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METALLOGRAPHY SECTION

THE TUBALLOY-THORIUM BINARY SYSTEM

PROBLEM ASSIGNMENT - #10

by

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Abstract

^{Q2U}
~~An~~ investigation of the Th-~~Pa~~ system 7
has been completed, and a constitutional diagram
has been drawn up. ~~(see Fig. 1)~~ A simple eutec-
tic exists with complete miscibility in the li-
quid state and complete heterogeneity in the
solid state. No intermetallic compound was
found nor was there any evidence of solid solu-
bility of one component in the other. The
~~Th~~-rich liquidus was not located. (auth)

I. Experimental Techniques

A survey of this system was begun before a quantity of thorium metal was obtainable. Therefore, the first few alloys were prepared by a co-reduction of the mixed fluorides of tuballoy and thorium with calcium. This method proved satisfactory for tuballoy-rich alloys but gave very poor reduction on thorium-rich alloys, and was abandoned when a supply of thorium became available. The procedure then adopted consisted of heating appropriate amounts of the metals self-inductively to a temperature of 1500 to 1900°C, depending upon the composition of the alloy. After testing several types of refractories, it was found that slip cast beryllia crucibles gave the best results. Alloy samples weighing about 600 grams (40 to 60 cc in volume) were prepared for each composition studied. While induction stirring usually provided adequate mixing of the melt, there was occasionally found slight segregation as the less dense thorium dendrites would tend to float to the surface.

The same furnace treatment was given all samples before studying them in order that comparable results might be obtained. Prior to thermal analysis, a thermocouple well was drilled into each casting and the drillings analyzed chemically. The sample was next annealed just below the eutectic temperature for 24 hours. The same apparatus was employed on all heating and cooling curves. This consisted of a graphite heater crucible packed with Norblack insulation (a special grade of lamp black) in a quartz vacuum jacket. The furnace was heated by induction to the desired temperature and then allowed to cool uncontrolled. This gave a smooth reproducible curve with an average cooling rate of about 6 to 8 degrees per minute. The eutectic and transformation breaks were obtained with a chromel-alumel couple using a Micromax automatic recorder. W-Mo and Pt-Pt 13 per cent Rh thermocouples were also used in unsuccessful attempts to locate the thorium-rich liquidus.

The degree of solid solubility of each component in the other has been estimated from the microstructures of annealed and quenched samples.

X-ray diffraction patterns were taken on powdered samples in a Debye-Scherrer camera with filtered copper K α radiation.

For chemical analysis separate samples were dissolved in HCl plus HClO_4 . The tuballoy was reduced in a Jones reductor and titrated with a standard ceric sulfate solution. The thorium was precipitated as the oxalate, ignited to the oxide and weighed.

II. Experimental Data and Interpretation of Results

While the completed system now appears extremely simple, early results were misleading and often confusing. For instance, at one time, it was believed that an intermetallic compound existed. This supposition was based upon (1) hardness values which showed an increase in hardness with an increase in thorium content, suggesting an intermetallic compound, and (2) upon x-ray data in which lines appeared which could not be indexed as either thorium or tuballoy.

TUBALLOY-THORIUM SYSTEM

FIG. 1

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THERMAL DATA ON TU-TH SYSTEM
FIG. 2

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It was later found, however, that as the samples which contained more thorium were heated longer at higher temperatures to insure equilibrium, there was more reaction of the thorium with the crucible and more carbon pick-up by the thorium which greatly increased the hardness of the thorium phase, sometimes resulting in hardness values above that of tuballoy. Using samples which have been prepared with great care to prevent oxygen and carbon contamination, it has been found that on a plot of hardness against composition, the curve rises from Rockwell B 92 for pure tuballoy to 100 B at the eutectic and then drops evenly to 70 B for cast thorium.

Continued x-ray studies identified most of the "compound lines" as impurities in the form of oxides, carbides and nitrides. An x-ray diffraction pattern of a 50-50 weight per cent sample which had been carefully prepared to prevent any contamination showed the following:

<u>Phase present</u>	<u>Lattice spacing</u>	<u>Intensity of Lines</u>
Thorium metal	$a_0 = 5.09 \pm 0.02 \text{ \AA}$	VS
$\propto$ tuballoy metal		M to S
Thorium dioxide	$a_0 = 5.59 \pm 0.02 \text{ \AA}$	W to VW

