several times and inverting them between melts. In some cases the γ-molybdenum dendritic phase was concentrated in the center of the button and was surrounded by the lower melting eutectic constituent. Further melting at higher arc power settings increased the homogeneity of these ingots. Weight losses during

Table 1

Analysis of the component metals

Impurity element	Content in molybdenum (ppm)	Content in thorium (ppm)
C	85 [a])	75-100 [a])
O	34 [b])	50-150 [b])
N	50 [c])	75-150 [c])
H	1 [b])	4 [b])

Spectrographic analysis for (1) molybdenum: Bi, Cr, Ni and Si - trace; Co, Cu and Fe - faint trace (2) thorium: Mn, Al, Be, Ca, Mg, Si, Zr and Ni - below the lower limit of standards - usually < 20 ppm.

[a]) Combustion-conductometric analysis
[b]) Vacuum fusion analysis
[c]) Kjeldahl type analysis

the melting procedures were negligible: therefore, the data obtained from this investigation are based on the intended compositions.

2.2 MELTING POINT DETERMINATIONS

The specimen dimensions, apparatus and procedure used to obtain solidus and liquidus data have been described by Williams et al. [4]. An optical pyrometer was used to measure both the surface and black-body temperature of the necked-down bar specimen which was heated in vacuum by its own resistance to an electric current. The solidus temperature was indicated by the appearance of a dark spot in the bottom of the sight hole due to disruption of the black-body conditions by molten metal. The surface temperature at which the bar melted in two was corrected for emissivity by use of the extrapolated black-body vs surface temperature relationship, and this was taken as the approximate liquidus temperature for the specimen.

2.3 ELECTRICAL RESISTANCE MEASUREMENTS

Anomalies in the resistance-temperature curves due to solid state transformations were detected by potentiometric methods. The emf drop across 0.03 to 0.05 in. diameter wire specimens about 5 in. in length was plotted vs temperature over the 800 to 1400°C range. A Pt-Pt+13%Rh thermocouple and 20 mil diameter tantalum potential leads, which had been spot welded to the specimen, were used in conjunction with a Moseley X-Y recorder. The potential drop was made proportional to the resistance of the specimen through the use of a constant current power supply. The specimen was heated in an evacuated tube in a resistance furnace having silicon carbide elements.

Tantalum cylinders placed in the heat zone and around the insulated leads were electrically grounded to eliminate the induced emf produced by the furnace elements. A massive piece of thorium located in the heat zone was used as an oxygen sink during the experiment.

2.4 X-RAY DIFFRACTION METHODS

A Debye-Scherrer camera and nickel-filtered copper radiation were used to obtain powder patterns. Filings from arc-cast samples were sealed in tantalum envelopes by spot welding before heat treatment. These powder specimens were heat treated at 700°C for 24 hours and slow cooled, at 1225°C for 8 hours and quenched, or at 1325°C for 8 hours and quenched. A vertically mounted molybdenum wound resistance furnace was used in the quenching operations. Envelopes containing powders were suspended in the furnace and dropped into a water-cooled brass crucible by severing the suspension wire. The thorium-rich powders heat treated at 1325°C were sintered. Therefore, powders were filed from these samples and stress-relieved at 700°C for 6 hours. An optical pyrometer was used to measure the quenching temperatures.

The a_{hkl} values for reflections at Bragg $\theta \geq 60°$ were plotted vs the Nelson-Riley function. The a_o value was obtained by fitting these data to a straight line by least squares methods and extrapolating to Bragg $\theta = 90°$. Solubility values were determined from the resulting lattice parameters assuming Vegard's Law to hold. The computations included the effects of the change in coordination number[5]) on the atomic diameters and are exemplified by Palmer et al.[6]). These calculations

showed that a 0.1 at.% (0.04 wt %) solid solution of molybdenum in thorium is represented by a decrease of 0.0011 Å in the lattice parameter of thorium, and an increase of 0.0009 Å in the lattice parameter of molybdenum is equivalent to 0.1 at.% (0.24 wt %) thorium solubility in molybdenum.

