HAFNIUM AND HAFNIUM COMPOUNDS

1. Introduction

Hafnium [7440-58-6], Hf, is in Group 4 (IVB) of the Periodic Table as are the lighter elements zirconium and titanium. Hafnium is a heavy gray-white metallic element never found free in nature. It is always found associated with the more plentiful zirconium. The two elements are almost identical in chemical behavior. This close similarity in chemical properties is related to the configuration of the valence electrons, $4d^2 5s^2$ and $5d^2 6s^2$ for zirconium and hafnium, respectively; and to the close similarity in ionic radii of the M^{4+} ions, Zr^{4+}, 0.084 nm and Hf^{4+}, 0.083 nm. The latter is a consequence of the lanthanide contraction. Hafnium and zirconium have more similar chemical properties than any other pair in the Periodic Table apart from the inert gases.

Whereas zirconium was discovered in 1789 and titanium in 1790, it was not until 1923 that hafnium was positively identified. The Bohr atomic theory was the basis for postulating that element 72 should be tetravalent rather than a trivalent member of the rare-earth series. Moseley's technique of identification was used by means of the x-ray spectra of several zircon concentrates and lines at the positions and with the relative intensities postulated by Bohr were found (1). Hafnium was named after *Hafnia*, the Latin name for Copenhagen where the discovery was made.

Hafnium is obtained as a by-product of the production of hafnium-free nuclear-grade zirconium (see NUCLEAR REACTORS; ZIRCONIUM AND ZIRCONIUM COMPOUNDS). Hafnium's primary use is as a minor strengthening agent in high temperature nickel-base superalloys. Additionally, hafnium is used as a neutron-absorber material, primarily in the form of control rods in nuclear reactors.

Table 1. **Physical Properties of Hafnium**

Property	Value	Reference
atomic number	72	
atomic weight	178.49	
density, at 298 K, kg/m^3	13.31×10^3	2
melting point, K	2504	3
boiling point, K	4903	3
specific heat, at 298 K, J/(kg · K)[a]	144	3,4
latent heat of fusion, J/kg[a]	1.53×10^5	3
electrical resistivity, at 298 K, $\Omega \cdot$ m	3.37×10^{-7}	5
Hall coefficient, at 298 K, V · m/(A · T)	-1.62×10^{-12}	6
work function, J[a]	6.25×10^{-19}	6
thermal conductivity, W/(m · K)		
at 273 K	23.3	7
at 1273 K	20.9	
Young's modulus, at 293 K, GPa[b]	141	8
shear modulus, at 293 K, GPa[b]	56	8
Poisson's ratio, at 293 K	0.26	8
thermal expansion coefficient, linear,[c] from 293 to 1273 K, 10^{-6}/K	6.1	9

[a] To convert J to cal, divide by 4.184.

[b] To convert GPa to psi, multiply by 145,000.

[c] For random polycrystalline orientation.

2. Physical Properties

Hafnium is a hard, heavy, somewhat ductile metal having an appearance slightly darker than that of stainless steel. The color of hafnium sponge metal is a dull powder gray. Physical properties of hafnium are summarized in Table 1. These data are for commercially pure hafnium which may contain from 0.2 to 3% zirconium. Although a number of radioactive isotopes have been artificially produced, naturally occurring hafnium consists of six stable isotopes (Table 2). Hafnium crystallizes in a body-centered cubic system which transforms to a hexagonal close-packed system below 2033 K.

Table 2. **Hafnium Isotopes**

Isotope mass number	Abundance, %	Thermal neutron cross section, m$^2 \times 10^{-28}$	Contribution to the total cross section
174	0.16	620	1.0
176	5.21	23	1.2
177	18.61	375	69.8
178	27.30	85	23.2
179	13.63	46	6.3
190	35.10	13	4.6
Total	*100.01*		*106.1*

3. Chemical Properties

Hafnium's normal stable valence is also its maximum valence of four. Hafnium exhibits coordination numbers of six, seven, and eight in its compounds. The aqueous chemistry is characterized by a high degree of hydrolysis, the formation of polymeric species, a very slow approach to true equilibrium, and the multitude of complex ions that can be formed. Partially reduced di- and trihalides have been produced by reducing anhydrous hafnium tetrahalides with hafnium metal.

Hafnium is a highly reactive metal. The reaction with air at room temperature is self-limited by the adherent, highly impervious oxide film which is formed. This film provides oxidation stability at room temperature and resistance to corrosion by aqueous solutions of mineral acids, salts, or caustics. Thicker oxide films are formed at higher temperature, but slowly enough that forging or hot rolling of hafnium ingots is conducted in air at a temperature between 900 and 1000°C, with subsequent removal of surface scale by sandblasting and then a nitric–hydrofluoric acid pickling. High surface area hafnium powder or porous sponge metal ignites quite easily in air. Clean hafnium metal ignites spontaneously in oxygen of about 2 MPa (300 psi).

Hafnium begins to react with nitrogen at about 900°C to form a surface nitride film, and reacts rapidly with hydrogen at about 700°C to form hydrides (qv). The hydrogen diffuses rapidly and converts the bulk metal into the brittle hydride.

Hafnium is readily soluble in hydrofluoric acid and is slowly attacked by concentrated sulfuric acid. Hafnium is unaffected by nitric acid in all concentrations. It is resistant to dilute solutions of hydrochloric acid and sulfuric acid. Hafnium is attacked by all mineral acids if traces of fluorides are present. Hafnium is very resistant to attack by alkalies.

4. Occurrence and Mining

Hafnium and zirconium are always present together in naturally occurring minerals. The primary commercial source is zircon [14940-68-2] (zirconium orthosilicate). Zircon sand is found in heavy mineral sand layers of ancient ocean beaches. Principal zircon sand producing countries are Australia, South Africa, the United States, and Ukraine. Other countries producing zircon include India, Sri Lanka, Russia, Malaysia, China, Thailand, Sierra Leone, and Brazil, and production is planned in Indonesia and Madagascar. Zircon is always a coproduct from the mining of rutile and ilmenite mineral sands to supply the titanium oxide pigment industry (see PIGMENTS, INORGANIC; TITANIUM COMPOUNDS, INORGANIC). Baddeleyite [1490-68-2], a naturally occurring zirconium oxide, is available from South Africa and Russia. World primary hafnium production statistics are not available. Table 3 gives data for zirconium production and reserves and hafnium reserves (10).

