Chapter 4
Zirconium

4.1 Introduction

Owing to zirconium's affinity for oxygen and nitrogen, which cause embrittlement, the isolation of the pure metal long eluded a satisfactory conclusion. German chemist Klaproth identified a new metal oxide in the mineral zircon in 1789. This compound was given the name zirconia and was recognized to contain a new element. In 1824 Berzelius produced first impure metallic zirconium (Zr) by the reduction of K_2ZrF_6 with potassium metal. But it was not until some 80 years later that a malleable zirconium metal was produced.

A notable feature of zirconium is its resistance to acids and alkalis. Zirconium metal is difficult to handle in the molten condition, since it either reduces or dissolves and becomes contaminated with most refractories; that metal becomes too brittle for any use.

Zirconium (Zr) based alloys find application in nuclear power reactors as the cladding material because of their high mechanical strength, corrosion-resistant properties and low capture cross-section for thermal neutron (0.18 barn). Hafnium (Hf), which co-occurs along with zirconium in the ore, and has a high absorption cross-section for thermal neutrons (105 barns). Nuclear grade zirconium contains less than 100 ppm of hafnium.

4.2 Sources

The chief source of zirconium minerals is the beach sands of Queensland in Australia, where the silicate mineral zircon occurs associated with rutile. Zircon is also present in the monazite sands of India. The occurrence of zirconium in the Earth's crust is greater than the total percentage of copper, lead and zinc.

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The major source of zirconium is zircon sand [$Zr(Hf)SiO_4$], which is found in Australia, USA and India, with the sea-beach sand. Baddeleyite ore (ZrO_2) is found in Brazil. This ore, when it contains some zircon, is often called zirkite.

Sea-beach sands are readily concentrated by gravity methods; the use of shaking tables, which are simpler and use less power. Final cleaning of the concentrate is accomplished with magnetic and electrostatic separators.

4.3 Exreaction of Zirconium

4.3.1 Separation of Zirconium and Hafnium

Zircon sand contains 0.5–2.0% Hf, and the hafnium has chemical properties so similar to zirconium that no separation is achieved in the usual chemical processes. Reactor grade zirconium is limited to a maximum of 0.01% Hf, because the later metal has such a high thermal neutron absorption cross-section. Zirconium has a cross-section of 0.18 barns, whereas hafnium has a cross-section of 115 barns which is more than 500 times that of zirconium. For this reason hafnium is used as control rods in reactors.

Many methods have been developed for the separation of zirconium and hafnium (flow sheet for the extraction of Zr and Hf metals is shown in Fig. 4.1), such as fractional distillation, ion exchange, fractional crystallization, liquid-liquid extraction etc. The last named procedure is the most widely used. In one process, crude zirconyl chloride is brought into contact with a counter-current stream of thiocyanate-rich methyl isobutyl ketone.

(a) Solvent Extraction: The solvent extracts of hafnium and the zirconyl chloride are mixed with H_2SO_4 and NH_4OH to produce zirconium hydroxide, which is subsequently heated to produce pure zirconium oxide (ZrO_2). Other solvents and procedures of precipitation are used. Increased interest has been shown in a process wherein $ZrCl_4$ is selectively reduced to $ZrCl_3$; the $HfCl_4$ is then sublimed and a separation is achieved.

(b) TBP- Nitric Acid process: Zircon sand is fused with NaOH at 600 °C to form zirconium-hafnium hydroxide which is leached with water to remove the solute sodium silicate.

$$Zr(Hf)SiO_4 + 4NaOH = Zr(Hf)(OH)_4 + Na_4SiO_4 \tag{4.1}$$

The cake is dissolved in nitric acid (50–60%) and form zirconium-hafnium nitrate solution.

