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SOLUBILITY OF CARBON IN THORIUM

By
Robert Mickelson
David Peterson

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Ames Laboratory
Ames, Iowa

Technical Information Service, Oak Ridge, Tennessee

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Robert Mickelson and David Peterson

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Ames Laboratory
at
Iowa State College
F. H. Spedding, Director
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ABSTRACT

The solubility of carbon in thorium has been investigated and the limit of solubility has been determined at four temperatures. Thorium-carbon samples, containing from 0.025 to 1.23 weight per cent carbon, were prepared by arc melting sponge thorium with high purity graphite. X-ray data, hardness readings, and metallographic examinations of heat treated specimens were combined to obtain the following solubility limits: room temperature - 0.35% carbon, 800°C - 0.43% carbon, 1018°C - 0.57% carbon, and 1215°C - 0.91% carbon.

I. INTRODUCTION

Carbon has been found to be the most effective alloying element in changing and improving the mechanical properties of thorium metal. Peterson¹ reports that additions of carbon to thorium increase the hardness and tensile strength without seriously reducing ductility. The investigation of the solubility of carbon in thorium was undertaken to provide basic information of value in understanding the effect of carbon on the physical properties of thorium.

The thorium-carbon system has been investigated by Chiotti,² who reports that thorium monocarbide is the stable phase in equilibrium with thorium at room temperature. Thorium and thorium monocarbide are reported to be completely soluble in the liquid and solid states at elevated temperatures. The exact limits of the solubility of carbon in thorium were not extensively investigated. Saller³ investigated the solubility of carbon in thorium and found considerable variation between the results of X-ray diffraction and metallographic examination. His conclusion was that the metallographic results were more accurate.

II. EXPERIMENTAL

A. Preparation of Samples.

The thorium-carbon samples used in this investigation were prepared by arc melting in a water-cooled copper crucible. The crucible was evacuated to less than 0.1 micron and filled with purified helium. A piece of zirconium metal was then melted to remove any oxygen or nitrogen still present in the furnace. The samples, which weighed about 100 grams, were prepared by melting Ames sponge thorium and dissolving high purity graphite in the molten metal. Each sample was turned and remelted three times to insure homogeneity.

The thorium sponge and the thorium-carbon samples were chemically analyzed for carbon and nitrogen. The thorium sponge contained 0.026 weight per cent carbon and 0.026 weight per cent nitrogen. The average nitrogen content of the seventeen samples was 0.032 weight per cent. The thorium sponge and five thorium-carbon samples were spectrographically analyzed for eleven different impurities.

B. Heat Treatment.

Samples used to determine the room temperature solubility limit were heated in a quartz tube evacuated to less than 0.02 micron. The samples were held at 900°C for six hours and cooled to room temperature over a period of five days.

A molybdenum tube resistance furnace was adapted to quench samples into molten Wood's metal placed on the furnace base directly beneath the cylindrical heater. The heating was done under a vacuum of 0.4 micron or lower. The samples were supported on a thorium disk which was allowed to fall into the quenching vessel with the samples. Since heating and quenching were done under vacuum and the samples were in contact only with thorium, the chances for contamination of the samples were reduced. The samples were held at temperature for 30 minutes or more before quenching. The Wood's metal was maintained at 80-100°C.

C. X-ray Study.

Lattice parameter determinations were made on a North American Phillips back-reflection camera which has a diameter of 12 cm. Samples containing less than 0.1 weight per cent carbon were hot-rolled to 1/16 inch sheet and shaped to the circumference of the camera before undergoing heat treatment. Samples containing more than 0.1 per cent carbon were too brittle to roll and blocks 1/16 inch thick and 1/4 inch wide were used in the X-ray camera. In

every instance, before the sample was exposed it was vigorously pickled in dilute nitric acid which contained a small amount of hydrofluoric acid. This pickling was performed to remove the surface metal which might have become contaminated during heat treatment.

