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1. Zirconium

1.1. Introduction

On analyzing the gem mineral known as jargon from Sri Lanka, in 1789 KLAPROTH found it contained an oxide which he could not identify and which he later called zirconerde". In 1824 BERZELIUS prepared the first zirconium metal, an impure black powder, by heating potassium hexafluorozirconate and potassium in a closed pot. LELY and HAMBURGER prepared the first relatively pure zirconium in 1904 by reduction of zirconium tetrachloride with sodium in a bomb, producing malleable, corrosion-resistant zirconium pellets. But it was a hundred years after BERZELIUS before VAN ARKEL, DE BOER, and FAST [1, 2] developed the iodide process which produced the first massive zirconium metal that could be

cold worked and which exhibited good ductility at room temperature.

Early uses for zirconium metal were in pyrophoric devices, such as fuses, ammunition primers, fireworks, photoflash powder, and flares. Zirconium powder was used extensively as a gettering material in vacuum tubes. By 1946 the consumption of zirconium for these purposes was about 5 t/a. Less than 50 kg of ductile iodide metal was sold, at ca. \$ 700 per kilogram.

W. J. KROLL carried out the first inert-atmosphere magnesium reduction of zirconium tetrachloride in his Luxembourg laboratory in 1938 [3]. In 1944 the U.S. Bureau of Mines started a project to make ductile zirconium economically. KROLL was assigned to take over direction of the project in January, 1945. By 1947, a pilot plant was producing 30 kg of zirconium sponge per week. Concurrently, researchers at Massachusetts

Institute of Technology and at Oak Ridge National Laboratory were evaluating the physical and atomic properties of metals as potential uranium fuel cladding materials for nuclear power stations. In 1948 hafnium-free zirconium was selected as most promising. By 1949 zirconium had been chosen as the structural material for the fuel core of the submarine thermal reactor, the land-based reactor prototype, and during 1949–1950 a satisfactory hafnium separation process was developed at Oak Ridge. By the end of 1950, 3000 kg of hafnium-free zirconium metal strip had been produced, and the zirconium metal producing industry was launched as an integral part of the beginning nuclear power industry.

1.2. Properties

Physical Properties. Zirconium [7440-67-7] is a lustrous, strong, ductile metal similar in appearance to stainless steel. Pure zirconium metal has three solid phases: ω -Zr, which is stable below 200 K at ambient pressure and up to 1000 K at 6 GPa [4]; α -Zr, which is stable from 200 K to 1125 K; and β -Zr, which is the stable form between 1125 K and the melting point. These transition temperatures change with the addition of α - or β -stabilizing alloying elements. The important physical properties are presented in the following:

Relative atomic mass	91.224
Atomic radius	15.90 nm (in metal lattice)
Ionic radius (Zr^{4+})	7.5 nm
Electronegativity	1.22
Standard potential M/MO_2	1.53 V
Melting point	$1852 \pm 2^\circ C$
Boiling point	$3850^\circ C$
Crystal structure	
ω -Zr	hexagonal open
α -Zr	hexagonal dense, a = 32.3 nm c = 51.5 nm
β -Zr	body-centered cubic, a = 36.1 nm
Transformation temperatures	
$\omega \rightarrow \alpha$	$-73^\circ C$
$\alpha \rightarrow \beta$	$862 \pm 5^\circ C$
Heat of fusion	2.30×10^4 J/mol
Heat of evaporation	5.96×10^5 J/mol
Electrical resistivity	$3.89 \times 10^{-5} \Omega \cdot cm$
Thermal conductivity	
at $25^\circ C$	$21.1 W m^{-1} K^{-1}$
at $100^\circ C$	$20.4 W m^{-1} K^{-1}$
at $300^\circ C$	$18.7 W m^{-1} K^{-1}$

Specific heat	
at $25^\circ C$	$0.285 J g^{-1} kg^{-1}$
at $865^\circ C$	$0.335 J g^{-1} kg^{-1}$
Thermal expansion coefficient	
α , bulk, at $25^\circ C$	$5.89 \times 10^{-6} K^{-1}$
α -Zr, parallel to the C axis	$6.4 \times 10^{-6} K^{-1}$
α -Zr perpendicular to C axis	$5.6 \times 10^{-6} K^{-1}$
β -Zr	$9.7 \times 10^{-6} K^{-1}$
Density	
α -Zr	6.50 g/cm
β -Zr	6.05 g/cm
Effective cross section for thermal neutrons	$1.9 \times 10^{-29} m^2$ (0.19 barns)