2.5 METALLOGRAPHY

Thorium-rich samples were electropolished in order to avoid the scratched surfaces usually produced by mechanical polishing. The electrolyte was a solution of 10 parts methanol, 7 parts butyl "Cellosolve" and 1 part perchloric acid (70%). The eutectic structure was best revealed by swabbing the surfaces with a chemical etchant of 1 part HF, 10 parts HNO_3 and 40 parts water for about 1 minute. The surfaces of the molybdenum-rich samples were prepared for microscopic examination by alternately mechanically polishing and etching. Murakamis' reagent, 10 g KOH and 10 g $K_3Fe(CN)_6$ dissolved in 100 ml water, was used as the etchant and was applied by swabbing the samples for 2-3 minutes.

3. Experimental Results and Discussion

3.1 SOLIDUS AND LIQUIDUS DATA

A eutectic reaction isotherm was established at 1380 ± 10°C for the thorium-molybdenum system. The solidus and liquidus points, both of which resulted from melting point determinations, are listed in Table 2 and are plotted in Fig. 1. The liquidus lines are dashed because of the ± 50°C uncertainty of the temperature measurements.

Table 2

Data from melting point determinations

Composition wt % molybdenum	Solidus, °C ± 10°C	Liquidus, °C ± 50°C
thorium	1750 ± 10°C	
1.0	1385	
2.0	1377 [a])	
5.0	1383 [a])	
8.0	1385	
10.0	1378	
12.0	1377	1410
15.0	1378	
25.0	1383	1450
34.8	1383	1465
40.0	1383	1550
57.0	1385	1700
60.0	1383	1800
70.0	1384	1800
80.0		1910
90.0		2225
92.0	1385	2250
95.0		2400
molybdenum	2620 ± 10°C	