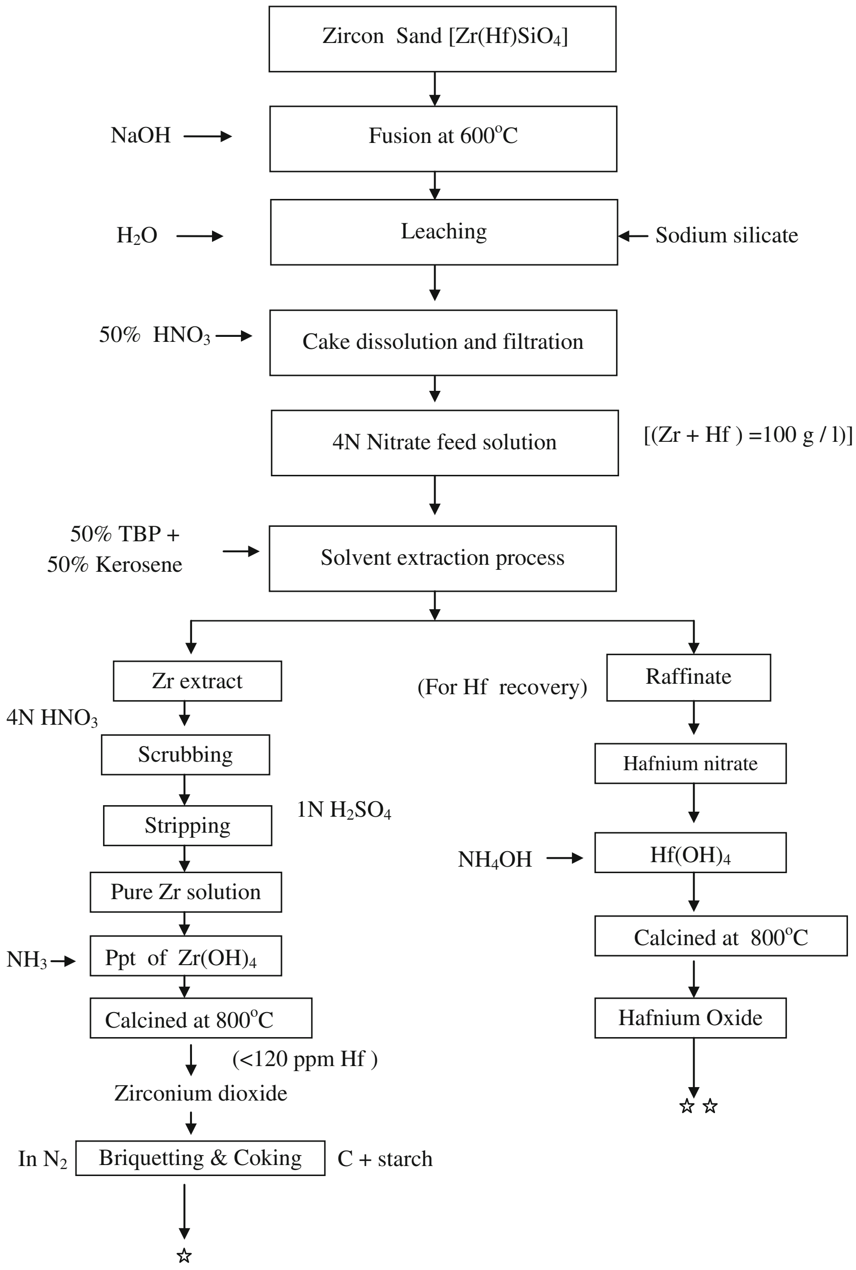

Fig. 4.1 Flow sheet for the extraction of zirconium and hafnium metals

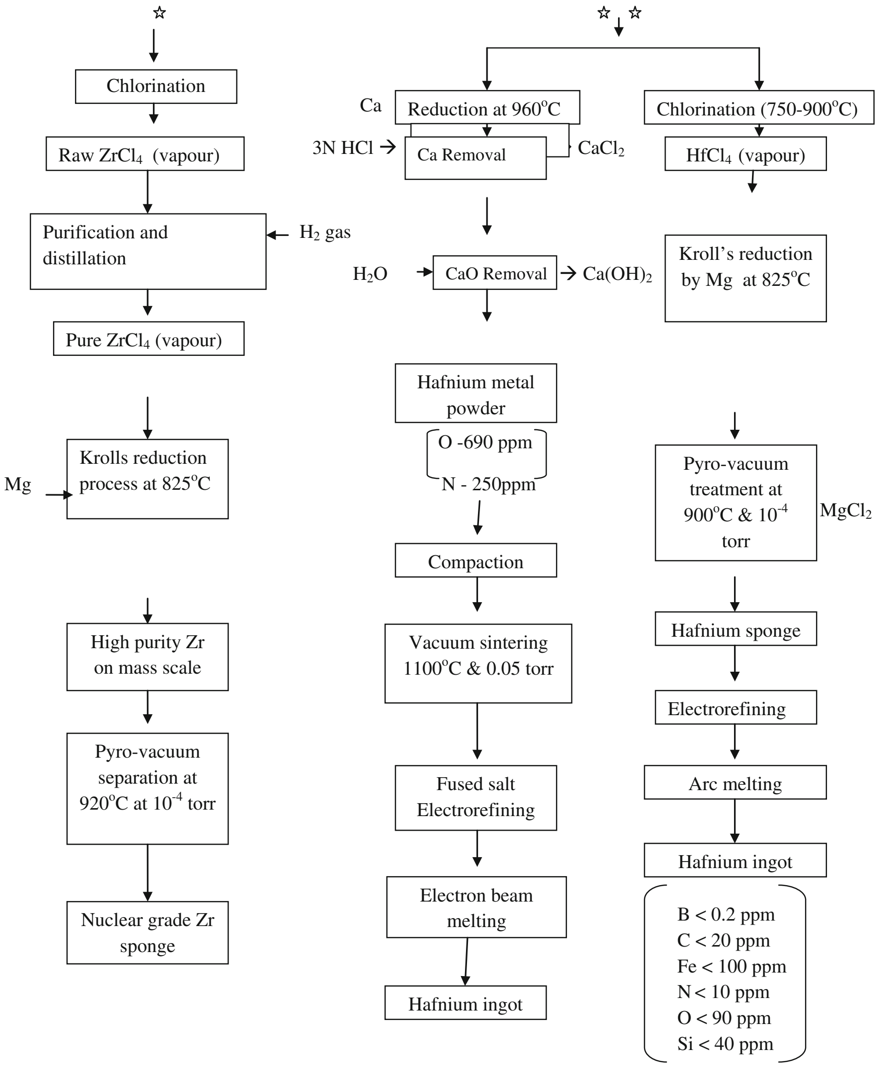

Fig. 4.1 (continued)

$$Zr(Hf)(OH)_4 + 4HNO_3 = Zr(Hf)(NO_3)_4 + 4H_2O \tag{4.2}$$

Now zirconium and hafnium are separated by solvent extraction method by using 50% TBP in kerosene. So zirconium is collected as an extract in organic phase and hafnium is separated as a raffinate in aqueous phase. The scrubbing of zirconium by concentrate (4 N) HNO_3 and stripping with dilute (1 N) H_2SO_4 brings zirconium back into the aqueous phase (pure zirconium solution).

4.3.2 Preparation of Zirconium Oxide

After getting the pure zirconium solution (nitrate), zirconium hydroxide is then precipitated by ammonia.

$$Zr(NO_3)_4 + NH_3 \rightarrow Zr(OH)_4 + HNO_3 \tag{4.3}$$

This zirconium hydroxide is calcined at 800 °C, to form ZrO_2.

$$Zr(OH)_4 = ZrO_2 + 2H_2O \tag{4.4}$$

4.3.3 Production of Zirconium Tetrachloride

Direct metallothermic reduction of zirconium oxide is not attractive for the production of ductile zirconium, since it is difficult to eliminate residual oxygen from the resultant powder zirconium. So the conversion of zirconium oxide to the metal on a commercial scale thus involves chlorination of zirconium oxide to obtain zirconium tetrachloride. Chlorination of zirconium oxide is carried out by reacting with chlorine and carbon mixture in a static chlorinator reactor.

Firstly, zirconium dioxide and carbon mixture (with starch as a binder) is briquetted in nitrogen atmosphere to form porous briquettes and heated in a silica lined furnace. This zirconium dioxide and carbon briquette possesses sufficient electrical conductivity, which improves with temperature, and with appropriate voltage and current control; the briquettes are slowly heated to the reaction temperature of 750 to 900 °C.

$$ZrO_2 + 2C + 2Cl_2 = ZrCl_4 + 2CO \tag{4.5}$$

$ZrCl_4$ vapour evolving from the chlorination is condensed as dense crystals in a double walled inconel condenser at 150–200 °C. The raw chloride is then purified by sublimation at 350 °C (boiling point of $ZrCl_4$ is 334 °C) in hydrogen atmosphere.

4.3.4 Reduction of $ZrCl_4$ by Mg or Na

Since zirconium is highly corrosive in the molten form and extremely so in the powder form, it is essential to produce it in the partially sintered condition as obtained in the Kroll process.