Mechanical Properties. Although zirconium is a high-melting metal, its mechanical properties are similar to those of much lower melting metals: its elastic modulus is quite low, and its strength diminishes rapidly with increasing temperature. The mechanical properties of zirconium are strongly dependent on purity, especially the oxygen and nitrogen content, the amount of cold work, and the crystallographic texture. Forged or rolled zirconium shows marked anisotropy in mechanical properties in both the as-formed and annealed conditions. Pure zirconium is ductile at liquid-nitrogen temperatures but the metal is subject to hydrogen embrittlement whenever the hydrogen content sufficiently exceeds the hydrogen solubility at the operating temperature. Tables 1 and 2 gives typical values of the more important mechanical properties of zirconium and of Zircaloy 2 and Zircaloy 4 (see also Section 1.9).

Chemical Properties. Zirconium is a very reactive metal that, in air or aqueous solution, immediately develops a surface oxide film. This stable, adherent film is the basis for zirconium's corrosion resistance. In most media, zirconium is more resistant than titanium or stainless steel. Its acid resistance approaches that of tantalum, but unlike tantalum, zirconium is also resistant to caustic media.

Table 1. Mechanical properties of zirconium

Property	20 °C	200 °C	300 °C
Tensile strength, MPa	300–450	220–250	150–180
Elastic limit (0.2%), MPa	200–300	110–130	75–85
Elongation, %	25–35	50–60	45–55
Modulus of elasticity, MPa	9.5×10^4	8.3×10^4	7.2×10^4
Brinell hardness	90–130		
Shear modulus	36 500		
Poisson's ratio	0.35		

Table 2. Mechanical properties of Zircaloy 2 and Zircaloy 4

Property	Annealed			Recrystallized		
	20 °C	200 °C	400 °C	20 °C	200 °C	400 °C
Tensile strength, MPa	785	440	380	520	290	190
0.2% yield strength, MPa	600	360	300	370	150	130
Ultimate elongation (50 mm),%	17	20	20	34	45	55

Fluoride ions bond strongly to zirconium, and even a trace of fluoride in most media will drastically reduce its corrosion resistance.

The corrosion resistance in sulfuric acid is excellent at temperatures up to 150 °C and acid concentrations up to 70%, except that welds and adjacent heat-affected zones are susceptible to corrosive attack above 60% concentration. This can be alleviated by annealing. Ferric, cupric, and nitrate ion impurities in sulfuric acid decrease the corrosion resistance at acid concentrations above 65%. Even at room temperature zirconium is rapidly attacked at concentrations above 75%.

The corrosion resistance in hydrochloric acid is excellent at temperatures up to 130 °C and concentrations up to 37%. However, even small amounts of ferric or cupric ions will lead to severe pitting and stress cracking.

The corrosion resistance in nitric acid is excellent at all concentrations up to 90% and temperatures up to 200 °C. In concentrations above 65%, stress corrosion cracking may occur if high tensile stresses are present [5].

The corrosion resistance in phosphoric acid is excellent in all concentrations up to 65 °C and, at concentrations below 40%, up to 185 °C.

Zirconium is rapidly attacked by hydrofluoric acid, even at concentrations below 0.1%.

The corrosion resistance in sodium hydroxide and potassium hydroxide is excellent at all concentrations, up to the boiling temperature. Zirconium is resistant to molten sodium hydroxide up to 1000 °C.

Zirconium is very resistant to most organic compounds at all concentrations and temperatures. But, when air or moisture are not available to reform the surface oxide film, zirconium is attacked by anhydrous chlorinated organics at elevated temperatures and is etched by bromine or iodine dissolved in anhydrous organics. Stress corrosion cracking may also occur.

Zirconium reacts with most gases at relatively low temperatures.