[a]) average of 3 determinations

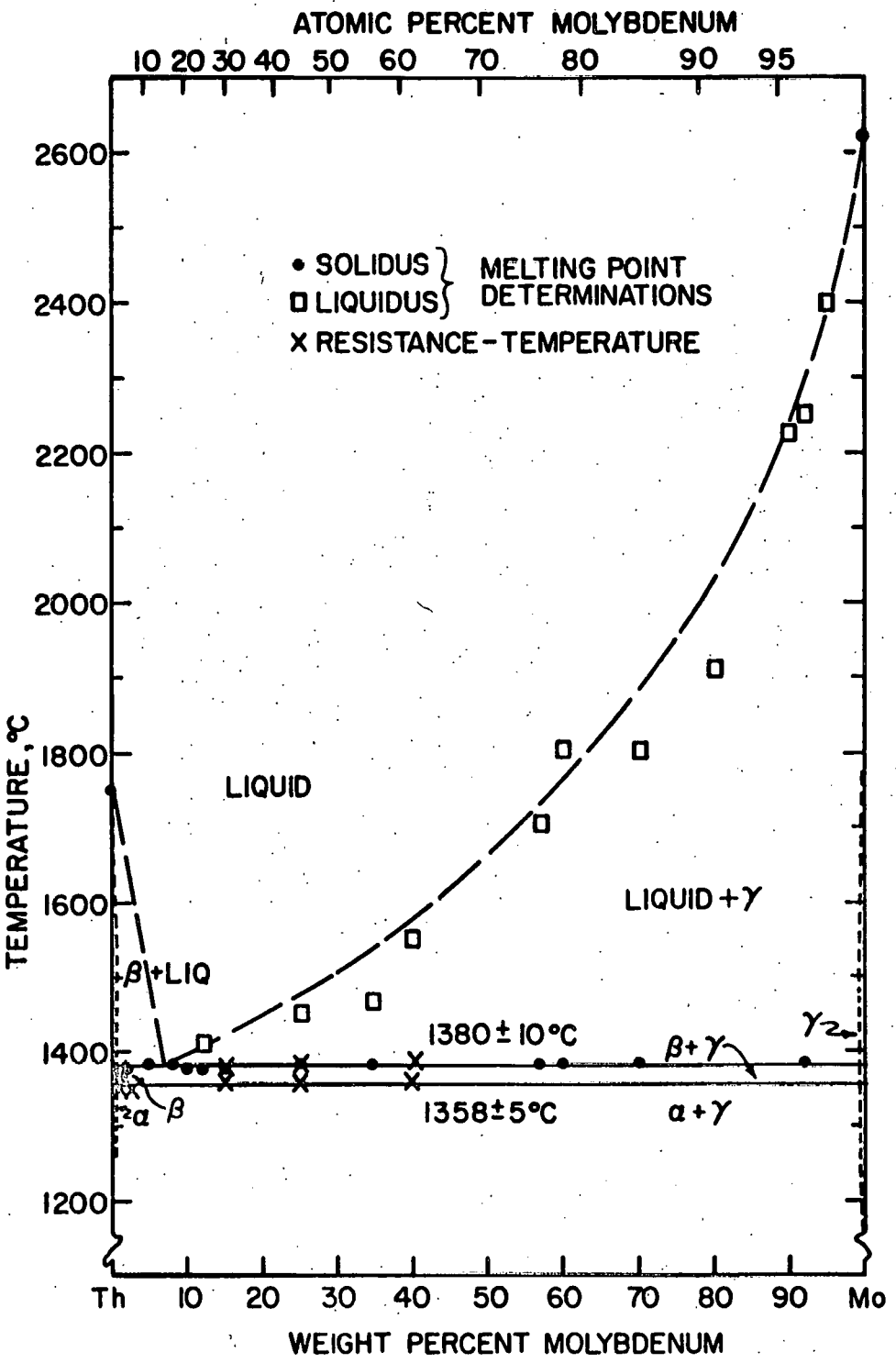

Fig. 1. The phase diagram of the thorium-molybdenum alloy system.

As indicated in Table 3, some solidus data were obtained in the resistance-temperature studies from plots similar to those shown in Fig. 2.

3.2 EFFECTS OF MOLYBDENUM ON THE TRANSFORMATION OF THORIUM

As determined from the resistance-temperature analyses, the 1365 ± 5°C thorium transformation temperature is slightly lowered to 1358 ± 5°C due to the alloying effects of molybdenum. The results listed in Table 3 are plotted in Fig. 1 and suggest that a eutectoidal arrangement is associated with the allotropic transformation of thorium. Fig. 2 shows the data obtained from a typical resistance-temperature experiment as plotted by a Moseley X-Y recorder.

Solubility data in support of the suggested eutectoidal arrangement could not be obtained because of the limited area of the beta plus gamma field. Attempts were made to quench powder specimens for X-ray diffraction analysis, but insufficient accuracy of the measurement of quenching temperatures left some doubt as to the temperature represented by the resulting solubility data. The solubility data listed in Table 4 show that molybdenum is only slightly soluble in alpha-thorium at 1325°C.

3.3 SOLUBILITY LIMITS

The solubility of molybdenum in thorium decreases from the 0.05 wt % detected at 1325°C to essentially zero at room temperature. No solubility of thorium in molybdenum was detected by X-ray diffraction in samples quenched from 1325°C or slow cooled to room

Table 3

Resistance-temperature data

Composition wt % molybdenum	Eutectoid temperature [a] ± 5°C	Eutectic temperature [a] ± 10°C
thorium	1365	
0.5	1354	1378
2.0	1352	1382
15.0	1362	1388
25.0	1359	1387
40.0	1360	1385

