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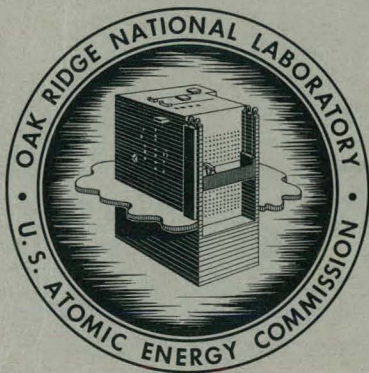
UC-25 - Metals, Ceramics, and Materials
TID-4500 (27th ed.)

MASTER

MONOCLINIC-CUBIC TRANSFORMATION

IN THORIUM DICARBIDE

N. A. Hill
O. B. Cavin



OAK RIDGE NATIONAL LABORATORY

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N. A. Hill¹ and O. B. Cavin

Abstract

Thorium dicarbide has been found to transform at $1415 \pm 10^\circ\text{C}$ from the low-temperature monoclinic structure to a face-centered cubic structure with $a_0 = 5.808 \pm 0.003 \text{ \AA}$ at 1500°C . It has not been possible to retain the high-temperature structure by quenching.

Introduction

Fissile-fertile nuclear fuels containing thorium-rich thorium-uranium dicarbide are of interest for use in graphite-base, high-temperature reactors. In connection with a study of the phase relations in this system, the crystal structure of thorium dicarbide was investigated as a function of temperature.

Arrests in heating and cooling curves of thorium dicarbide at 1430 and 1480°C have been reported by Langer,² and Accary³ has reported a marked change in thermal expansion at 1230 – 1300°C .

In this paper, the results of x-ray diffraction from thorium dicarbide with excess graphite at temperatures up to 1700°C and the results of differential thermal analysis (DTA) up to 1500°C are presented.

Experimental Method

High-Temperature X-Ray Diffraction

Arc-melted thorium dicarbide (analysis in Table 1) was crushed to powder under argon and mixed with graphite powder and dry kerosene. A

¹A.E.R.E., Harwell, England, presently assigned to ORNL.

²S. Langer, Physicochemical Properties of Carbides for Nuclear Applications - A Review, GA-4450 (1963).

³Private communication.

Table 1. Chemical Analysis of Thorium Dicarbide

	Arc-Cast Material	Microspheres
Thorium	87.7%	84.9%
Carbon	10.2%	14.15%
Oxygen		0.04%
Nitrogen	0.02%	Silicon 130 ppm Iron 160 ppm Other impurities < 30 ppm

few drops of this slurry were placed on the tantalum strip heater in an "M.R.C." high-temperature x-ray diffraction camera⁴ Model X-86-N mounted on a "Norelco" x-ray diffractometer. The camera was evacuated to 4×10^{-5} torr and the specimen scanned from $2\theta = 22$ to 60° at room temperature.

The tantalum strip and carbide specimen were heated slowly until the kerosene distilled off, then heated rapidly to 1200°C . Diffractometer scans were obtained at 1200°C , at 100°C intervals up to the maximum strip temperature (2000°C), and back to 1200°C . This heating and cooling cycle was repeated three times, and finally the strip was cooled to room temperature and the specimen scanned once more.

Temperatures were measured with a "Pyro" micro-optical, disappearing-filament pyrometer which could be focused on the heating strip or on different areas of the specimen.

Differential Thermal Analysis

Thorium dicarbide microspheres (200- μ diam) (analysis in Table 1) were coated with a 10- μ shell of pyrolytic carbon to reduce oxidation and loaded into one of the platinum buckets of a "Stone" DTA apparatus. The

⁴D. K. Smith, "Techniques of High-Temperature X-Ray Diffraction Using Metal Ribbon Furnaces," Norelco Rept. 10(1), 19 (1963).

other platinum bucket was filled with powdered alumina as a standard. The chamber containing the specimen, standard, and furnace was evacuated to 10^{-2} torr and backfilled with argon several times.

Under argon at 1-atm pressure, the specimen and the alumina standard were heated at $10^{\circ}\text{C}/\text{min}$ to 1500°C and cooled at the same rate. The difference in output between thermocouples in contact with the two platinum buckets was recorded, and any transformation which absorbed or emitted heat produced a peak in the curve of differential output vs time. The temperature of the sample was recorded from a separate thermocouple.