Most of the heavy mineral sands operations in the world are similar. Typically the quartz sand overburden is bulldozed away to reach the heavy mineral sand layer, which usually has 2 to 8% heavy minerals. The excavation is flooded and the heavy mineral sands layer is mined by a floating dredge with a cutter-

Table 3. **World Statistics for Zirconium and Hafnium**[a]

	Zr mine production × 10^3t					
	2002	2003[a]	Zr reserve[b]	Zr reserve base[b]	Hf reserve[c]	Hf reserve base[c]
United States[d]	100	100	3.4	5.3	68	97
Australia	408	400	9.1	30	180	600
Brazil	21	30	2.2	4.6	44	91
China	15	15	0.5	3.7	NA	NA
India	19	20	3.4	3.8	42	46
South Africa	224	280	14	14	280	290
Ukraine	34	34	4.0	6.0	NA	NA
other countries	9	10	0.9	4.1	NA	NA
World total [e]	*830*	*890*	*38*	*72*	*610*	*1,100*

[a] Ref. 1.
[b] As $ZrO_2 \times 10^6$t.
[c] As $HfO_2 \times 10^3$t, NA = not available.
[d] Estimated.
[e] Rounded.

head-suction. The sand slurry is pumped to a wet-mill concentrator mounted on a barge behind the dredge. Wet concentration using screens, cones, spirals, and sluices removes roots, coarse sand, slimes, quartz, and other light minerals. The tailings are returned to the back end of the excavation. Rehabilitation of worked-out areas is about a 10-year project which includes replacing the overburden and topsoil to pre-existing levels and contours, and reestablishing the natural vegetation, usually from company-owned nurseries (see MINERAL PROCESSING AND RECOVERY).

The heavy mineral sand concentrates are scrubbed to remove any surface coatings, dried, and separated into magnetic and nonmagnetic fractions (see SEPARATION, MAGNETIC). Each of these fractions is further split into conducting and nonconducting fractions in an electrostatic separator to yield individual concentrates of ilmenite, leucoxene, monazite, rutile, xenotime, and zircon. Commercially pure zircon sand typically contains 64% zirconium oxide, 34% silicon oxide, 1.2% hafnium oxide, and 0.8% other oxides including aluminum, iron, titanium, yttrium, lanthanides, uranium, thorium, phosphorus, scandium, and calcium.

Zircon sands containing 3% hafnium oxide (6% Hf/(Hf + Zr)) have been found in Brazil and Nigeria, and higher concentrations of hafnium oxide have been found in altered zircons such as cyrtolite, malacon, alvite, and naëgite. In general, zircon sands containing higher amounts of hafnium also contain higher amounts of radioactivity.

5. Manufacture

5.1. Decomposition of Zircon.

Zircon sand is inert and refractory. Therefore the first extractive step is to convert the zirconium and hafnium portions into active forms amenable to the subsequent processing scheme. For the production of hafnium, this is done in the United States by carbochlorination as shown in Figure 1. In the Ukraine, fluorosilicate fusion is used. Caustic fusion is the usual starting procedure for the production of aqueous zirconium chemicals, which usually does not involve hafnium separation. Other methods of decomposing zircon such as plasma dissociation or lime fusions are used for production of some grades of zirconium oxide.

Carbochlorination. Milled zircon and coke are reacted with hot chlorine gas in a fluidized bed using chlorine as the fluidizing medium:

$$(\mathrm{ZrHf})\mathrm{SiO_4} + 4\ \mathrm{C} + 4\ \mathrm{Cl_2} \xrightarrow{1100^\circ\mathrm{C}} (\mathrm{ZrHf})\mathrm{Cl_4} + \mathrm{SiCl_4} + 4\ \mathrm{CO}$$

This reaction is endothermic and additional energy must be provided to sustain it, usually by induction heating, or by adding silicon carbide grain which chlorinates exothermically. The product gases are cooled below 200°C to condense and collect the zirconium–hafnium tetrachloride as a powder. The offgas stream then is refrigerated to obtain by-product silicon tetrachloride liquid.

Fluorosilicate Fusion. Milled zircon and potassium hexafluorosilicate are heated together to yield potassium hexafluorozirconate and silica (11):

$$(\mathrm{ZrHf})\mathrm{SiO_4} + \mathrm{K_2SiF_6} \xrightarrow{700^\circ\mathrm{C}} \mathrm{K_2(ZrHf)F_6} + 2\ \mathrm{SiO_2}$$

The addition of potassium carbonate or chloride to the fusion mix reduces the loss of volatile silicon tetrafluoride, improving the conversion efficiency. The fused product is cooled, crushed, and leached with acidified hot water. The resulting hot solution of potassium hexafluorozirconate–hafnate is filtered to remove silica, then cooled to allow crystallization of the potassium hexafluorozirconate–hafnate. Many of the impurity metals remain in solution.

5.2. Separation of Hafnium. Many methods have been proposed for the separation of hafnium and zirconium; three different industrial methods are in use.

