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PHASE EQUILIBRIA IN THE THORIUM-TANTALUM SYSTEM*

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SUMMARY

X-ray, electrical resistance, thermal and metallographic methods were used to determine the phase diagram of the thorium-tantalum system. The diagram is of the simple eutectic type with a eutectoid reaction associated with the thorium α-β transformation. The eutectic point occurs at 1565±10°C and 4.0±0.5 wt % tantalum. No evidence of intermetallic compounds was found and only slight terminal solid solubility was found at either end of the diagram, even at elevated temperatures. The solubility of tantalum in thorium at the eutectic temperature is about 0.4 wt % and below 1340°C is less than 0.2 wt %. The solubility of thorium in tantalum was found to be less than 0.2 wt % at the eutectic temperature.

INTRODUCTION

This investigation was undertaken in order to establish the constitutional diagram of the thorium-tantalum alloys and to increase the

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DISCLAIMER

knowledge of thorium and tantalum metallurgy. Chiotti[1] has reported that thorium has a face centered cubic structure at temperatures up to 1360±10°C and a body centered cubic structure from 1360°C to the 1750±10°C melting point. The lattice spacing for the face centered cubic form at room temperature is 5.0843 Å according to Evans and Raynor[2]. Williams and Pechin[3] report that tantalum exists in the body centered cubic form up to the 2940°C melting point.

The behavior of tantalum upon alloying with thorium and other elements is predicted by Miller[4]. The collective results from several considerations predicted that thorium is a marginal case for liquid immiscibility with tantalum. Also, the size factor of thorium is unfavorable for solid solution formation and compounds are unlikely to form with tantalum. That the thorium-tantalum alloy system is most probably of the eutectic type was deduced from the diagrams of the thorium-group V-B alloy systems as compiled by Rough and Bauer[5].

PREPARATION OF ALLOYS

Component metals

The tantalum used in the preparation of the alloys was supplied by the Fansteel Metallurgical Corporation and was specified as high purity sheet. The impurity content of this metal and that of the thorium is given in Table I. The crystal-bar thorium used in this investigation was prepared by McMasters in the Ames Laboratory. The iodide process as described by Veigel, et al.[6] was duplicated on a 200-300 gram batch basis.

TABLE I

ANALYSIS OF THE COMPONENT METALS

Impurity element	Content in tantalum(ppm)	Content in thorium(ppm)
Carbon	16*	75-100*
Oxygen	50**	50-150**
Nitrogen	22**	75-150*
Hydrogen	1**	4**
Iron	40*	<20

*Chemical analysis.
**Vacuum fusion analysis.
Spectrographic analysis for: (1) tantalum, Ti and Si <20 ppm, Mg and Nb - faint trace; (2) thorium, Mn, Al, Be, Ca, Mg, Si, Zr, and Ni - below lower limit of standards, usually <20 ppm.

Melting and homogenizing

A tungsten-electrode arc-furnace, as described by Levingston and Williams[7], was used to melt the alloys. Charges of intended compositions were melted several times and were turned over between melts in an attempt to make them homogeneous. Weight losses during the melting procedures were negligible and the data from this investigation are based on the intended compositions. The large difference between the melting points of the component metals made melting and homogenizing of the alloys difficult. Splattering of the molten charge necessitated power reductions in the arc in order to avoid sample losses and to facilitate ingot shaping. The resulting ingots were not homogeneous since the lower melting eutectic constituent tended to form a shell around

the higher melting center portion which was dendritic in nature. Cold-working and homogenizing heat treatments usually preceded the taking of data.

Fabrication

Melting point bars, as shown by Williams[8], were prepared by milling. Resistance-temperature specimens were prepared by swaging 0.250-in. diameter arc-cast rods into 0.030-in. wires. Flaking of the dendritic phase during swaging of 10 mil wire to be used for x-ray diffraction specimens was avoided by choosing samples in the 1.0 to 10 and 90 to 99 wt % Ta-Th composition ranges.

APPARATUS AND PROCEDURES

Melting point determinations

The apparatus and procedure used to obtain solidus data have been described by Williams[8]. The eutectic temperature data obtained from the necked-down bar specimens were determined by observing the temperature at which the molten metal disrupted the black-body conditions by causing a dark spot to appear at the bottom of the pyrometer sight hole. The liquidus lines were located by observing the temperature at which the specimens melted in two. Since only surface temperatures are available above the solidus, the liquidus temperatures were corrected for emissivity by extrapolating the black-body versus surface temperature data obtained below the solidus. The extrapolation required the assumption that the surface temperature dependence of the emissivity is the same both below and above the solidus temperature.