Results

X-Ray Diffraction

The initial room-temperature trace showed peaks from graphite, monoclinic thorium dicarbide, and a little thorium dioxide. At a surface temperature of 1200°C , the specimen gave the same peaks (slightly displaced by thermal expansion); but at 1300°C surface temperature (1500°C maximum within the specimen as discussed below), a new set of lines appeared, corresponding to a face-centered cubic lattice and quite distinct from the thorium oxide lines. At a surface temperature of 1500°C , the monoclinic thorium dicarbide lines had disappeared, leaving graphite lines, weak thorium dioxide lines, and strong lines from the new face-centered cubic material. To correct for any shift in 2θ from misalignment of the specimen or the x-ray beam, the thorium dioxide lines were used as standards for the adjacent new face-centered cubic lines. The corrected values are given in Table 2. Over the range $2\theta = 26-54^{\circ}$, the unit cell edges calculated from each diffraction line are in very close agreement, giving

$$a_0 = 5.808 \pm 0.003 \text{ \AA} \text{ (at } 1500^{\circ}\text{C)}$$

for the new face-centered cubic thorium dicarbide phase. No higher 2θ values were obtainable so it was not possible to apply any systematic correction, but the consistency of better than $\pm 0.1\%$ shown in Table 2 over the range $2\theta = 26-54^{\circ}$ indicates that this data should give a reliable and accurate lattice parameter value.

Table 2. High-Temperature X-Ray Diffraction Results
from Arc-Cast Thorium Dicarbide at 1500°C

(CuK $_{\alpha}$ radiation: $\lambda = 1.54178$ A)

2θ (deg)	d (A)	a_o (A)	I/I_o
26.57	3.355	5.811	100
30.78	2.905	5.810	80
44.08	2.054	5.810	50
52.25	1.750	5.804	40
54.76	1.676	5.806	10

Average $a_o = 5.808 \pm 0.003$ A for
face-centered cubic.

On holding the specimen at a surface temperature of 1600°C, the thorium oxide lines weakened and eventually disappeared, leaving graphite and the new face-centered cubic thorium dicarbide lines.

There was no evidence for any further transformation on heating to the maximum temperature of approximately 1700–1800°C in the center of the specimen. The thorium dicarbide was cycled three times between surface temperatures of 1100 and 1600°C, and each time the monoclinic-cubic-monoclinic transformations occurred, confirming that the transformation is reversible. Comparison of the diffractometer traces of the face-centered cubic thorium dicarbide in the presence and the absence of thorium dioxide showed no detectable difference, indicating that there is no major solubility of oxygen in this structure. Once the oxide had transformed to carbide at high temperatures, it did not reappear during subsequent cycling.

Throughout the work, a marked temperature gradient existed in the specimen. When the tantalum strip was at 2000°C, the adjacent layers of the specimen were at approximately 1800°C and the surface at 1600–1700°C. It was not possible, therefore, to measure the transformation temperature although the temperatures at which the transformation began and ended during heating and cooling could be estimated as 1390 and 1440°C, respectively. As there were large temperature differences within the specimen, no emissivity or absorption corrections were applied to the temperature measurements.

Differential Thermal Analysis

On heating the pyrolytic carbon-coated thorium dicarbide spheres, a peak due to a transformation began at 1425°C; on cooling, a similar peak in the reverse direction began at 1405°C, indicating a transformation temperature of $1415 \pm 10^\circ\text{C}$. The heating and cooling rates were both $10^\circ\text{C}/\text{min}$; and, as shown in the trace reproduced in Fig. 1, the peaks are virtually identical in size and shape.

In some of the early runs before the argon atmosphere was dried, a large peak occurred at 1470–1500°C; subsequent peaks at 1415°C were smaller and finally disappeared. These samples showed mainly thorium oxide on x-ray diffraction analysis after the DTA runs were completed. This indicates that the large peak observed is in some way connected with the oxidation of the particles, and the diminution of the peak at 1415°C was due to a proportion of the thorium carbide being oxidized.