4.3.4.1 Kroll Process (by Mg)

The reduction of $ZrCl_4$ with Mg produces a high purity zirconium metal. This method was developed by scientist W.J. Kroll and his co-workers at the United States Bureau of Mines, hence this method is known as Kroll process. The Kroll process comprises a specially designed three-zone furnace with provision to maintain temperature in each zone. The unique feature of the Kroll process is the heating of the zirconium chloride so that only the vapours come in contact with the magnesium which is the reducing agent.

Zirconium chloride ($ZrCl_4$ sublimate at 334 °C) and magnesium are loaded in separate containers in the retort. The chloride is purified by eliminating volatile impurities at 300 °C and temperature of Mg is raised to 850 °C. The chloride is distilled under control to react at the surface of molten Mg (melting point 651 °C). For optimum reduction rates the process has to be controlled in the temperature range 800–875 °C.

$$ZrCl_4 + 2Mg = Zr + 2MgCl_2 \tag{4.6}$$

At the end of the reduction the crucible contains a sponge like network of zirconium crystals covered with $MgCl_2$ and unreacted Mg. Mg and $MgCl_2$ are then removed by pyro-vacuum separation at 920 °C and 10^{-4} torr pressure in a separate distillation retort to get nuclear grade zirconium sponge which contain impurities (B < 0.5, C − 400, N − 85, O − 865, Hf − 120 ppm).

4.3.4.2 Modified Kroll Process (by Na)

Reduction by sodium has certain advantages in that its low melting point (97.5 °C) makes it possible to handle it in liquid form; this facilitates purification, handling, and feeding to the reactor. The reaction products zirconium and NaCl can be leached with water or weak acids.

$$ZrCl_4 + 4Na = Zr + 4NaCl \tag{4.7}$$

The use of sodium has certain disadvantages: (a) nearly twice as much mono-valent sodium is used per kg of zirconium as compared to di-valent magnesium; (b) there is a greater quantity of by-product NaCl is to be disposed of; and (c) low boiling point of sodium (883 °C) and high melting point of NaCl (801 °C) also created some problems.

4.3.4.3 Bimetal Reduction

The use of a small percentage of sodium along with magnesium has been found to form a purer product. This is attributable to the guttering ability of sodium, reduced iron contamination (iron coming from the crucible of the reactor), better flexing ability of NaCl with impurity chlorides (such as $FeCl_3$, $AlCl_3$) and better removal of $MgCl_2 - NaCl$ slag (which is more fluid than $MgCl_2$ alone).

4.4 Properties

Zirconium is found to be steel-grey in colour, not quite so heavy as iron, with tensile properties similar to mild steel. Zirconium has an atomic weight of 91.22. The specific gravity of zirconium is 6.45, its melting point and boiling point are 1852 ± 10 °C and 3580 – 3700 °C respectively. Zirconium has an allotropic transition HCP to BCC ($\alpha \rightarrow \beta$) at 862 ± 5 °C. Transition from $\alpha \rightarrow \beta$ will be increased with present of O, N, Sn and Al; and decreased with Ta, Cb, Th and U. Zirconium, if sufficiently pure, is soft and ductile. Hardness of zirconium is increased with increasing oxygen.

Zirconium reacts readily with oxygen, the rate of reaction varying with particle size, temperature presence of impurities, and the nature of the surface. It was found that large amounts of oxygen, up to 60 atomic%, can be dissolved in solid solution in zirconium without showing any ZrO_2 structure. The equilibrium vapour pressure of saturated solutions of oxygen in zirconium is so low that there is no possibility of removing oxygen from zirconium by vacuum treatment. Of the oxygen content in zirconium, 50–90% can be removed by heating in molten Ca or in Ca vapour.

The reaction of nitrogen gas and zirconium occurs very slowly at 400 °C, but increases rapidly at 800 °C and above; the reaction is insensitive to pressure. Amount up to 20 atomic% form solid solution; above this ZrN is formed. Nitrogen gas cannot be removed by vacuum treatment or with calcium.

Hydrogen gas is absorbed rapidly by zirconium at temperatures from 300 to 1000 °C. In contrast to oxygen and nitrogen gases, hydrogen gas can be completely removed by prolonged heating in a vacuum above 1000 °C. The absorption of hydrogen gas embrittles zirconium to the extent that it can be crushed, thus providing one method for producing zirconium powder.