Liquid–Liquid Extraction. In the United States, both Teledyne Wah Chang Albany Corp. and Western Zirconium Division of Westinghouse use a liquid–liquid extraction process first proposed in Germany as an analytical procedure (12) (see EXTRACTION, LIQUID–LIQUID). This was modified into an industrial method at the Oak Ridge National Laboratory, and subsequently put into production at the U.S. Bureau of Mines, Albany, Oregon (13). In this process ammonium thiocyanate is added to an acidic solution of zirconium–hafnium hydroxide chloride [22196-48-1], $(\mathrm{ZrHf})(\mathrm{OH})_2\mathrm{Cl}_2$. This solution is contacted with an immiscible methyl isobutyl ketone solution containing thiocyanic acid in a series of countercurrent stages. Both hafnium and zirconium thiocyanate complexes are soluble in both phases, but hafnium is preferentially distributed in the ketone phase. Hafnium is recovered from the ketone by scrubbing with dilute sulfuric acid which is then neutralized to precipitate hydrous hafnium oxide which is filtered and calcined to hafnium oxide. The reaction of milled hafnium oxide with carbon and chlorine in a fluidized bed at 900–1000°C produces hafnium tetrachloride. Before being reduced the hafnium tetrachloride is purified by sublimation in a nitrogen–hydrogen atmosphere.

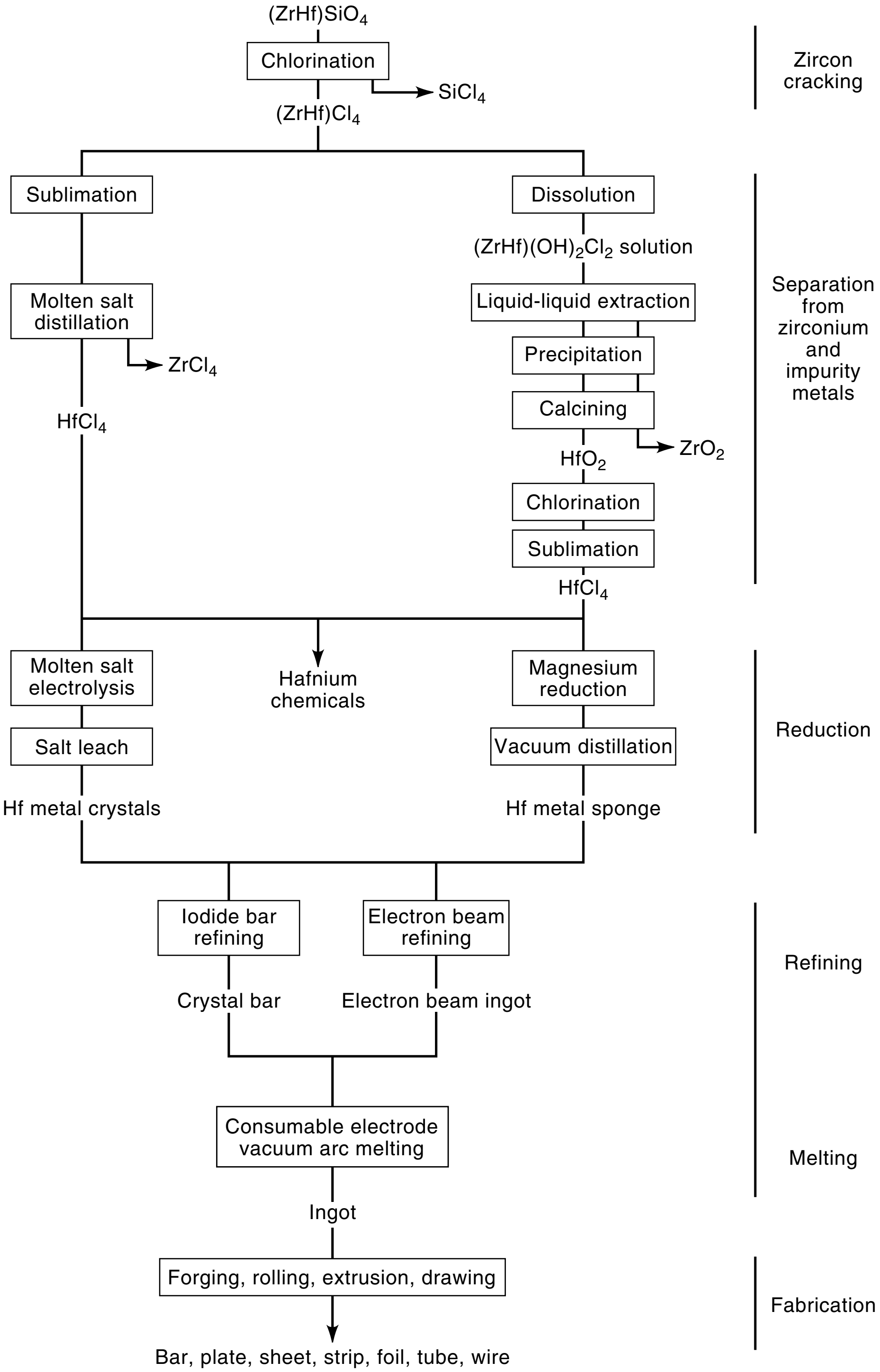

Fig. 1. Flow sheet for hafnium production.

Molten Salt Distillation. Hafnium tetrachloride is slightly more volatile than zirconium tetrachloride, but a separation process based on this volatility difference is impractical at atmospheric pressures because only solid and vapor phases exist. The triple point for these systems is at about 2.7 MPa (400 psia) and 400°C so that separation of the liquids by distillation would necessarily require a massive pressurized system (14).

In France, Compagnie Europèene du Zirconium (CEZUS) uses a separation (15) based on the extractive distillation of zirconium–hafnium tetrachlorides in a molten potassium chloride–aluminum trichloride solvent at atmospheric pressure at 350°C. For feed, the impure zirconium–hafnium tetrachlorides from the zircon chlorination are first purified by sublimation. The purified tetrachlorides are again sublimed to vapor feed the distillation column containing the solvent salt. Hafnium tetrachloride is recovered in an enriched overhead fraction which is accumulated and reprocessed to pure hafnium tetrachloride.

Fluorozirconate Crystallization. Repeated dissolution and fractional crystallization of potassium hexafluorozirconate was the method first used to separate hafnium and zirconium (16), potassium fluorohafnate solubility being higher. This process is used in the Prinieprovsky Chemical Plant in Dnieprodzerzhinsk, Ukraine, to produce hafnium-free zirconium. Hafnium-enriched (about 6%) zirconium hydrous oxide is precipitated from the first-stage mother liquors, and redissolved in acid to feed ion-exchange columns to obtain pure hafnium (11).

