Ternary Compounds Between Thorium Monocarbide
and Thorium Dihydride*

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Abstract-- The thorium-hydrogen-carbon system was studied by measuring hydrogen equilibrium pressures at various compositions and temperatures. Two compounds, $\text{ThC} \cdot \text{ThH}_2$ and $\text{ThC} \cdot 2\text{ThH}_2$, were found and characterized. $\text{ThC} \cdot \text{ThH}_2$ has a hexagonal closest-packed lattice with $a_0 = 3.816\text{\AA}$ and $c_0 = 6.302\text{\AA}$. $\text{ThC} \cdot 2\text{ThH}_2$ had a monoclinic lattice with $a_0 = 6.50\text{\AA}$, $b_0 = 3.80\text{\AA}$, $c_0 = 10.91\text{\AA}$ and $\beta = 119^\circ$. The enthalpies of formation for each compound were determined.

INTRODUCTION

An investigation of the solid solubility of thorium dihydride in thorium by Peterson and Westlake⁽¹⁾ indicated that this solubility was

(1) D. T. Peterson and D. G. Westlake, Trans. AIME, 215, 444 (1959).

increased by carbon dissolved in the thorium. The thorium-hydrogen-carbon system was investigated to determine whether this apparent increase in solubility was due to an interaction between carbon and hydrogen

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in solution which decreased the activity of hydrogen or whether it was due to the formation of a compound containing carbon and hydrogen. Measurement of the equilibrium-hydrogen pressure over thorium specimens containing varying amounts of carbon as a function of hydrogen concentration was chosen as the experimental method because it would clearly distinguish between these two cases and would give valuable thermodynamic data.

EXPERIMENTAL METHODS AND MATERIALS

Materials—The thorium specimens were prepared from calcium-reduced thorium identical to that used by Peterson and Westlake. (1) This metal was arc melted with spectrographic graphite to obtain the desired carbon content. The specimens, cut from the arc-melted buttons, were cylinders about 6 mm in diameter and 15 mm long which weighed ~5 grams. The carbon content of the specimens was determined by the combustion method. Pure hydrogen was obtained by thermal decomposition of uranium hydride as described by Spedding et al. (2)

(2) F. H. Spedding, A. S. Newton, J. C. Wharf, O. Johnson, R. W. Nottorf, I. B. Johns and A. H. Daane, Nucleonics, 4, 4 (1949).

Apparatus—The apparatus is shown in Fig. 1. The furnace tube was 8 mm inside diameter and extended into the stainless steel block in the center of the furnace. The temperature was measured by a thermocouple between the furnace tube and the stainless steel block. The

Fig. 1 Schematic diagram of the apparatus.

temperature for an axial distance of 5 cm within the block was uniform within 1°C. The specimen was centered in this region and, consequently, the existence of an appreciable thermal gradient in the specimen was unlikely. The temperature of the furnace was held constant to within 2°C by an autotransformer and a constant voltage transformer. The volumes of the various portions of the gas system were determined so that it could be used to measure the amount of hydrogen added to or taken from the system. The amount of gas in the furnace tube at constant pressure decreased with increasing furnace temperature so an effective volume was determined at several furnace temperatures. The amount of hydrogen in the specimen was the difference between the known total quantity of hydrogen in the system and the amount of hydrogen in the gas phase. The mercury manometer could be read to ± 0.3 mm and the McLeod gage, to ± 6 microns up to 900 microns. The pressure was measured at a given temperature and composition after it had been constant within 3 mm for at least 12 hours. This often required several days at the lower temperatures because the attainment of equilibrium required diffusion of carbon as well as the diffusion of hydrogen.

RESULTS

The pressure-composition isotherms showed that two compounds of thorium, hydrogen and carbon were formed which were more stable than thorium dihydride. The equilibrium hydrogen pressures over a sample with a 0.46 atomic ratio of carbon to thorium is shown in Fig. 2.

Fig. 2 Pressure-composition isotherms for a specimen with a 0.46 C/Th ratio.

As the hydrogen content of the sample was increased the hydrogen first went into solid solution in both the metal and carbide phases. Formation of the ternary compound started at a fixed pressure at each temperature and continued at a constant pressure until the metal or the carbide phase disappeared. Subsequently, the hydrogen content of the ternary compound increased as the hydrogen pressure increased. This compound is not of fixed composition but apparently exists from $\text{ThC} \cdot \text{ThH}_{1.8}$ to $\text{ThC} \cdot \text{Th}_{2.0}$. This variation in hydrogen content is quite similar to that observed in thorium dihydride.