Zirconium reacts rapidly with CO_2 gas above 800 °C; zirconium also reacts with CO gas and H_2O vapour above 1000 °C. Zirconium oxide (ZrO_2) is formed by all these gases, and at high temperature CO and CO_2 gases also lead to zirconium carbide formation. Zirconium reacts readily with all of the halogens in the range of 200–400 °C to form volatile halides. Zirconium also reacts with S, C, Si, P, B and Al at elevated temperatures.

A notable feature of zirconium is its resistance to acids, hot nitric and sulphuric acids having little effect; it is insoluble in hydrochloric acid in concentrations up to 20%. Resistance to alkalis is also a prominent characteristic.

Reactor grade unalloyed zirconium is sufficiently pure to withstand the corrosive attack of water indefinitely at temperature up to 260 °C. Above this temperature, the behaviour becomes erratic. For this reason, the zircaloy alloys were developed for use in pressurized water reactors. The principal alloy in use is zircaloy-2, which consists of 1.5 wt% Sn, 0.12 wt% Fe, 0.1 wt% Cr and 0.05 wt% Ni in Zr. The presence of Fe, Cr and Ni retard accelerated corrosion and film failure. The corrosion behaviour of Zr-alloys in high temperature water and steam is very sensitive to the cleanliness of the metal surface. Although the material is readily machinable, it is easily overheated, and the surface layer becomes contaminated by nitrogen.

Complete solid solubility is found in the Zr-Hf and Zr-Ti systems. An eutectic and an eutectoid are obtained with H, W, V, Ag, Be, Co, Cr, Cu, Fe, Mn, Mo and Ni. The tensile strength of Zr is as low as 17.575 kg/mm^2. Addition of Mo, Sn and Nb to Zr improves tensile strength (140.6 kg/mm^2) and results in a fair amount of ductility (6–10%). Unalloyed uranium was extrusion clad with two of these alloys Zr-5 wt% Mo-2 wt% Sn, and Zr-5 wt% Nb-2 wt% Sn. Al may replace Sn in the later alloy, and strength may be maintained.

Zirconium is inert to pure liquid sodium, and its reaction with liquid metal coolant is confined to guttering the oxygen impurity from sodium. An adherent oxide is formed on the zirconium, and oxygen diffuses into the metal. The rates for both oxidation and diffusion of oxygen in zirconium are strongly temperature-dependent.

Zirconium ingot can be heated to 850 °C in ordinary furnace atmosphere and rolled or forged. Seamless tubing is made by extruding billets coated with glass or encased in copper. Salt bath heating permits extrusion temperature up to 1000 °C. Zirconium must be welded in an inert atmosphere to prevent harmful contamination by atmospheric gases.

4.5 Applications

The chief consumption of zirconium metal has been for nuclear energy applications. These result from its excellent corrosion resistance combined with a low absorption cross-section for neutrons. The cross-section for zirconium is 0.18 barn (1 barn = 10^{-24} sq cm/nucleus) as compared with 0.22 barn for aluminium, and 3 barns for stainless steel, and 120 barns for hafnium. Zirconium can be used in the core of a nuclear reactor as a cladding material for the fuel elements, as an alloying metal with uranium.

The general commercial application of zirconium depends mainly on its corrosion resistance. It combines outstanding resistance to both mineral and organic acids as well as to strong alkaline solutions. Pumps, valves, heat exchangers, filters, piping, and other components are produced by commercial grade zirconium. These components are used in chemical industry. Other uses, such as in vacuum tubes, in photoflash bulbs, and for surgical use, make it a popular metal.

High strength zirconium alloys are developed for two reasons:

1. In natural uranium fueled heavy water moderated reactors, neutron economy is of prime consideration. If a reduction of cladding thickness could be achieved by using a high strength zirconium alloy to replace zircaloy-2, which is only a

little stronger than zirconium, then a decrease in parasitic neutron capture by the cladding would be achieved.

2. High strength claddings may be used to constrain the swelling associated with irradiation of uranium alloy fuels and thereby increase the allowable fuel burn-up.

For chemical industry use, zirconium combines extreme resistance to corrosion in both alkaline and acids exposures. Its low corrosion rates in acids, dry chlorine (below 200 °C), alkalis, sea water, halide salts, and sodium hypochlorite are outstanding. These factors, combined with its fine mechanical properties, make its use attractive in chemical equipment.