Electrical resistance versus temperature

The apparatus, basic circuit and procedure used to obtain resistance-temperature data are reported by Rogers and Atkins[9]. Two specimens, usually one thorium and the other a thorium-tantalum alloy, were connected in series with a standard resistor and a 6-volt storage battery. Ten mil diameter tantalum potential leads were spot welded, under a helium atmosphere, to the specimens. The specimens were heated under vacuum in an electric furnace having silicon-carbide resistance heating elements. Resistance values were determined by measuring the voltage drop across the specimens and the standard resistance. The temperature was measured by a Pt-Pt+13% Rh thermocouple giving data over a range from 30°C to 1425°C.

X-ray diffraction methods

Powders were filed from the melting point specimens and given a stress-relief anneal at 650°C for 36 hours. Thin sheet specimens prepared by rolling were stress-relieved by heat treatments prior to quenching and were used in conjunction with a focusing back-reflection camera. A diffractometer was used for phase identification in some metallographic specimens using standard procedures.

The more significant x-ray data were obtained from quenched wire specimens using a Debye-Scherrer camera and copper K_α radiation. Ten mil diameter wire specimens were heated by their own resistance between two water-cooled copper electrodes and quenched by thermal conduction when the power was turned off.

Metallography

The polishing and etching procedures were complicated by the nature of the alloys. The eutectic constituent is more readily attacked by etchants than is either dendritic phase, thus leaving the dendrites in relief. An electropolish was used in the final stages in order to avoid the scratches produced by the mechanical polishing.

A cathodic etching apparatus described by Carlson, et al.[10] was used for some of the metallographic specimens.

EXPERIMENTAL RESULTS

Solidus and liquidus data

Melting point determinations were used to establish the temperature of the eutectic reaction isotherm and to approximate the position of the liquidus lines. The data listed in Table II and plotted in Fig. 1 placed the eutectic temperature at 1565±10°C. The liquidus data are listed in Table II and the liquidus lines appear as dashed lines in the diagram, since the data were only reliable to about ±50°C.

Effects of tantalum on the transformation of thorium

Resistance-temperature data and x-ray diffraction results were used to determine the nature of the reaction associated with the allotropic transformation of thorium. This portion of the diagram is shown in the insert in Fig. 1.

Table III lists the results obtained from several resistance-temperature experiments and Fig. 2 is a plot of the data from a typical