Thermal data and microscopic study have established the eutectic in this system to be at 5 wt.% thorium, freezing at 1085°C. (See Figures 3-9). The eutectic structure tends to become very obscure in the high thorium alloys due to the diffusion and agglomeration of the particles in the eutectic when the sample is cooled slowly or annealed at high temperatures. From photomicrographs of alloys on the thorium-rich side of the eutectic composition, which have been cooled, the eutectic phase seems to have disappeared leaving two clear phases. However, if the sample is quenched at the eutectic temperature, the structure is retained before the finely divided particles have time to agglomerate. Fig. 15 shows the 15.5 wt.% Th sample which has been cooled slowly and in which very little eutectic is apparent. Fig. 16 shows the same sample which has been cooled rapidly before diffusion could take place. Other accompanying photomicrographs show an increase in the thorium phase and a corresponding decrease in the tuballoy phase across the system (Figures 9-14).

The thermal data taken on this system show but little scatter of points and is in good agreement with the diagram as drawn. Points for the thorium melting point and liquidus line have not been picked up in the thermal analyses which may be due to any combination of the following:

- (1) The high melting point of thorium and its apparently low heat of fusion
- (2) The limiting temperature range of the Pt-Pt 13% Rh couple
- (3) The extremely poor sensitivity of the W-Mo thermocouple

Two or three very questionable indications of liquidus breaks in the rich alloys were found but these were not reproducible and so this portion of the diagram has been dotted in. Thorium production at Ames has shown that a temperature of about 1840°C is necessary to obtain metal fluid enough for pull-rod casting from BeO crucibles. Recent thermal studies on such metal have shown a break at around 1810°C, although it is suspected that the actual melting point of pure Th is lower than this figure and that the higher temperature necessary for casting is due to dissolved oxygen. In all of the Th-rich samples in which Ames cast thorium was used, a thermal arrest was found at about 1160°C. This arrest was quite distinct and amounted to about 2.5 calories per gram in cast thorium. It was first thought that it might be due to a solid transition in thorium but careful work showed that it was connected with the oxygen in thorium and that when great care was exercised to prevent oxygen contamination, this break was not observed.

Solid solubility, as stated above, was determined mostly from microstructures although the fact that there is no depression of the tuballoy transformations provides good evidence that there is very little solubility of thorium in tuballoy. Microscopic study of 0.7 and 0.9 per cent thorium alloys revealed a considerable amount of a second phase along the grain boundary and quenching from 800°C did not produce any noticeable change in the amount of that phase (Figures 3 and 17). A quench from 1000°C dispersed the grain boundary phase. This change is not believed to be due to solubility, however, but rather to spheroidization of the thorium during the anneal prior to quenching (Fig. 18).

Very little is known definitely about the degree of solubility of tuballoy in thorium. Chemical analyses show that there is about 3 per cent of impurities in the best thorium available, and these impurities prevented any careful microscopic or x-ray study of the degree of solid solubility of tuballoy in thorium. X-ray diffraction studies on thorium-rich samples show no change in the lattice parameter which could be identified with solubility of tuballoy and there is no microscopic evidence for any precipitation from solution at higher temperatures (Figures 13 and 14). If there is any solid solubility of tuballoy in thorium, it is estimated that it is definitely less than 2 per cent.

Fig. 3
0.9% Th X 100

Fig. 4
0.9% Th X 250

Thorium eutectic along grain boundaries in Tuballoy matrix. (All alloys have been given a H_3PO_4 elec. polish and an elec. oxalic acid etch.)

Fig. 5
3.0% Th X 100

Fig. 6
3.0% Th X 250

Approaching eutectic composition

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Fig. 7
9.0% Th X 100

Light thorium dendrites in tuballoy-rich eutectic matrix

Fig. 9
15.5% Th X 100

Fig. 10
38.1% Th X 100

Impurities can be seen in thorium dendrites

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Fig. 11
49% Th X 100

Fig. 12
74% Th X 100

Fig. 13
90% Th X 100

Dark lakes of tuballoy, also
impurities along grain boundaries.
Light oxalic etch.

Fig. 14
Cast Th X 100

Dark dendritic inclu-
sions and eutectic-like
grain boundaries believed
to be oxides.

Fig. 15
15.5% Th X 250

Slow cooled sample.
Eutectic structure faint

Fig. 16
15.5% Th X 250

Quenching retains
eutectic structure

Fig. 17
0.9% Th X 100

Quenched from 800°
No change in structure
Oxalic etch

Fig. 18
0.9% Th X 100

Quenched from 1000°
Nearly one phase, shows
light areas of spheroidi-
zed thorium, Heavy oxalic
acid etch.

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