[a]) average values of 2 to 5 data points

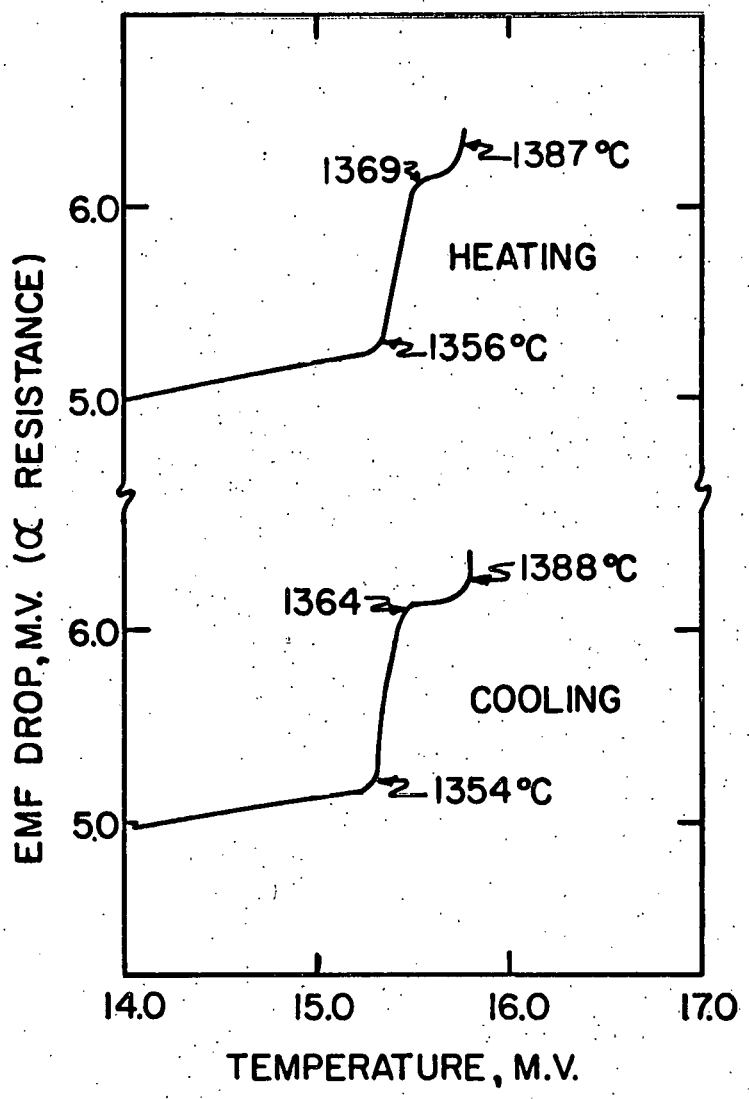

Fig. 2. Electrical resistance vs temperature curves for a 2.0 wt % Mo-Th alloy.

Table 4

X-ray diffraction solubility data

Composition	Number of patterns	Temperature before quench, °C	Lattice parameter a_o, Å	Δa_o, Å	Solubility at. %	Solubility wt %
thorium	2	1225	5.0872			
1.0 wt % Mo-Th	2				Mo in Th	
2.0 wt % Mo-Th	1	1225	5.0865	-0.0007	0.06	0.025
5.0 wt % Mo-Th	2					
thorium	4	1325	5.0920			
5.0 wt % Mo-Th	3	1325	5.0907	-0.0013	0.12	0.050
molybdenum	5	1325	3.1469			
96.0 wt % Mo-Th	2				Th in Mo	
99.0 wt % Mo-Th	2	1325	3.1469	0.0000	none detected	
99.5 wt % Mo-Th	2					

temperature. Solubility data obtained from quenched powder specimens by X-ray diffraction methods are listed in Table 4.

The two phase microstructures of the 0.5 and 99.5 wt % Mo-Th metallographic specimens were not noticeably changed during the heat treatment of the arc-cast specimens at 1300°C for 50 hours. On the basis of the relative proportions of the two constituents observed in these heat treated specimens, the solubility limits at 1300°C were determined to be considerably less than 0.5 wt % alloying component.