The formation of a second ternary compound is shown in Fig. 3 which is a pressure-composition isotherm at 851° for a specimen with a 0.24 carbon to thorium ratio. $\text{ThC} \cdot \text{ThH}_2$ was formed first as the hydrogen content increased. At a higher hydrogen content and pressure, the $\text{ThC} \cdot \text{ThH}_2$ reacted with thorium metal and hydrogen to form $\text{ThC} \cdot 2\text{ThH}_2$. Because there was thorium metal in excess of the amount required to combine with all of the carbon, ThH_2 was formed when the hydrogen pressure became high enough for this compound to be stable. This specimen initially consisted of ThC and thorium metal saturated with ThC and finally consisted of ThH_2 and $\text{ThC} \cdot 2\text{ThH}_2$. Consequently, all of the equilibrium phases between ThC and ThH_2 should be shown by this isotherm.

Specimens of each compound were prepared by equilibrating a sample having the proper carbon to thorium ratio with hydrogen at one atmosphere and 850°C . These compounds were quite brittle and -200

Fig. 3 Pressure-composition isotherm for a specimen with a 0.24 C/Th ratio.

mesh powder for x-ray diffraction examination was prepared by crushing in a diamond mortar. Powder diffraction patterns were taken on a 11.46 cm Debye-Scherrer camera. $\text{ThC} \cdot \text{ThH}_2$ was found to be hexagonal with $a_0 = 3.816 \text{ \AA}$ and $c_0 = 6.302 \text{ \AA}$. The thorium atoms were arranged in a hexagonal closest-packed structure but the positions of the carbon and hydrogen atoms could not be established by x-ray methods. The compound $\text{ThC} \cdot 2\text{ThH}_2$ had a more complex structure. Examination of a single crystal showed the lattice to be monoclinic with $a_0 = 6.50 \text{ \AA}$, $b_0 = 3.80 \text{ \AA}$, $c_0 = 10.91 \text{ \AA}$ and $\beta = 119^\circ$. The arrangement of the thorium atoms was a slightly distorted hexagonal closest-packed array.

The activity of hydrogen in specimens below the solubility limit⁽³⁾

(3) R. Mickelson and D. T. Peterson, Trans. ASM, 50, 340 (1958).

of ThC in thorium was determined. A pressure-composition isotherm at 800° for two carbon compositions below the solubility limit are shown in Fig. 4 with the data of Mallet and Campbell⁽⁴⁾ for pure thorium.

(4) M. W. Mallet and I. E. Campbell, J. A. C. S., 73, 4850 (1951).

The equilibrium hydrogen pressure over all the specimens fell on the same straight line until the hydrogen pressure at which $\text{ThC} \cdot \text{ThH}_2$ began to form was reached. This pressure in the specimen with a 0.060 carbon-to-thorium ratio was only slightly above the pressure for formation of $\text{ThC} \cdot \text{ThH}_2$ from ThC and thorium because this specimen

Fig. 4 Pressure-composition isotherms for specimens with carbon contents below saturation

was nearly saturated with ThC. The pressure at which ThC·ThH₂ began to form in a specimen with a 0.024 carbon-to-thorium ratio was higher, as would be expected from the law of mass action. As the hydrogen pressure increased further, the hydrogen concentration in solid solution in the thorium increased and ThC·ThH₂ also continued to precipitate. At a fixed higher pressure both specimens showed the formation of ThC·2ThH₂, and finally the formation of ThH₂ appeared at essentially the same pressure as for thorium with a very low carbon content.

A ternary section at 850°C for the Th-ThC-ThH₂ system, shown in Fig. 5, has been constructed. The ternary section allows a more accurate estimate of the composition ranges of the ternary compounds to be made. The effect of the stability of ThC·ThH₂ in limiting the solid solubility of both hydrogen and carbon in thorium is quite striking. Due to this restricted solubility, ThC·ThH₂ is the first phase to appear on adding hydrogen to thorium unless the carbon content is extremely low. A calculation based on constant activity coefficients for carbon and hydrogen in thorium indicated that at 800°C ThC·ThH₂ would be formed if the carbon content were above 40 ppm. The ternary section also shows that thorium and hydrogen together dissolve to a significant extent in ThC. The absorption of hydrogen by pure ThC was found to be very small but when thorium metal was present ThC would dissolve more than 20 a/o hydrogen.