Thorium oxide lines appeared on most of the X-ray photographs. These lines were more sharply defined than the thorium lines and, consequently, they could be measured with greater accuracy. Thus, thorium oxide was used as an internal standard to eliminate systematic errors in the determination of the lattice constant. If the thorium oxide lines indicated that there was an appreciable error in a given film, this error was eliminated by a graphical extrapolation against $\sin^2 \theta$.

The samples of thorium containing more than 0.5 per cent carbon were very coarse-grained, particularly when quenched from the higher temperatures. As a result, the X-ray diffraction patterns were very spotty and the accuracy of film measurement was poor. Since massive samples were used, there was no way of eliminating this difficulty.

A maximum probable error in the measurement of the lattice constant was calculated from a reasonable assumed error in measuring the film. A larger assumed error was used for samples containing more than 0.5 per cent carbon because of the spotty lines from these samples. The systematic error in many of the determinations was less than this maximum probable error and, in these cases, no correction was made.

D. Metallographic Examination.

The samples for metallographic examination were ground on 320, 400, 500, and 600 grit paper. They were polished with Linde B on Microcloth. Etching was used to improve the contrast between thorium monocarbide and thorium. The presence of thorium carbide could usually be detected before etching, but the improved contrast made the pictures clearer. The etching solution was 2 molar nitric acid, 0.02 molar hydrofluoric acid, and 0.005 molar thorium nitrate. The etching solution was applied by swabbing for ten to thirty seconds.

III. RESULTS AND DISCUSSION

The spectroscopic analyses of the thorium metal used in preparing the samples and of a number of the samples are given in Table I. Most of these results are an upper limit since the

actual content was below the limit of measurement of the methods used. The principal difference in purity between these samples and Ames production thorium metal was in the beryllium content. These samples contain less than 20 ppm beryllium while Ames thorium, due to being melted in beryllia, usually contains 100 ppm or more.

The chemical analyses of the thorium-carbon samples for nitrogen and carbon are presented in Table II. The oxygen content of these samples was not determined but must have been above the solubility limit since thorium oxide was observed in the microstructures of all these samples. The thorium oxide content was probably between one and two per cent. In graphing the results of this investigation, the error in the carbon analysis was assumed to be five per cent of the absolute value of the carbon content.

Table I
Spectroscopic Analysis of Thorium-Carbon Samples

Sample Number	Impurity Content ppm										
	Be	Al	Ca	Mg	Si	Fe	Mn	B	Cd	Zn	Zr
Sponge	<20	<25	<50	<20	<50	40	<20	0.75	<0.2	110	<100
1	<20	<25	<50	<50	<50	35	<20	<0.3	0.3	<10	<100
2	<20	<25	<50	<50	<50	30	<20	<0.3	<0.2	<10	<100
3	<20	<25	<50	<20	<50	105	<20	0.45	2.1	12	<100
5	<20	<25	<50	<20	<50	35	<20	<0.3	0.3	<10	<100
6	<20	<25	<50	<20	<50	45	<20	<0.3	<0.2	<10	<100

The solid solubility limits of carbon in thorium were established from the X-ray data and confirmed by microscopic examination. The observed lattice constants of the samples after various heat treatments are reported in Table III and are plotted in Figure 1 against the carbon content. The solubility limit at each temperature was taken as the carbon content above which there was no further increase in lattice constant. The experimental error is indicated by horizontal and vertical lines through each point.

The solid solubility limits of carbon in thorium are shown in Figure 2 as a function of temperature.

Table II

Analysis and Hardness of Thorium-Carbon Samples

Sample Number	Nitrogen Content, ppm	Carbon Content Weight Per Cent	Atomic Per Cent	Rockwell A Hardness			
				Heated at 900°C and slow cooled	Quenched from 800°C	Quenched from 1018°C	Quenched from 1215°C
1	471	0.025	0.47	23	-	24	25
2	344	0.054	1.03	-	27	29.5	-
3	344	0.026	0.49	26	-	-	28
4	203	0.035	0.67	-	-	-	-
5	482	0.042	0.81	-	-	29	-
6	241	0.104	1.98	-	38	36	-
7	301	0.132	2.49	-	-	-	43.5
8	1,015	0.163	3.06	38	44	48.5	50
9	332	0.208	3.87	41.5	-	48.5	-
10	293	0.239	4.44	44	-	52	54
11	253	0.300	5.50	46	49	51	-
12	224	0.350	6.36	50	54	55.5	-
13	143	0.408	7.37	-	-	60	-
14	215	0.556	9.82	53	-	62.5	-
15	178	0.736	12.59	55	58.5	64	-
16	168	0.959	15.78	57.5	60	64	-
17	182	1.228	19.40	-	-	66.5	-

