Enthalpy of Formation of Hafnium Dioxide

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The enthalpy of formation of hafnium dioxide has been determined by means of an oxygen bomb calorimeter and is $\Delta H^{\circ}_{f\,298.15^{\circ}\,\mathrm{K.}}$ = −273.6 ± 0.3 kcal. per mole.

THE two values in the literature (*3, 5*) for the enthalpy of formation of hafnium dioxide differ by about 2%. One of the values is based on only two runs which were widely separated. In addition, a combustion aid contributed more than 80% of the evolved heat. The other determination was performed on a sample of metal, which contained 2.4% zirconium in addition to other impurities. No analysis was made for oxygen in either case.

With a purer material now available together with better analytical techniques, it seemed wise to redetermine this datum. With a melting point exceeding 2800° C., hafnium dioxide may find increasing use in high temperature environments.

MATERIAL

Reactor grade hafnium metal (Leytess Metal & Chemical Corp., N.Y.) was obtained as 13-mil thick sheet. Analyses performed at this laboratory showed the following impurities: C, 0.004%; O, 0.058%; N, 0.006%; Fe, 0.02%. No other metals were detected. Both Nb and Zr were listed as being less than the limit of detection which was 0.1%. No hydrogen was found.

The material was calculated to be (weight %): Hf, 99.23; HfC, 0.06; HfO, 0.60; HfN, 0.08; Fe_2O_3, 0.03. No impurities were detected by x-ray analysis. The unit cell dimensions were a = 3.1982 and c = 5.0613 A.

METHOD AND RESULTS

The method involved the determination of the amount of heat evolved from the combustion of a weighed sample of hafnium metal in a bomb calorimeter at a known initial pressure of oxygen. The method and equipment have been described (*1, 2*). The sample was burned in oxygen at 25 atm. pressure on sintered disks of HfO_2. Ignition was made by passing an electrical current through a 10-mil diameter hafnium fuse wire. The average initial temperature was 25.02° C. with an average temperature rise of 1.23° C.

The completeness of combustion was determined by heating each sample to constant weight in oxygen at 1000° C. A gain in weight, after correction for adsorbed carbon dioxide and water, would indicate unburned hafnium metal. Absorption of the water was made in a tube containing magnesium perchlorate. Carbon dioxide was absorbed by another tube containing Ascarite, a sodium hydrate asbestos. Blank corrections were made in each case. The amount of water and carbon dioxide evolved averaged 1.1 and 1.0 mg., respectively. Although these amounts seem small, they are significant since a gain in weight of 1 mg. in the combustion product indicates approximately 5½ mg. of unburned hafnium metal. The completeness of combustion averaged 99.92% and was never less than 99.72%. The specific heat of HfO_2 was taken as 0.0669 cal. per gram per degree. Thirteen runs were made on the sample; the last three runs were made more than a year after the first ten. The runs are listed in Table I.

The average combustion value of −1523.4 was increased to −1529.4 cal. per gram (0.39% larger) after making correction for the impurities. These corrections were made assuming that each combustible impurity contributed to the over-all heat according to the difference between its enthalpy of formation and the enthalpy of formation of the combustion products. The enthalpies of formation (kilocalories per mole) used were: ΔH°_{f}(HfC) = −52.3 (*4*); ΔH°_{f}(HfO) = −135 (estimated), ΔH°_{f}(HfN) = −88.2 (*3*), $\Delta H^{\circ}_{f\,298.15^{\circ}\,\mathrm{K.}}$($HfO_2$) = −273.6 ± 0.3 (this work), ΔH°_{f}(CO_2) = −94.05 (*6*). No correction was made for the possible presence of Nb and Zr. If the assumption is made that each of these elements is present in amounts of 0.05%, the corrected value for the heat of combustion of hafnium metal is reduced by 0.07%. The atomic weight of Hf was taken as 178.49. The correction for impurities introduced an uncertainty of 0.03% which, when combined with other

Table I. Energy of Combustion of Hafnium Metal

Mass Burned, Grams	Wt. HfO_2, Grams	Energy Equiv., Cal./Deg., Total	ΔT, ° C.	Energy from: Firing, cal.	Energy from: Hf, cal./gram	Dev. from Mean, Cal./Gram
1.99217	49.3	2391.0	1.2745	2.5	−1528.4	5.0
1.95466	49.4	2391.0	1.2449	2.2	−1521.7	1.7
1.83460	49.3	2391.0	1.1705	3.2	−1523.8	0.4
1.99424	50.0	2391.0	1.2725	3.3	−1524.0	0.6
1.92660	49.7	2391.0	1.2288	2.3	−1523.8	0.4
1.97597	46.7	2390.8	1.2581	2.2	−1521.1	2.3
1.82755	57.4	2391.5	1.1695	2.4	−1529.1	5.7
1.87561	35.1	2390.0	1.1922	2.6	−1517.8	5.6
2.03469	34.9	2390.0	1.2973	2.6	−1522.5	0.9
1.95209	34.9	2390.0	1.2443	2.8	−1522.0	1.4
1.89274	34.6	2390.0	1.2071	3.6	−1522.3	1.1
1.91198	34.8	2390.0	1.2201	2.9	−1523.6	0.2
1.81873	34.9	2390.0	1.1621	2.1	−1524.3	0.9
				Av.	−1523.4	2.0
			Std. dev. of the mean			0.8