3.4 EUTECTIC COMPOSITION

The microstructures of arc-cast thorium-molybdenum samples, similar to those shown in Figs. 3, 4 and 5 established the eutectic composition at 7.0 ± 0.5 wt % Mo-Th. Identification of the primary dendrites on either side of the eutectic composition was made by observing the easily recognizable differences of appearance of these dendrites after they had been subjected to an acidic etchant treatment. The γ-molybdenum dendrites were quite vigorously attacked by a 1-HF:10-HNO_3:40-H_2O solution applied for 1 minute, while the thorium dendrites were only slightly affected.

Acknowledgments

The authors wish to express their appreciation to Mr. D. E. Williams for his counsel and advice during this investigation.

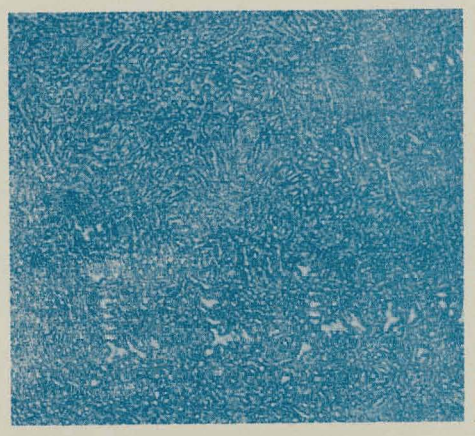

Fig. 3. - 9 wt % Mo-Th.
Gamma molybdenum solid solution dendrites in a eutectic matrix. X750.
Etchant: Murakamis' reagent.

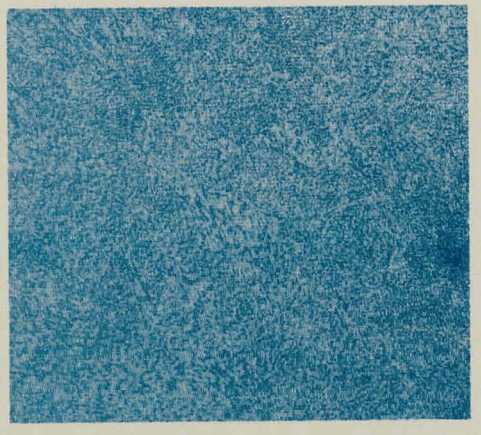

Fig. 4 - 7 wt % Mo-Th.
Eutectic. X300.
Etchant: $HF:HNO_3:H_2O$ (1:10:40).

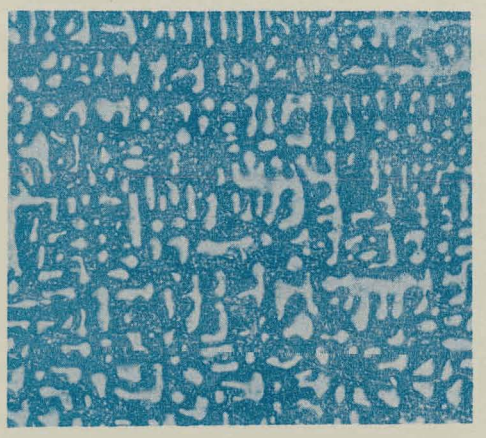

Fig. 5 - 5 wt % Mo-Th.
Alpha thorium solid solution dendrites in a eutectic matrix. X500.
Etchant: Same as Fig. 4.

All samples are in their as-cast condition.

References

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Figure Captions

Fig. 1. The phase diagram of the thorium-molybdenum alloy system.

Fig. 2. Electrical resistance vs temperature curves for a 2.0 wt % Mo-Th alloy.

Fig. 3. 9 wt % Mo-Th. Gamma molybdenum solid solution dendrites in a eutectic matrix. X750. Etchant: Murakamis' reagent.

Fig. 4. 7 wt % Mo-Th. Eutectic. X300. Etchant: $HF:HNO_3:H_2O$ (1:10:40).

Fig. 5. 5 wt % Mo-Th. Alpha thorium solid solution dendrites in a eutectic matrix. X500. Etchant: Same as Fig. 4.
All samples are in their as-cast condition.