5.3. Reduction. Hafnium oxide can be reduced using calcium metal to yield a fine, pyrophoric metal powder (see CALCIUM AND CALCIUM ALLOYS). This powder contains considerable oxygen contamination because of oxygen's high solubility in hot hafnium, and cannot be consolidated into ductile metal. To obtain low oxygen ductile hafnium, the feed must be an oxygen-free halide compound such as hafnium tetrachloride or potassium hexafluorohafnate [16871-86-6].

Kroll Process. Hafnium tetrachloride vapor is reduced by liquid magnesium in an inert atmosphere in a batch operation. Hafnium tetrachloride powder is charged into the annular upper chamber of a vertical cylindrical steel retort. Cast ingots of pure magnesium are placed inside a stainless-steel liner within the lower chamber. After the retort has been closed, evacuated, and backfilled with argon, heat is applied to the lower retort zone to melt the magnesium. Then the reaction is initiated by heating the upper zone to gradually sublime the hafnium tetrachloride. Hafnium tetrachloride vapors pass into the lower chamber and react with the liquid magnesium to form three micrometer-sized spheres of hafnium metal which settle to the bottom of the chamber as a hafnium–magnesium mud. The rate of this exothermic reaction is controlled by adjusting the upper zone temperature, thereby controlling the rate of tetrachloride sublimation. After the reaction, the reduction retort is cooled and unloaded. The reduction mass is placed in the upper portion of a vacuum distillation furnace which is then evacuated to a pressure of about 0.1 Pa (75 μm Hg) before heating. As the temperature passes above 700°C the magnesium chloride melts and drains into the cooler lower zone, and the magnesium begins to distill from the mud, allowing the hafnium spheres to slowly sinter into a porous sponge. The distillation is complete after several hours at 980°C. After the furnace is cooled, the sponge is broken by a hydraulic chisel operating in an argon atmosphere box.

The sponge chunks are visually graded, then chopped to less than 19 mm and sampled (17).

Electrolysis. Electrowinning of hafnium, zirconium, and titanium has been proposed as an alternative to the Kroll process. Electrolysis of an all chloride hafnium salt system is inefficient because of the stability of lower chlorides in these melts. The presence of fluoride salts in the melt increases the stability of Hf^{4+} in solution and results in much better current efficiencies. Hafnium is produced by this procedure in France (18).

5.4. Refining. Kroll-process hafnium sponge and electrowon hafnium do not meet the performance requirements for the two principal uses of hafnium metal. Further purification is accomplished by the van Arkel-de Boer, ie, iodide bar, process (19) and by electron beam melting.

For van Arkel-de Boer refining, hafnium sponge or crystals are loaded around the interior periphery of a vertical cylindrical Inconel vessel. The vessel lid supports insulated electrodes from which hafnium wire filaments in hairpin shape are suspended. Iodine is added to the evacuated vessel which then is heated to 300°C. The iodine reacts with the sponge forming hafnium tetraiodide vapor which diffuses to the hafnium filament which is resistance-heated to 1300–1600°C. The tetraiodide thermally dissociates at the hot filament, depositing

Table 4. **Analysis of Kroll Process, Electrowon, and Refined Hafnium, ppm**

Impurities	Kroll process sponge	Electrowon crystals	Refined from Kroll sponge: Electron beam ingot	Refined from Kroll sponge: Iodide bar
Al	65	15	<10	<10
B	<0.2	<0.2	<0.2	<0.2
C	35	35	35	<20
Cd	<1	<1	<1	<1
Co	<5	<5	<5	<5
Cr	40	30	<10	<10
Cu	40	<40	<40	<40
Fe	250	100	<50	50
Mg	370	<10	<10	<10
Mn	<10	10	<10	<10
Mo	15	10	<10	<10
N	25	15	15	<10
Ni	15	35	<10	<10
Nb	<50	<50	<50	<50
Pb	<5	<5	<5	<5
O	900	600	300	90
Si	40	<40	<40	<40
Ta	<100	<50	<50	<50
Ti	95	30	<30	40
U	1	<1	<1	<1
V	<5	<5	<5	<5
W	<20	<20	<20	<20

a film of hafnium and releasing iodine to react again with additional sponge.

$$\mathrm{Hf} + 2\,\mathrm{I_2} \xrightarrow{300^\circ\mathrm{C}} \mathrm{Hf\,I_4} \xrightarrow{1400^\circ\mathrm{C}} \mathrm{Hf} + 2\,\mathrm{I_2}$$

Oxygen and nitrogen stay gettered by the residual sponge, and other metals transfer poorly under these conditions so that the filament product, hafnium crystal bar, is much purer and therefore softer than the starting sponge. Crystal bar growth is slow and this refining procedure is costly.

Electron beam melting of hafnium in a high vacuum removes those impurities having partial pressure at the surface of the melt greater than the vapor pressure of hafnium, about 0.1 Pa (0.075 μm Hg) at 2500 K. Some oxygen is removable because hafnium monoxide is more volatile than hafnium. Only nitrogen and higher melting point metals, such as tantalum and tungsten, are not removed. To obtain the very purest hafnium, both refining procedures are used in sequence. Typical analyse of as-produced and refined hafnium are shown in Table 4.

Many of the impurities are much lower than the values shown in Table 4, but these analytical lower limits are typical and more than sufficient for all but special applications. Zirconium content can be from 0.01 to 4.5%, and is typically 0.5–2%, but this is a function of how far the separation process was carried, not a function of the reduction or refining processes.

6. Economic Aspects

World resources of hafnium are associated with those of zircon and baddeleyite and exceed 1×10^6 t. Resources of hafnium in the United States are estimated to be about 130×10^3 t, available in the 14×10^6 t of the domestic resources of zircon.