The enthalpy of formation of these compounds was calculated

Fig. 5 Ternary section at 850° of the Th-ThC-ThH₂ system.

from the variation of the equilibrium hydrogen pressure with temperature. The plot of the logarithm of the equilibrium pressure against reciprocal temperature is shown in Fig. 6. The data were treated by a least squares method to obtain the constants for the linear equations. The reactions for the respective equations given below are $\text{Log } P_{(\text{mm Hg})} = \frac{-10,580}{T} + 10.20$ and $\text{Log } P_{(\text{mm Hg})} = \frac{-8,365}{T} + 9.84$. The reaction for the formation of $\text{ThC} \cdot \text{ThH}_2$ is $\text{Th}_{(\text{s})} + \text{ThC}_{(\text{s})} + \text{H}_{2(\text{g})} \rightleftharpoons \text{ThC} \cdot \text{ThH}_{2(\text{s})}$ and for $\text{ThC} \cdot 2\text{ThH}_2$ is $\text{Th}_{(\text{s})} + \text{ThC} \cdot \text{ThH}_{2(\text{s})} + \text{H}_{2(\text{g})} \rightleftharpoons \text{ThC} \cdot 2\text{ThH}_2$. The enthalpy of formation of $\text{ThC} \cdot \text{ThH}_2$ by the reaction given above is -48.4 kcal per mole. The enthalpy of formation of $\text{ThC} \cdot 2\text{ThH}_2$ by the reaction given above is -38.3 kcal per mole.

DISCUSSION

The positions of the carbon and hydrogen atoms in the $\text{ThC} \cdot \text{ThH}_2$ structure have not been determined and, consequently, the bonding in this compound can not be deduced from the bond distances and arrangement. However, the bonding in this compound is probably quite similar to the bonding in ThC and ThH_2 . The volume of $\text{ThC} \cdot \text{ThH}_2$ is very nearly equal to the sum of the volumes of the ThC and ThH_2 that it contains. The volume of one $\text{ThC} \cdot \text{ThH}_2$ unit cell is $79.5 \text{ \AA}^3$ and the sum of one fourth of the face-centered-cubic⁽⁵⁾ ThC unit cell and one half

(5) H. A. Wilhelm and P. Chiotti, Trans. ASM, 42, 1925 (1950).

of the body-centered tetragonal⁽⁶⁾ ThH_2 unit cell is $79.3 \text{ \AA}^3$. The

Fig. 6 Logarithm of equilibrium hydrogen pressure vs. reciprocal temperature.

(6) R. E. Rundle, C. G. Shull and E. O. Wollan, Acta Cryst., 5, 22 (1952).

metallic luster and relatively high electrical conductivity of ThC and ThH₂ are also shown by ThC·ThH₂.

The hexagonal closest-packed γ phase reported in the zirconium-hydrogen system by Hagg⁽⁷⁾ may have been an analogous compound formed

(7) G. Hägg, Z. für physikalische Chemie, Vol. B11, 433 (1931).

by zirconium. It is interesting that the volume of the unit cell reported for this compound is $52.94\text{\AA}^3$ and the sum of the volumes of ZrC and ZrH₂ is $52.83\text{\AA}^3$. The presence of carbon in the specimens examined by Hagg is supported by his observation in a sample containing 9 a/o hydrogen of a face-centered-cubic phase with a lattice constant of $4.669\text{\AA}$ which is very nearly equal to the lattice constant of ZrC in equilibrium with zirconium metal. It appears quite likely that the β phase reported by Hagg was zirconium carbide and the γ phase was a ternary zirconium-hydrogen-carbon compound rather than non-equilibrium phases formed by zirconium and hydrogen. The similarity of the hydrides and carbides of Ti and Hf to those of Zr and Th makes the formation of similar compounds with these metals likely.

FIGURE CAPTIONS

Fig. 1—Schematic diagram of the apparatus.

Fig. 2—Pressure-composition isotherms for a specimen with a 0.46 C/Th ratio.

Fig. 3—Pressure-composition isotherm for a specimen with a 0.24 C/Th ratio.

Fig. 4—Pressure-composition isotherms for specimens with carbon contents below saturation.

Fig. 5—Ternary section at 850° of the Th-ThC-ThH₂ system.

Fig. 6—Logarithm of equilibrium hydrogen pressure vs. reciprocal temperature.

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