Table III

Lattice Constants of Thorium-Carbon Samples

Sample Number	Carbon Content, Weight Per Cent	Lattice Parameter, Angstroms			
		Heated at 900°C and Slow-Cooled	Quenched from 800°C	Quenched from 1018°C	Quenched from 1215°C
1	0.025	5.0871	5.0877	5.0920	5.0900
2	0.054	5.0886	5.0922	-	-
3	0.026	5.0871	5.0875	-	5.0867
4	0.035	5.0873	5.0926	5.0905	-
5	0.042	5.0859	-	-	-
6	0.104	5.0953	5.0958	-	-
7	0.132	5.0964	-	5.1064	5.1075
8	0.163	5.0966	5.1033	-	5.1107
9	0.208	5.1004	-	-	-
10	0.239	5.1020	-	5.1203	5.1183
11	0.300	5.1058	5.1140	5.1196	-
12	0.350	5.1077	5.1211	5.1272	5.1216
13	0.408	5.1077	5.1305	5.1356	5.1325
14	0.556	5.1092	5.1270	5.1380	5.1433
15	0.736	-	5.1250	5.1425	5.1532
16	0.959	5.1077	5.1243	5.1447	5.1613
17	1.228	-	-	5.1436	5.1573

Fig. 1 Lattice Constants of Thorium-Carbon Samples with Various Heat Treatments.

Fig. 2 Solubility of Carbon in Thorium of Various Temperatures.

The solubility limits established by X-ray methods were checked by microscopic examination. Thorium carbide could be identified as small particles which tend toward a square form. The thorium oxide particles were much larger and darker in color.

Figures 3 and 4 show samples above and below the solubility limit at each temperature. These pictures show the precipitation of thorium carbide in samples above the solubility limits.

An anomalous effect was observed in samples which contained less than 0.35 per cent carbon and hence were not saturated with carbon. These quenched samples showed an increase in lattice constant over the slow-cooled samples of the same carbon content, and, up to 1000°C, the higher quenching temperatures resulted in an increased lattice constant. A similar effect was observed in the increased hardness of unsaturated samples quenched from various temperatures. The most likely explanation is that the samples were saturated with nitrogen at room temperature and heating to higher temperatures caused more thorium nitride to dissolve in the thorium. Thorium nitride has been reported by Chiotti² to be appreciably soluble in thorium at elevated temperatures.

IV. CONCLUSIONS

The solubility of carbon in thorium was established as 0.35 per cent at room temperature, 0.43 per cent at 800°C, 0.57 per cent at 1018°C, and 0.91 per cent at 1215°C. Increasing the carbon content causes an increase in the hardness of thorium by solid solution hardening. An impurity in these samples, believed to be nitrogen, caused an increased lattice constant and hardness of quenched alloys below the carbon solubility limit.

V. LITERATURE CITED

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3. Grenell, L. H. and H. A. Saller, "The Solubility of Carbon in Thorium," CT-3411, (1946).

Fig. 3 Thorium-Carbon Samples. Nitric Acid Etch. X500.
A - 0.30% Carbon. Slow-Cooled. B - 0.408% Carbon. Slow-Cooled. C - 0.350% Carbon. Quenched from 800°C. D - 0.736% Carbon. Quenched from 800°C.

A

B

C

D

Fig. 4 Thorium-Carbon Samples. Nitric Acid Etch. X500.
A - 0.408% Carbon. Quenched from 1018°C. B - 0.736% Carbon. Quenched from 1018°C. C - 0.736% Carbon. Quenched from 1215°C. D - 0.959% Carbon. Quenched from 1215°C.