Discussion

From the results, it is evident that above approximately 1400°C thorium dicarbide has a face-centered cubic structure with $a_0 = 5.808 \pm 0.003 \text{ \AA}$ (at 1500°C); and, since DTA results show a reversible structure change in thorium dicarbide particles (coated with pyrolytic carbon) at $1415 \pm 10^\circ\text{C}$, it seems most likely that the reversible monoclinic-cubic transformation causes this peak. Hence it is concluded that the cubic phase is the stable phase in thorium dicarbide above $1415 \pm 10^\circ\text{C}$, and no other transformation occurs in the presence of excess graphite up to 1700°C (the upper temperature limit of the x-ray diffraction runs).

In the low-temperature monoclinic thorium dicarbide, Hunt and Rundle⁵ concluded that the carbon atoms are arranged in pairs. In the present work, attempts to retain the high-temperature cubic form by quenching failed, indicating that the cubic-monoclinic transformation is very rapid and may be diffusionless as suggested by Chang⁶ for the

⁵E. B. Hunt and R. E. Rundle, "The Structure of Thorium Dicarbide by X-Ray and Neutron Diffraction," J. Amer. Chem. Soc. 73, 4777 (1951).

⁶R. Chang, "A Diffusionless UC_2 (Cubic) to UC_2 (Tetragonal) Transformation," Acta Cryst. 14, 1097 (1961).

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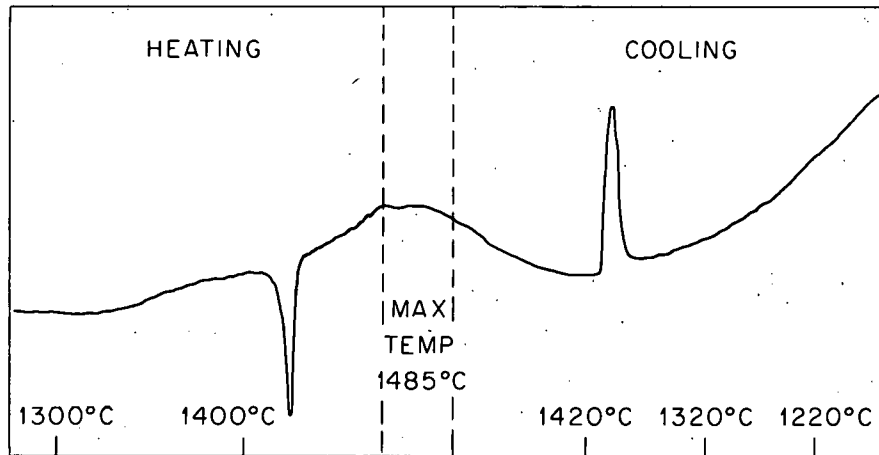


Fig. 1. Differential Thermal Analysis Trace from Thorium Dicarbide Showing Transformation Peaks on Heating and Cooling.

cubic-tetragonal UC_2 transformation. In this case, provided the paired carbon groups in monoclinic thorium dicarbide exist at $1400^\circ C$, it is likely that the high-temperature cubic structure also contains these groups.

Metallography of arc-cast thorium dicarbide shows that there is marked twinning visible under polarized light as shown in Fig. 2. These twins may well be formed by the cubic-monoclinic transformation on cooling from the melting temperature. There is no evidence of fine graphite or other precipitate within the grains, indicating that there is no marked change in stoichiometry associated with the phase transformation; all the excess graphite is in the form of massive stringers.

Conclusions

High-temperature x-ray diffraction results showed that thorium dicarbide has a face-centered cubic structure with $a_0 = 5.808 \pm 0.003 \text{ \AA}$ at $1500^\circ C$. Differential thermal analysis of thorium dicarbide showed a peak both on heating and on cooling at $1415 \pm 10^\circ C$, corresponding to the reversible monoclinic-cubic transformation observed by x-ray diffraction. No cubic structure was retained on quenching to room temperature, indicating a diffusionless transformation which may cause the twins observed in the microstructure of thorium dicarbide.

Acknowledgments

R. E. MacDonald provided the arc-melted material; G. B. Marrow provided the microspheres which were coated by R. L. Beatty; the metallography was directed by R. J. Gray. W. O. Harms and H. L. Yakel gave advice and encouragement throughout the work.



Fig. 2. Microstructure of Thorium Dicarbide under Polarized Light Showing Extensive Twinning and Massive Stringers of Graphite. 1000X.

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