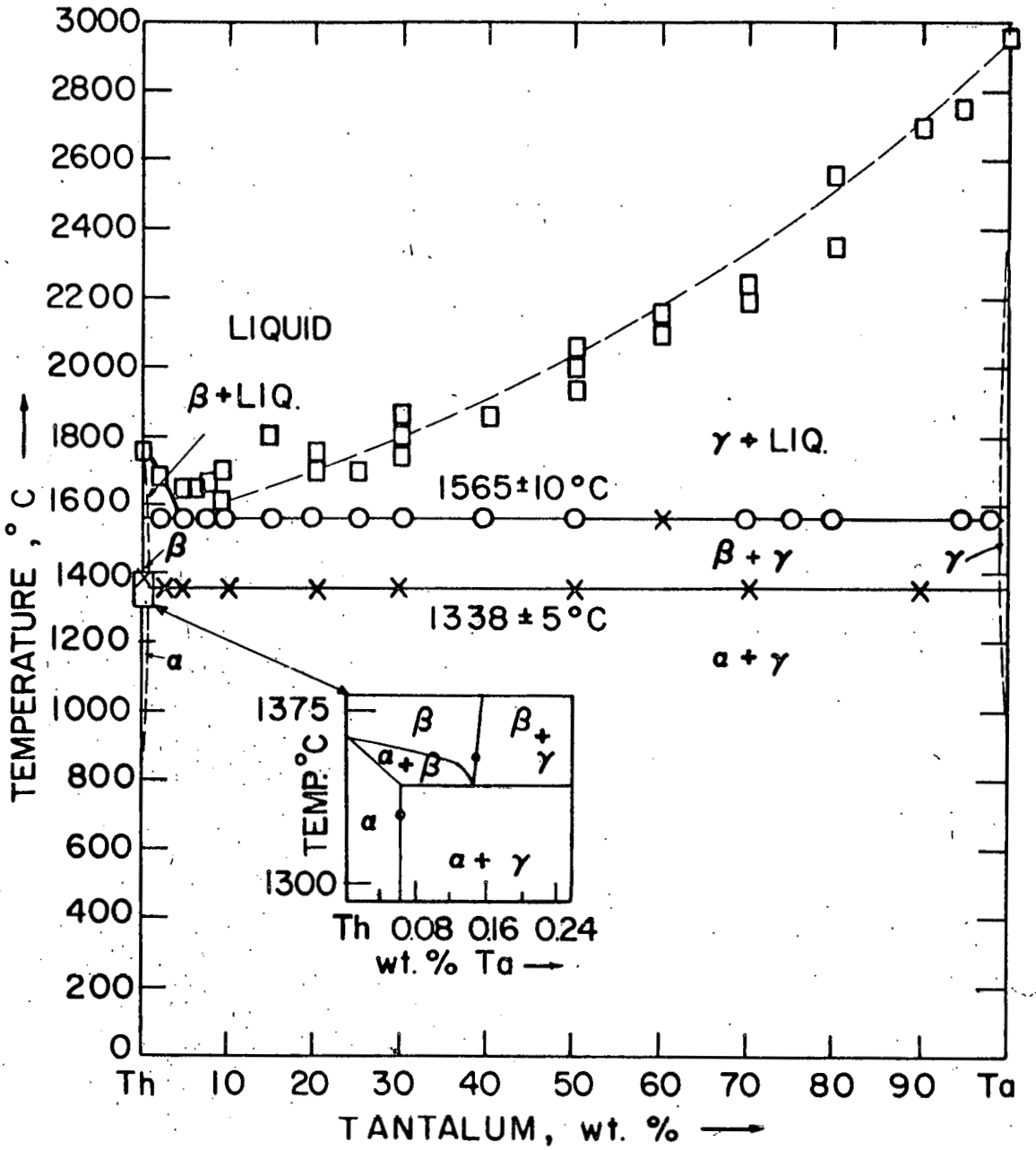

Figure 1. Plot of data from which the thorium-tantalum diagram was drawn.

- o solidus data from melting point determinations
- □ liquidus data from melting point determinations
- x electrical resistance versus temperature results
- • data from x-ray diffraction patterns

TABLE II

DATA FROM THE MELTING POINT DETERMINATIONS

wt % Ta-Th	solidus, °C	liquidus, °C
thorium	melting points of 1700°C and 1725°C	
3.1	1563*	1685
5.0	1565*	1640
6.0	1565	1650
7.5	1563*	1620
9.0	1563	1680
10.6	----	1700
15.0	1565	1800
20.0	1565*	1725
25.0	1570**	1700
30.0	1566**	1800
40.0	1565	1850
50.0	1566**	1975
60.0	----	2125
70.0	1573	2230
75.0	1568	2025
80.0	1568*	2475
90.0	1570	----
95.0	1570	2750
98.0	1575	----
tantalum	melting point 2940°C+	

*average of two measurements
**average of three measurements
+reported by Williams and Pechin[3]

