Chapter 5
Hafnium

5.1 Introduction

Hafnium (Hf) occurs in nature in small amounts associated with zirconium in all the zirconium minerals. The hafnium content of the Earth's crust has been estimated to be greater than that of mercury, niobium, and tantalum or silver. Although hafnium was not discovered until 1923, claims of evidence of the concentration of this element were made many years earlier. The evidence was considered inconclusive by Bohr and by Coster and von Hevesy, who were convinced that element 72 was not one of the rare earths but that it was quadrivalent and a homologue of zirconium and thorium. Coster and von Hevesy reasoned that element 72 was more likely to occur with zirconium than with the rare earths. Coster and von Hevesy announced the discovery of element 72, proposing the name *hafnium* (from *Hafnia*, Latin for Copenhagen) in honour of the city where the discovery was made.

There has been considerable interest in the use of hafnium (Hf) metal as a control rod material in nuclear reactors. This use has been made possible in large measure by the somewhat greater availability of the metal as a by-product of the increased production of reactor grade zirconium. Hafnium excels in this application because of its excellent hot water corrosion resistance, good ductility, machinability and high thermal neutron absorption cross-section (105 barns).

5.2 Sources

Hafnium occurs in nature in small to moderate amounts associated with zirconium in all types of zirconium-bearing minerals. The ratio of hafnium to zirconium in the Earth's crust has been estimated at about 0.02. The principal commercial sources of hafnium are the minerals zircon [$Zr(Hf)SiO_4$] and baddeleyite (ZrO_2), which are processed primarily for their zirconium content. These minerals contain 0.5–2.0% Hf.

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5.3 Extraction of Hafnium

5.3.1 Separation of Zirconium and Hafnium

Hafnium and zirconium are always extracted together and since the separation of hafnium from zirconium is an important step in the production of reactor grade zirconium. The flow sheet for the extraction of Zr and Hf metals is shown in Fig. 4.1. TBP-nitric acid process (as described in Sect. 4.3.1 in extraction of Zr). The raw material for production of metal is hafnium oxide obtained as a by-product in the production of hafnium free zirconium.

5.3.2 Preparation of HfO_2

Hafnium nitrate in aqueous phase is achieved from solvent extraction process, then $Hf(OH)_4$ is precipitated by NH_4OH.

$$Hf(NO_3)_4 + 4NH_4OH = Hf(OH)_4 + 4NH_4NO_3 \tag{5.1}$$

This $Hf(OH)_4$ is calcinated at 800 °C, to form HfO_2.

$$Hf(OH)_4 = HfO_2 + 2H_2O \tag{5.2}$$

5.3.3 Production of Hafnium Metal

Hafnium metal is prepared by the same methods which are used into the production of zirconium: (a) Kroll process; (b) Modified Kroll process (using Na as the reducing agent); (c) reduction of HfO_2 by Si/Al/Ca.

5.3.3.1 Kroll Process

Chlorination of HfO_2 is done by chlorine gas in presence of carbon at 750–900 °C.

$$HfO_2 + 2C + 2Cl_2 = HfCl_4 + 2CO \tag{5.3}$$

Sublimation point of $HfCl_4$ is 316 °C, so resublimed at 325 °C of $HfCl_4$ in an inert atmosphere for purification.

$HfCl_4$ and Mg (40% excess) are taken in Kroll reduction furnace at the temperature of 825 °C for reduction.

$$HfCl_4 + 2Mg = Hf + 2MgCl_2 \tag{5.4}$$

The produced hafnium metal is covered by the excess magnesium and molten $MgCl_2$. Then by pyro-vacuum treatment at 900 °C and 10^{-4} torr pressure separate $MgCl_2$ and excess Mg to get hafnium metal sponge (which contain 1000 ppm of O). The sponge metal is pressed into bars and cast into ingots, using the consumable electrode arc technique.

De-Boer or hot wire process or iodide refining: This process developed by Van Arkel and De Boer. The product of the hot wire process is a rod, or crystal bar of compact, ductile hafnium. The crude metal is maintained at 600 °C and the filament at 1600 °C. The iodine process must be considered a refining method rather than a basic reduction step.

5.3.3.2 Reduction of $HfCl_4$ by Na

The use of Na to replace Mg for the large-scale reduction of the tetrachlorides of Zr and Hf are developed. The main advantage of Na reduction method is its lower cost.

$$HfCl_4 + 4Na = Hf + 4NaCl \tag{5.5}$$

The reduction step is followed by leaching of the product with water to remove salt and excess Na from the hafnium metal sponge.

5.3.3.3 Reduction of HfO_2 by Si/Al

(a) Attempts have been made at the metallothermic reduction of the oxides of hafnium in a vacuum, using Si, $CaSi_2$ and Al as reducing agents. During the reduction in a high vacuum (use of an electron beam furnace) mainly gaseous suboxides like SiO and Al_2O are formed. Besides these the volatile suboxide of Hf(HfO) is also formed.