Price history for hafnium sponge is for the period 1999–2000 range was \$165–290 and for the period 2001–2003 range was \$119–141 (10).

Table 5. **U.S. Imports for Consumption of Hafnium, Unwrought, Waste, and Scrap,[a] and Country[b]**

	2001		2002	
Country	Quantity, t	Value, $\$ \times 10^3$	Quantity, t	Value, $\$ \times 10^3$
Canada			2	296
China	[c]	5	1	65
France	4	931	1	296
Germany	1	330		
Japan	[c]	15	1	10
United Kingdom	[c]	17		
Total	*5*	*1,300*	*5*	*668*

[a] Harmonized code (8112.92.2000) (2002) and (8112.91.2000) (2001).

[b] Ref. 20.

[c] Less than 1/2 unit.

Imports of hafnium, unwrought, waste and scrap were 9 t in 1999; 11 t in 2000; and 5 t for the period 2001–2003. Data are not available as to the reliance of these imports on net consumption. See Table 5 for further import data (20).

7. Specifications and Standards

Several ASTM Standard Specifications have been promulgated for hafnium materials: B737-90 for Hot-Rolled or Cold-Finished Hafnium Rod and Wire; B776-91 for Hafnium and Hafnium Alloy Strip, Sheet, and Plate; G2-88 and G2M-88 (metric) for Corrosion Testing of Products of Zirconium, Hafnium, and Their Alloys in Water at 680°F (633 K) or in steam at 750°F (673 K); C1076-92 for Nuclear-Grade Hafnium Oxide Pellets; and C1098-88 for Nuclear-Grade Hafnium Oxide Powder.

In addition, the following ASTM Standard Specifications are for the Nb–10Hf–1Ti–1Zr alloy known commercially as C103: B652-92 Niobium–Hafnium Alloy Ingots; B654-92 Niobium–Hafnium Alloy Foil, Sheet, Strip, and Plate; B655-92 Niobium–Hafnium Alloy Bar, Rod, and Wire.

8. Analytical Methods

Analyses of alloys or ores for hafnium by plasma emission atomic absorption spectroscopy, optical emission spectroscopy (qv), mass spectrometry (qv), x-ray spectroscopy (see X-RAY TECHNOLOGY), and neutron activation are possible without prior separation of hafnium (21). Alternatively, the combined hafnium and zirconium content can be separated from the sample by fusing the sample with sodium hydroxide, separating silica if present, and precipitating with mandelic acid from a dilute hydrochloric acid solution (22). The precipitate is ignited to oxide which is analyzed by x-ray or emission spectroscopy to determine the relative proportion of each oxide.

Hafnium metal is analyzed for impurities using analytical techniques used for zirconium (21,23,24). Carbon and sulfur in hafnium are measured by combustion, followed by chromatographic or ir measurement of the carbon and sulfur oxides (21). Chromatographic measurement of liberated hydrogen follows the hot vacuum extraction or fusion of hafnium with a transition metal in an inert atmosphere (25,26).

Oxygen and nitrogen also are determined by conductivity or chromatographic techniques following a hot vacuum extraction or inert-gas fusion of hafnium with a noble metal (27,28). Nitrogen also may be determined by the Kjeldahl technique (21). Phosphorus is determined by phosphine evolution and flame-emission detection. Chloride is determined indirectly by atomic absorption or x-ray spectroscopy, or at higher levels by a selective-ion electrode. Fluoride can be determined similarly (29,30). Uranium and U-235 have been determined by inductively coupled plasma mass spectroscopy (31).

Inductively coupled plasma (icp) emission, direct current plasma (dcp), and inductively coupled plasma mass spectrometry (icp/ms) have taken over as the methods of choice for the simultaneous detection of metallic impurities in hafnium and hafnium compounds (31–33).

9. Health and Safety Factors

High surface area forms of hafnium metal such as foil, fine powder, and sponge are very easily ignited, and fine machining chips can be pyrophoric. If ignited, hafnium can be extinguished with a blanket of argon or a layer of dry salt or dry sand. The use of water to extinguish burning hafnium is extremely hazardous. The resulting steam and hydrogen may disperse the burning fragments and spread the fire. Damp hafnium sponge or powder burns more quickly and completely than dry hafnium. Methods for safe handling of both hafnium and zirconium are discussed in the literature (34).

Most hafnium compounds require no special safety precautions because hafnium is nontoxic under normal exposure. Because hafnium is poorly soluble in water and thus is not absorbed efficiently. Many hafnium compounds are poisons, however. OSHA PEL and ACGIH TLV for hafnium TWA is 0.5 mg m^3 (35). Acidic compounds such as hafnium tetrachloride hydrolyze easily to form strongly acidic solutions and to release hydrogen chloride fumes, and these compounds must be handled properly. Whereas laboratory tests in which soluble hafnium compounds were injected into animals did show toxicity, feeding test results indicated essentially no toxicity when hafnium compounds were taken orally (36,37).

10. Uses

10.1. Alloying. The largest use of hafnium as an alloying element in high temperature application alloys such as superalloys and refractory metal alloys where hafnium additions improve the high temperature tensile and creep strength (see HIGH TEMPERATURE ALLOYS). Hafnium reacts with carbon, nitrogen, or oxygen in these alloys to form a fine dispersion of hafnium carbide, nitride, and oxide which provide second-phase particle dispersion strengthening. This effect is maintained at high temperature because of the high melting points and thermodynamic stability of these components. It is used as a 1–2% addition in the superalloys used for cast vanes and turbine blades placed in the hottest stages following the combustion zone of jet aircraft engines. Small additions of hafnium and carbon react to form second-phase dispersions in tantalum, molybdenum, and tungsten alloys (38–40), including the tantalum alloys T-111, T-222, and Astar 811C, and the molybdenum alloy MHC.