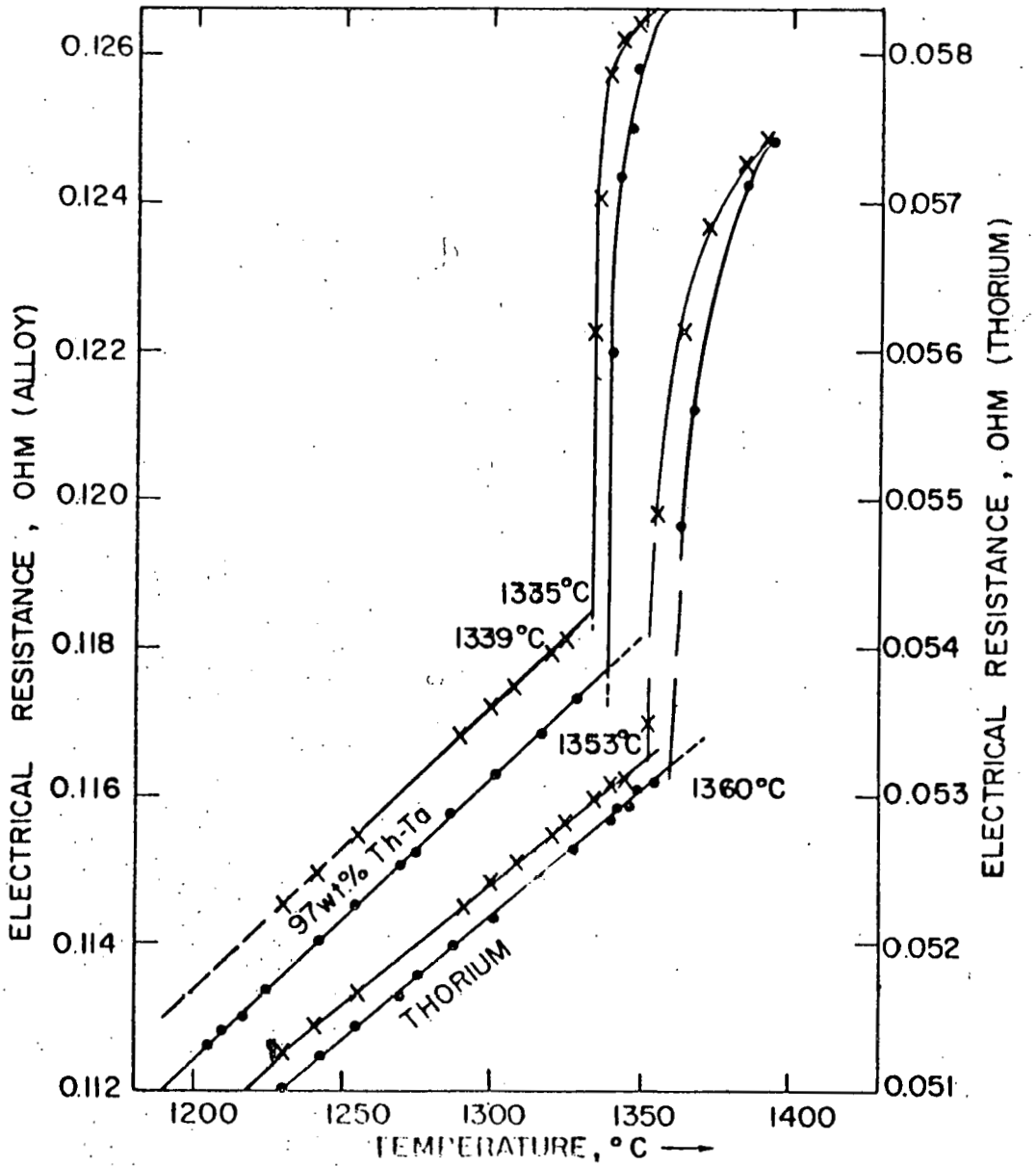

Figure 2. Electrical resistance versus temperature graphs for unalloyed thorium and 3 wt % Ta-Th specimens.

• heating data
x cooling data

TABLE III

RESISTANCE-TEMPERATURE DATA

Experiment number	Composition	Transformation Temperature heating, °C	cooling, °C
1	Th	1365	----
	10.0 wt % Ta	1335	----
2	Th	1367	1362
	10.0 wt % Ta	1338	----
3	Th	1369	1373
	20.0 wt % Ta	1339	1342
4	Th	1360	1358
	10.0 wt % Ta	1338	1342
5	Th	1365	----
6	Th	1368	1353
	3.2 wt % Ta	1339	1335
7	7.5 wt % Ta	1338	1333
average for unalloyed thorium		1363±10°C	
average for alloyed thorium		1338± 5°C	

experiment. The temperature of the transformation in pure thorium was obtained by averaging the heating curve and cooling curve values from several runs and is 1363±10°C. A temperature of 1338±5°C was obtained in a similar manner for the alloyed specimens. The addition of tantalum to thorium thus lowers the transformation temperature and a eutectoidal arrangement is strongly suggested. The greater precision of the data for alloy samples suggests that some of the tantalum may be removing

carbon from solution in the thorium to give Ta_2C [1]. While the presence of carbon or other impurities may thus be affecting the transformation temperatures observed, it is not expected that the form of the diagram is other than eutectoidal.