known sources of errors, gave an over-all uncertainty of 0.12%. The enthalpy of combustion of hafnium metal under bomb conditions was −272.98 ± 0.32 kcal. per mole. Correction to unit fugacity of oxygen and to constant pressure leads to $\Delta Hf^{\circ}_{298.15^{\circ}\mathrm{K.}}(\mathrm{HfO_2}) = -273.6 \pm 0.3$ kcal. per mole as the enthalpy of formation of hafnium dioxide: $\mathrm{Hf(c)} + \mathrm{O_2(g)} = \mathrm{HfO_2(c)}$. The uncertainty attached to the value is twice the standard deviation of the mean. This value is 7.5 kcal. more negative than Humphrey's value (*3*) and 2.1 kcal. more negative than Roth's and Becker's value (*5*).

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Enthalpies of Formation of Thorium Mono- and Dicarbides

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A series of analyzed thorium carbides has been burned in an oxygen bomb calorimeter. The enthalpies of formation of $\mathrm{ThC}_{1.00 \pm 0.01}$ and $\mathrm{ThC}_{1.91 \pm 0.01}$ were −29.6 ± 1.1 and −29.9 ± 1.1 kcal. per mole, respectively, at 298.15° K.

THE refractory nature of the thorium carbides with melting points above 2600° C. is an important consideration for their use in nuclear reactors. Recent reviews on the thorium–thorium carbide system (*3, 10*) describe the methods of preparation of the mono- and dicarbides (no sesquicarbide has been synthesized), phase relationships, structures, and some thermochemical properties. Heats of formation values in the literature are in wide disagreement. They rely mostly on vapor pressure measurements with estimated free energy functions or e.m.f. measurements on cells at elevated temperatures combined with estimated heat capacities.

This paper describes the results obtained from the combustion of four samples of the monocarbide phase and two samples of the dicarbide phase of thorium. The combustions were carried out in an oxygen bomb calorimeter at a known initial pressure of oxygen (*5*). The energy equivalent of the calorimeter as determined by the combustion of standard benzoic acid was 2384.3 ± 0.6 cal. per degree.

PREPARATION OF THORIUM CARBIDES

The thorium carbides were prepared by a fusion reaction in an arc furnace (*3, 10*). Thorium metal rods from Oak Ridge National Laboratory were used. The surface was cleaned using anodic electropolishing in a bath of 75% $\mathrm{H_2SO_4}$ containing chromic acid (10 grams per liter). The metal was then washed with distilled water and dried. Chemical analysis gave the following results: Th, 99.7%; $\mathrm{O_2}$, 0.13%; and in parts per million, the following: Li, < 0.1; Be, 3; B, 0.8; Na, 2; Mg, 20; Al, 3; Si, 30; Ca, 3; V, < 40; Cr, 30; Mn, 1; Fe, 80; Co, < 2; Ni, 70; Cu, 30; Pb, 2. Spectrographic quality graphite rods were used as the source of carbon for the preparation.

The arc furnace was of water-cooled copper construction. It had a movable cathode with a 1-inch diameter Type AUC graphite tip (Carbon Products Division of the Union Carbide Corp.). The furnace could be evacuated by an oil diffusion pump backed by a mechanical pump to approximately 10^{-6} mm. The power for melting of samples came from a 34.5-kw. welding generator of the rectifier type. A high frequency unit was used to initiate the arc.

The thorium carbides were prepared by placing the thorium metal rods and spectrographic quality graphite rods side by side on the copper hearth and closing the furnace. Each batch totaled approximately 60 grams. After evacuation of the system, helium was admitted to a pressure approximately 8 to 10 cm. below the ambient atmospheric pressure. Next, a button of zirconium metal was melted in the arc furnace as a "getter" for the impurities in the helium. The thorium was then melted in contact with the graphite to form the carbide. After the carbide piece had cooled, it was turned over in the hearth by means of the movable cathode without opening the furnace to the atmosphere. What was previously the bottom side of the sample could now be melted. This procedure was repeated three times for each of the compositions. The carbides have a gold cast, and are shiny, metallic, and brittle. Their analyses are summarized in Table I.

There was a small amount of hydrogen, 0.004%, in the second dicarbide sample, and the higher carbides had some free carbon present. X-ray patterns of the monocarbides gave a = 5.3137, 5.3268, 5.3387, and 5.3438 A., respectively, for these face centered cubic materials. The patterns of the two dicarbides showed only the monoclinic (α) form.

Metallography was conducted on each of the samples using polarized light. Polishing and etching was attempted on each sample. Photomicrographs showed some grain boundary precipitate and some contamination.

The oxygen impurity was assumed to be combined with the metallic impurities and the nitrogen and any excess oxygen with the thorium. The calculated compositions are shown in Table II. There is an estimated uncertainty of ± 0.01 in the coefficient of the carbon in the formula of each carbide.