The reduction of hafnium oxide by Si proceeds at temperatures between 2200 and 3200 °C according to:

$$HfO_2(s) + 2Si(l) = Hf(l) + 2SiO(g) \tag{5.6}$$

A slight deficiency in silicon should be maintained in the starting mixture in order to avoid residual silicon content in the final product which is difficult to remove. Excess oxygen is mainly removed as gaseous HfO. The composition of the evaporated oxide changes with increasing reaction time, and also the losses in metal owing to evaporation increase.

The metal obtained is workable only within limits. Reduction by $CaSi_2$, which appears to be more favourable, results in a more thorough deoxidation, but the nitrogen content of the $CaSi_2$ (0.04%) is entirely transferred into the hafnium, which will contain 0.15% N.

$$3HfO_2(s) + 2CaSi_2(l) = 3Hf(l) + 2CaO(s) + 4SiO(g) \tag{5.7}$$

(b) **Ca Reduction of HfO_2 or BARC process**: This process was developed at the Metallurgy Division, Bhabha Atomic Research Centre (BARC), Trombay, India. HfO_2 is reduced by Ca at 960 °C:

$$HfO_2 + 2Ca = Hf + 2CaO \tag{5.8}$$

The excess Ca is removed by (N) HCl as $CaCl_2$ and by-product CaO is removed by water.

$$Ca + 2HCl = CaCl_2 + H_2 \tag{5.9}$$

$$CaO + H_2O = Ca(OH)_2 \tag{5.10}$$

After removal of excess Ca and CaO, Hf metal powder is washed by acetone and dried in vacuum. This dried hafnium powder (which contain 6900 ppm O and 250 ppm N) is compacting and vacuum sintering at 1100 °C, and 0.05 torr pressure. Now sintered hafnium metal is refined by fused salt electro-refining process; after that impurities contain 10% Zr, 126 ppm O and 10 ppm N. Hence, hafnium metal is again remelted by electro beam melting for refining to get hafnium ingot.

5.4 Properties

Metallic hafnium has a bright lustre. It is harder and less easily workable than zirconium. Like zirconium, it crystallizes in the close packed hexagonal system, and in many other physical properties is similar to zirconium. Properties of hafnium are very much dependent on the impurity content in hafnium. The atomic weight of hafnium is 178.5. The specific gravity of arc melted crystal hafnium bar (which contain less than 100 ppm Zr) is 13.29. Melting point of that hafnium bar is 2150 °C, and melting point of crystal bar hafnium (which contains 80 ppm Zr) is 2222 ± 30 °C. Boiling point of hafnium is 4600 °C. It can be hot and cold worked in much the same manner as zirconium.

Allotropic transition temperature from α (hexagonal close packed) to β (body centred cubic) is vary from as low as 1310 ± 10 °C to as high as 1950 ± 10 °C (which is close to the melting point of hafnium).

Chemical properties of hafnium are much closed to zirconium. Unlike zirconium, however, it is less sensitive to pick-up of nitrogen and oxygen. Hafnium is oxidized under 1 atm of O_2 pressure in the range of 350 to 1200 °C. The resistance of hafnium to air oxidation at elevated temperature is fairly good and somewhat greater than that of zirconium. Hafnium has good resistance to high temperature, high pressure water up to 399 °C and 2.46 kg/mm^2.

5.5 Applications

Hafnium has few commercial uses because of its limited supply and high price, which have been due to the difficulty in separating hafnium from zirconium. Hafnium's main use has been for making rods in controlling the energy level in nuclear reactors and as structural material in water-cooled nuclear reactors where its corrosive resistance has proved superior to that of zirconium. In addition to having an adequate absorption cross-section for thermal neutrons, hafnium has excellent mechanical properties and is extremely corrosion resistance.

Hafnium has been used as a filament in incandescent lights, as a cathode in X-ray tubes, and as an electrode (alloyed with W or Mo) in high pressure discharge tubes. Powder hafnium has been used with Ba or Sr oxide in cathodes for high vacuum discharge tubes.

Hf–Ti alloys which are free from O, N, C and Si may be used as gas filled devices such as lamps, radio-tubes, and television tubes. Hafnium has been used also in rectifiers. Alloys of hafnium with Mn, Cr, Fe, Co, Ni, Cu and Ag have been prepared. An alloy containing 0.5% Hf with about 80% Ni and 19.5% Cr is used for electrical resistance heating elements.

The hafnium oxide is a valuable insulation for very high temperature and also serves as a raw material for high temperature ceramics. The carbide in conjunction with tantalum carbide provides a compound which possesses the highest recorded melting point (4000 °C) for ceramics.