X-ray diffraction data obtained from quenched wire specimens yielded solubility values which are in agreement with the suggested eutectoidal arrangement. Precautions were taken to minimize the contamination of the freshly prepared specimens used in the final analysis. Three x-ray patterns from different portions of each quenched wire were measured and the lattice parameters calculated from the individual reflections, (a_{hkl}) were averaged. These average a_{hkl} values and their corresponding Nelson-Riley functions were used to calculate a_o by the method of least squares, as described by Cullity[11]. These lattice parameters are listed in Table IV. The solubility data given in Table IV resulted from the calculations based on the lattice parameter values assuming that Vegard's Law holds for this dilute solution case. Calculations included correction factors for co-ordination numbers and for atomic diameter differences. Solubilities of Ta in Th are based on the computation which shows that 1.0 wt % Ta dissolved in Th produces a lattice contraction, Δa_o, of 0.0092 Å. A lattice parameter of 5.0854 ± 0.0004 Å was determined for unalloyed thorium by averaging values obtained from several specimens quenched from various temperatures. Evans and Raynor[2] listed a number of lattice parameters reported by various investigators and discussed the necessary precautions that must be taken if accurate values are to

TABLE IV

SOLUBILITY DATA OBTAINED BY X-RAY DIFFRACTION METHODS

Composition	Temperature before quench ±15°C	a_o, Å	Δa_o, Å	Solubility wt %
Thorium	1330	5.0853		
	1375	5.0855		
5.1 wt % Ta	1330	5.0846		
	1375	5.0838		
10.0 wt % Ta	1330	5.0848		
	1375	5.0844		
				Ta in Th
Alloyed Thorium	1330	5.0847	0.0006	0.06
(average)	1375	5.0841	0.0014	0.15
Tantalum	1350	3.3030		
				Th in Ta
95.0 wt % Ta	1350	3.3032	0.0002	0.02

be obtained. The evidence of their work pointed toward an a_o of 5.0843 Å as the preferred lattice spacing for iodide thorium at room temperature.

The solubility and resistance-temperature data are consistent with the requirements of a simple eutectoidal arrangement but the effort required to obtain the additional information needed to positively establish such an arrangement did not appear to be warranted in light of its limited contribution to the practical value of the investigation. Thus a simple eutectoidal arrangement was postulated as the most probable form of this reaction as shown in Fig. 1.

Solubility limits

On the basis of the data of Table IV, the β to $\beta+\gamma$ solvus in the eutectoidal region of the diagram has been placed at less than 0.2 wt % Ta-Th. A solubility of 0.4 wt % Ta-Th at the eutectic temperature was estimated from diffraction data of α-thorium obtained from samples quenched from 1525°C. As indicated by the parameter values, there is virtually no solid solubility of thorium in tantalum at 1350°C and less than 0.2 wt % Th in Ta at the eutectic temperature was detected by use of back-reflection equipment.

Room temperature solubility data were obtained by x-ray diffraction methods using powder specimens. No differences in parameter values could be detected between alloyed and unalloyed specimens, so it was concluded that the solubility at room temperature must be less than 0.1 wt % on both sides of the diagram.

Metallographic results

Metallography was used to establish the eutectic composition. The as-cast structures of samples with decreasing amounts of tantalum were observed microscopically. The eutectic composition was approached from the tantalum rich side since the gamma tantalum dendrites that formed on freezing were easily identified. The eutectic composition pictured in Fig. 4 was established at 4.0 ± 0.5 wt % Ta-Th by this method. The 6 wt % Ta-Th microstructure shown in Fig. 3 exhibits a few γ-Ta dendrites and the 2 wt % Ta-Th microstructure shown in Fig. 5 displays thorium solid solution in a eutectic matrix. A relatively harsh electrolytic

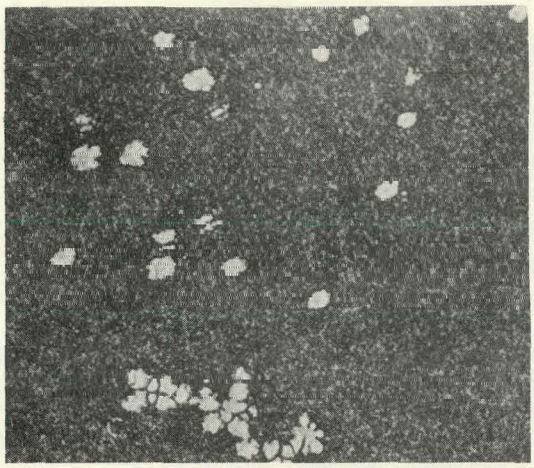

Fig. 3 - 6 wt % Ta-Th. Gamma tantalum solid solution dendrites in a eutectic matrix.