In larger proportions, hafnium provides both dispersed particle strengthening and solid solution strengthening in niobium-base alloys (41), including such as C103 (Nb–10 Hf–1 Ti–1 Zr), C-129Y (Nb–10 W–10 Hf–0.7 Y), and WC 3015 (Nb–30 Hf–15 W–1.5 Zr). Hafnium-based alloys containing 20–27% tantalum and up to 2% molybdenum are unique refractory alloys which exhibit high oxidation resistance.

Hafnium is an effective solid solution strengthener at higher temperatures for other alloys such as nickel aluminides (42,43).

10.2. Nuclear. A primary market for many years has been for control rods in the pressurized light water reactors which power many naval vessels. Hafnium excels in this application because of its excellent hot water (450°C) corrosion resistance, good ductility and machinability, and large neutron absorption cross section. It absorbs both thermal and epithermal neutrons and its absorption cross section decreases slowly after long periods of neutron irradiation. The existence of several successive hafnium isotopes having large cross sections permits the neutron absorption by one hafnium isotope to result in the formation of a new hafnium isotope which also has a large absorption cross section (see Table 2). The ability of hafnium to absorb neutrons above thermal energies (resource energy absorption) makes it more effective as an absorbing material. Hafnium has not been used significantly in commercial nuclear power reactors.

Hafnium neutron absorption capabilities have caused its alloys to be proposed as separator sheets to allow closer spacing of spent nuclear fuel rods in interim holding ponds. Hafnium is the preferred material of construction for certain critical mass situations in spent fuel reprocessing plants where hafnium's excellent corrosion resistance to nitric acid is also important.

10.3. Other Uses as Metal. Very pure hafnium forms effective diffusion barriers for multilevel integrated circuits (qv). Hafnium metal stubs are being used in water-cooled copper holders as cathodes for plasma arc cutting, and hafnium is replacing tungsten in copper coated welding (qv) tips. It is used in high temperature ceramics. Hafnium has been proposed as an ingredient in permanent magnets (see MAGNETIC MATERIALS).

10.4. Uses as Compounds. Hafnium oxide is a very refractory compound which has found some use in specialized refractories (qv) such as insulating sheaths for tungsten tungsten–rhenium thermocouples above 1500°C. Hafnium oxide [12055-23-1] sputtering targets are used for depositing coatings (qv) on optical components for lasers (qv) (44). Hafnium oxide is one of several hafnium compounds proposed as luminescents and phosphors during uv and x-ray excitation (45–49). Hafnium oxide is reactively sputtered on the surface of a magnetic recording disk as a wear-resistant coating (50).

A method to form zirconium oxide and hafnium oxide for high dielectric constant materials has been described (51). Precursors for zirconium and hafnium oxide for a thin film formed by chemical vapor deposition processes have has been disclosed (52).

Hafnium oxide 30–40 mol% titanium oxide ceramics (qv) exhibit a very low coefficient of thermal expansion over the temperature range of 20–1000°C. A 45–50 mol% titanium oxide ceramic can be heated to over 2800°C with no crystallographic change (53).

Hafnium nitride [25817-87-2], which has been used as a chemically stable surface coating on steel-grade cemented-carbide cutting tools (54–55), does not weld to the steel being cut, thereby reducing friction and tool wear (see TOOL MATERIALS). Hafnium nitride's gold coloring has been used as a decorative coating, and its optical properties (56) make it a candidate for wavelength-selective optical films that could be used on solar collectors (see SOLAR ENERGY). Hafnium nitride's high emissivity in the visible spectrum at high temperature has led to a proposed use (57) as a coating on incandescent light filaments to improve visible light output.

A field effect semiconductor device comprising a high permittivity hafnium nitride gate has been disclosed (58).

Hafnium carbide [12069-85-1] can be used as surface coating on cemented-carbide cutting tools, shows promise as a stable field emission cathode (59), and has been alloyed with niobium carbide to produce a substitute for tantalum carbide as a constituent of cemented carbide tool bits (see CARBIDES) (60).

High temperature ablation resistant ceramic composites of hafnium carbide and hafnium diboride have been made (61).

Hafnium tetrafluoride [13709-52-9] is one component in the cladding layer of a proposed zirconium fluoride glass optical waveguide fiber composition which is expected to have a lower intrinsic light absorption than fused quartz optical fiber (see GLASS; FIBER OPTICS).

After the discovery of isotactic polymerization of propylene using zirconocene catalysts, structurally analogous hafnium catalysts produced from hafnium tetrachloride [13499-05-3] were found to produce high yields of high molecular weight polypropylene (62), but not enough to lead to commercial development.

11. Hafnium Compounds

Most hafnium compounds have been of slight commercial interest aside from intermediates in the production of hafnium metal. However, hafnium oxide, hafnium carbide, and hafnium nitride are quite refractory and have received considerable study as the most refractory compounds of the Group 4 (IVB) elements. Physical properties of some of the hafnium compounds are shown in Table 6.

11.1. Hafnium Boride. Hafnium diboride [12007-23-7], HfB_2, is a gray crystalline solid. It is usually prepared by the reaction of hafnium oxide with carbon and either boron oxide or boron carbide, but it can also be prepared from mixtures of hafnium tetrachloride, boron trichloride, and hydrogen above 2000°C, or by direct synthesis from the elements. Hafnium diboride is attacked by hydrofluoric acid but is resistant to nearly all other reagents at room temperature. Hafnium dodecaboride [32342-52-2], HfB_{12}, has been prepared by direct synthesis from the elements (63).

11.2. Hafnium Tetrahydridoborate. Hafnium tetrahydridoborate [25869-93-6], $Hf(BH_4)_4$, is the most volatile compound of hafnium: mp, 29°C; bp, 118°C; and vapor pressure, 2 kPa (14.9 mm Hg) at 25°C. It is prepared by the reaction of hafnium tetrachloride with lithium tetrahydridoborate, followed by distillation of the hafnium tetrahydridoborate and separation from lithium chloride.