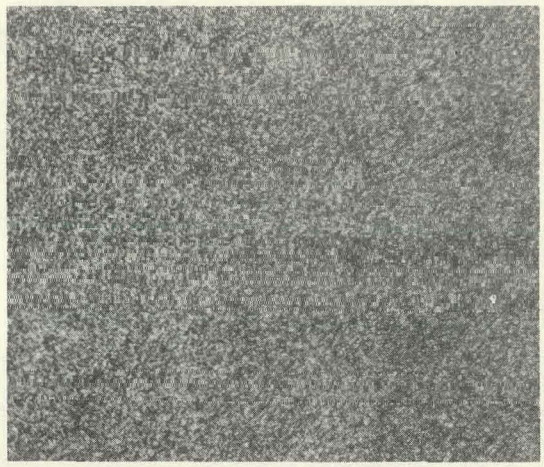

Fig. 4 - 4 wt % Ta-Th. Eutectic.

Above samples etched by swabbing the surfaces for one minute with a 1:5 conc. nitric acid to water solution to which was added 0.25 gm. sodium fluosilicate for each 100 ml.

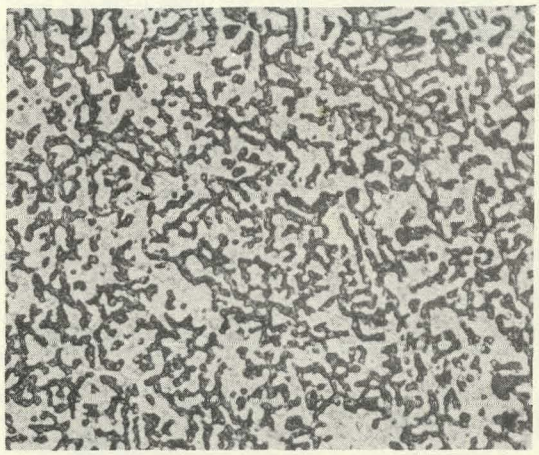

Fig. 5 - 2 wt % Ta-Th. Alpha thorium solid solution (light) in a eutectic matrix. X 500.

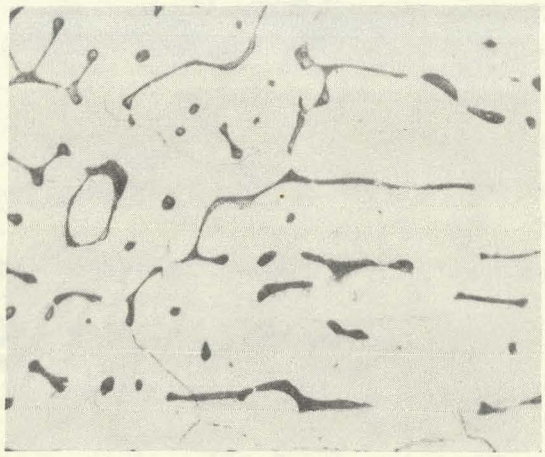

Fig. 6 - 1 wt % Ta-Th. Alpha thorium solid solution plus eutectic (dark). X 500.

Above samples etched electrolytically. Electrolyte: 1:1 85% orthophosphoric acid to 90% formic acid. Exposures of 30 seconds at 35 volts and 0.6 amperes.

All samples are in their as-cast condition. X 500.

etching treatment was required to disclose the thorium solid solution, while the γ-Ta dendrites were prominent after the application of a mild etchant for a brief period of time.

All alloy samples prepared in this investigation exhibited two-phase microstructures. The microstructure of an arc-cast 1 wt % Ta-Th sample is shown in Fig. 6. Samples of compositions 1 wt % Ta-Th and 99 wt % Ta-Th which were heat treated at 1300°C and 1540°C for several hours displayed two-phase microstructures which were not detectably different from those of the arc-cast samples. Therefore, solubility limits of less than 1 wt % at 1540°C were deduced from this analysis.

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