11.3. Hafnium Carbide. Hafnium carbide, HfC, is a dark gray brittle solid. This carbide can be prepared by heating an intimate mixture of the elements or by the reaction of hafnium tetrachloride with methane at 2100°C, but is commonly produced by the reaction of hafnium oxide with lampblack in graphite crucibles in hydrogen at 1900–2300°C or under vacuum at 1600–2100°C. The carbide is not a true stoichiometric compound, but a solution of carbon at preferred interstitial sites in a face-centered cubic hafnium lattice. The

Table 6. **Physical Properties of Some Hafnium Compounds**

Property	HfB_2	HfC	HfO_2	HfN	HfP
CAS Registry number	[12007-23-7]	[12069-85-1]	[12055-23-1]	[25817-87-2]	[12325-59-6]
melting point, °C	3370	3830	2810	3330	
sublimation point, °C					
specific gravity, g/cm^3					
theoretical	11.2	12.7		13.84	9.78
measured	10.5	12.2	9.68		
resistivity at RT, $\mu\Omega \cdot$cm	8.8	37	$>10^8$	33	
color	gray	gray	white	gold	
coefficient of thermal expansion, 10^{-6}	5.7	6.59	6.1	6.9	
hardness,[b] kgf/mm^2	2900[c]	2300[d]	1050[e]	1640[f]	
structure	hexagonal	face-centered cubic	monoclinic[f]	cubic	hexagonal
lattice parameters, nm					
a	0.3141	0.4640	0.51156	0.452	0.365
b			0.51722		1.237
c	0.3470		0.52948		

[a] At 3.34 MPa (33 atm).

[b] See Hardness; 1 kgf/mm^2 = 9.8 MPa.

[c] Vicker's hardness.

[d] Knoop hardness.

[e] Diamond pyramid hardness (DPH), 2 kg.

[f] Microhardness, 50 gf/mm^2 = 490 kPa.

[g] Tetragonal above 1600°C.

hafnium—carbon phase diagram shows that hafnium carbide is homogeneous over the composition range of 34–48 atomic% carbon at 2200°C (64).

Hafnium carbide is inert to most reagents at room temperature, but is dissolved by hydrofluoric acid solutions which also contain an oxidizing agent. Above 250°C, hafnium carbide reacts exothermically with halogens to form hafnium tetrahalide, and above 500°C, with oxygen to form hafnium dioxide. At higher temperatures in a flow of hydrogen, hafnium carbide slowly loses some of its carbon.

11.4. Hafnium Halides. Hafnium tetrafluoride, HfF_4, can be prepared by careful thermal decomposition of ammonium fluorohafnate in an oxygen-free atmosphere, or by passing anhydrous hydrogen fluoride over hafnium tetrachloride at 300°C. The direct synthesis from the elements is incomplete because the product fluoride forms a film on the metal.

Ammonium fluorohafnate [16925-24-9], $(NH_4)_2HfF_6$, or potassium fluorohafnate [16871-86-6], K_2HfF_6, can be prepared by crystallization from an aqueous

Table 6. (*Continued*)

HfS_2	$HfSe_2$	$HfSi_2$	HfF_4	$HfCl_4$	$HfBr_4$	HfI_4
[18855-94-2]	[12162-21-9]	[12401-56-8]	[13709-52-9]	[13499-05-3]	[13777-22-5]	[13777-23-6]
		1750	>968	432^a	424^a	449^a
			968	317	322	393
		8.03			5.09	
6.03	7.46	7.2			4.90	
	20	60				
purple-brown	dark brown		white	white	white	yellow-orange
hexagonal	hexagonal	rhombic^g	monoclinic	monoclinic	cubic	cubic
		930^f				
hexagonal	hexagonal	rhombic^g	monoclinic	monoclinic	cubic	cubic
0.364	0.375	0.3677	0.957	0.631	1.095	1.176
0.584	0.616	1.455	0.993	0.7407		
		0.3649	0.773	0.6256		

hydrofluoric acid solution by addition of ammonium fluoride or potassium fluoride, respectively.

Hafnium tetrachloride, $HfCl_4$, can be made by reaction of chlorine with hafnium above 317°C or with an intimate mixture of hafnium oxide and carbon above 700°C, or by reaction of carbon tetrachloride and hafnium oxide above 450°C. Hafnium tetrachloride reacts with water, forming hafnium oxide chloride and hydrochloric acid. It reacts with almost all hydroxide-containing organic compounds to form addition compounds with the subsequent evolution of hydrogen chloride. Hafnium tetrachloride vapor reacts with steam to form finely divided hafnium dioxide. It forms addition compounds with molten alkaline halides, eg, $2KCl \cdot HfCl_4$ [19381-63-6], iron chloride, and aluminum chloride. These addition compounds decompose at higher temperatures. Hafnium tetrachloride can be reduced to lower chlorides by reaction with hafnium metal or by reaction with aluminum metal in liquid aluminum chloride (65). Hafnium tetrachloride is the starting material used in preparation of hafnium-containing organometallic compounds (66).

Hafnium hydroxide chloride heptahydrate [93245-94-4], $Hf(OH)_2Cl_2 \cdot 7H_2O$ occurs as white tetragonal crystals. On heating, it first dissolves in its hydration water but rapidly loses both water and hydrogen chloride. On continued heating, further decomposition yields hafnium dioxide. The hydroxide chloride is produced by adding hafnium tetrachloride to water or by dissolving hydrous hafnium oxide in hydrochloric acid. Hafnium hydroxide chloride is soluble in water. The solubility in hydrochloric acid decreases with increasing acid strength to a minimum solubility at 8.5 M hydrochloric acid. The solubility in hydrochloric acid is increased greatly at elevated temperatures. Repeated crystallization of hafnium hydroxide chloride from hot concentrated hydrochloric acid is the classical method to obtain hafnium salts free of all metallic impurities except zirconium. The hydroxide chloride is the common starting material for the preparation of other aqueous hafnium compounds.

Hafnium tetrabromide [13777-22-5], $HfBr_4$, is very similar to the tetrachloride in both its physical and chemical properties. Hafnium tetraiodide [13777-23-6], HfI_4, is produced by reaction of iodine with hafnium metal at 300°C or higher. At temperatures above 1200°C, the iodide dissociates to hafnium metal and iodine. These two reactions are the basis for the iodide-bar refining process. Hafnium iodide is reported to have three stable crystalline forms at 263–405°C (67).

11.5. Hafnium Hydride. Hafnium reacts reversibly with hydrogen to form hafnium hydride [12656-74-5], $HfH_{1.6-2.0}$. Below 250°C, the reaction rate becomes quite slow. The proportion of hydrogen depends on the temperature and pressure of hydrogen at which the hafnium is exposed. As hydrogen is absorbed, the hafnium transforms from hexagonal metal to face-centered cubic hydride and then to face-centered tetragonal hydride. At room temperature, the face-centered cubic form exists as a single phase at an H/Hf ratio of 1.7–1.8 (68). The face-centered tetragonal form exists as a single phase above H/Hf of 1.87 at room temperature. The face-centered tetragonal phase has been reported to be stable only below 407°C.

Hafnium hydride is brittle and easily crushed to very fine particle sizes. It is usually produced as an intermediate in the process of making hafnium powder from massive hafnium metal. The hydrogen can be removed by high vacuum pumping above 600°C.

11.6. Hafnium Nitride. Hafnium nitride, HfN, a gold-colored brittle solid, is prepared by heating hafnium metal to 1000–1500°C in an atmosphere of nitrogen or ammonia. The higher temperatures yield a product with a nitrogen-to-metal ratio approaching one, but the reaction is slow because of the slow diffusion of nitrogen through the protective nitride layer. Hafnium nitride also can be prepared by the reaction of hafnium tetrachloride vapor with nitrogen in a hydrogen atmosphere at $>1000°C$. This is the basis for a chemical vapor deposition process used to deposit a thin layer of hafnium nitride on steel-grade cemented-carbide cutting tools. The hafnium nitride layer reduces the frictional forces and wear, thereby increasing the life of the tool by a factor of 6–8. A straw-colored higher nitride, Hf_3N_4 [104382-33-4], is produced by dual ion beam sputter deposition (69) and by low temperature chemical vapor deposition at 250–400°C (70).

11.7. Hafnium Oxide. Two oxides of hafnium, hafnium monoxide [12029-22-0], HfO, and HfO_2, are known to exist but only the dioxide is stable under ordinary conditions. Gaseous hafnium monoxide can be present at $>2000°C$, especially when the partial pressure of oxygen is low. Hafnium monoxide is probably the compound form in which oxygen is evolved when hafnium metal is melted in an electron-beam melting furnace. HfO(g) is the species observed mass spectrometrically when hafnium dioxide vaporizes.

Hafnium dioxide is formed by ignition of hafnium metal, carbide, tetrachloride, sulfide, boride, nitride, or hydrous oxide. Commercial hafnium oxide, the product of the separation process for zirconium and hafnium, contains 97–99% hafnium oxide. Purer forms, up to 99.99%, are available.

Pure hafnium dioxide transforms into the tetragonal structure at about 1700°C. The difference between the heating transformation temperature and the cooling transformation temperature is 40–80°C, considerably less than for zirconia. The hafnium dioxide undergoes a shrinkage of about 3% upon transforming into the tetragonal phase. The tetragonal form converts to a cubic polymorph having the fluorite structure above 2600°C. The fluorite structure can be rendered stable at lower temperatures by addition of erbium oxide, yttrium oxide, calcium oxide, or magnesium oxide. Compared to zirconium oxide, the higher transformation temperature of hafnium oxide, pure or stabilized, aroused considerable interest. Reference 71 is a thorough review of hafnium oxide and hafnium oxide-toughened ceramics.

At room temperature, hafnium dioxide is slowly dissolved by hydrofluoric acid. At elevated temperatures, hafnium dioxide reacts with concentrated sulfuric acid or alkali bisulfates to form various sulfates, with carbon tetrachloride or with chlorine in the presence of carbon to form hafnium tetrachloride, with alkaline fluorosilicates to form alkali fluorohafnates, with alkalies to form alkaline hafnates, and with carbon above 1500°C to form hafnium carbide.

The hydrous oxide, $HfO_2 \cdot xH_2O$, is precipitated from acidic solutions by addition of ammonium hydroxide or dilute alkaline solutions. However, the hydrous oxide exhibits a limited solubility in strongly alkaline solutions (72). The existence and relative stability of soluble alkaline peroxy compounds has been demonstrated (73).

11.8. Hafnium Sulfides. Several sulfides of hafnium have been prepared, including Hf_2S, HfS, and HfS_2, by the reaction of the mixed elements at 500°C or by passing hydrogen sulfide over heated hafnium powder. Of these, hafnium disulfide [18855-94-2] is fairly well characterized. The disulfide is a layered compound reported to have good lubricating properties similar to other layered chalcogenide compounds such as NbS_2, MoS_3, and WS_3. The electrical resistance and sulfur vapor pressure are given as a function of temperature and composition in Reference 74.

11.9. Hafnium Carbonate. Basic hafnium carbonate [124563-80-0], $Hf_2(OH)_4CO_3 \cdot XH_2O$, is prepared as a wet paste by reaction of a slurry of basic hafnium sulfate [139290-14-5], $Hf_5O_7(SO_4)_3 \cdot XH_2O$, and sodium carbonate, then filtering. The basic carbonate has a short shelf life and is preferably prepared as needed. It is a starting material for the preparation of various hafnium carboxylates.

11.10. Hafnium Acetate. Hafnium acetate [15978-87-7], $Hf(OH)_2(CH_3COO)_2$, solutions are prepared by reacting the basic carbonate or freshly precipitated hydroxide with acetic acid. The acetate solution has been of interest in preparing oxide films free of chloride or sulfate anions.

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RALPH H. NIELSEN
Teledyne Wah Chang Corporation