Zirconium forms a visible interference color film in air starting above 200 °C. Above 400 °C the adherent oxide film is black. Above 540 °C a loose gray-white oxide forms; the oxide layer becomes thicker as oxygen diffuses into the underlying metal, and the metal can become embrittled after prolonged exposure. The maximum continuous operating temperature of zirconium in air is ca. 450 °C. Short-term hot working, such as forging, rolling, and extrusion are conducted at 550–1000 °C. Afterwards, the surface oxide and embrittled metal layer are mechanically and chemically removed. While solid zirconium metal is slowly oxidized in air, the oxidation is exothermic, and for high-surface-area forms, such as powder or sponge metal, the large heat release may cause ignition (see Section 1.8).

Oxygen-containing gases, such as carbon dioxide, carbon monoxide, sulfur dioxide, steam, and nitrogen oxides, oxidize zirconium somewhat slower than air. The maximum continuous operating temperature is about 400 °C.

Zirconium reacts more slowly with nitrogen than with oxygen because the reaction is less exothermic.

Zirconium readily absorbs hydrogen above 300 °C. The rate of absorption varies inversely with the thickness of the surface oxide film. Hydrogen solubility increases with temperature. On cooling, when the solubility is exceeded, zirconium hydride platelets precipitate, embrittling the metal. The reaction is reversible: hydrogen is removed on heating the metal above 600 °C in a high vacuum.

Zirconium's oxide film protects it from dry chlorine gas at room temperature, but any impact or abrasion that exposes a fresh metal surface may initiate an exothermic reaction producing zirconium tetrachloride vapor.

More information on the chemical behavior of zirconium metal can be found in [6].

1.3. Occurrence, Ores, and Mining

Zirconium is the ninth most abundant metal in the earth's crust, with an estimated concentration of 0.016–0.025 wt% [7], about one twentieth that of titanium but more plentiful than nickel, copper, or zinc. Zirconium occurs only in fully oxidized form, never as free metal.

There are over 40 known zirconium minerals which can be grouped:

1. Zirconium orthosilicates Zircon and its metamict varieties
2. Zirconium dioxide: baddeleyite and its altered varieties
3. Zirconsilicates with sodium, calcium, iron, and other elements: eudialyte, eucolite, gittinsite and others
4. Zirconium carbonates with sodium, calcium, and other elements: weloganite and others
5. Others, including zirconolite ($\text{CaZrTi}_2\text{O}_7$)

Zircon is the predominant commercial zirconium mineral, but the minerals baddeleyite and eudialyte are also being used. All are obtained as byproducts of other mineral recovery operations.

Zircon [1490-68-2], ZrSiO_4 , occurs as an accessory mineral in silica-rich igneous rocks, particularly granite, nepheline syenite, and pegmatite, and also in metamorphic and sedimentary rocks. Zircon is rarely found in rocks in economically minable concentration. Weathering and erosion of these rocks frees the zircon grains, and the combined action of rivers, seas, and wind concentrate the heavier minerals by natural gravitation processes in placer deposits, deltas, and ocean beaches. As an ore, zircon is recovered from unconsolidated sands in beach deposits.

Large heavy mineral sands deposits are being extensively mined in Florida, West Australia, South Africa, India, Russia, and Kazakhstan, with smaller operations in Sierra Leone, Sri Lanka, Madagascar, Malaysia, Brazil, Indonesia, Thailand, Ukraine, and Vietnam. In Canada, some zircon is obtained from the processing of Athabasca tar sands. Undeveloped heavy mineral beach sand reserves containing zircon exist in New Jersey, the Carolinas, Georgia, Tennessee, Colorado, New Mexico, Oregon, Utah, Wyoming, Egypt, Malawi, Senegal, and Tanzania.

These heavy mineral sands deposits are mined to obtain the titanium minerals rutile, leucoxene, and ilmenite to supply the titanium metal and titanium oxide pigment industries. Depending on the deposit's composition and current market pricing, zircon and other minerals are viable byproducts. Australia and South Africa are major zircon exporters.

Mining of heavy mineral sands involves first removing a light sand overburden, followed by removal of the heavy sands layers using elevating scrapers and bulldozers, or by flooding the excavation and using dredges in the pond. The heavy minerals are concentrated by gravity separation, and the quartz, light minerals, fines, clay, and silt are returned to the back end of the excavation. Since the heavy mineral sands are only 4–7% of the deposit, the site can be rehabilitated close to the original elevation, topsoil replaced, and native vegetation replanted. The concentrate is hauled to an ore-dressing site where the grains may be scrubbed to remove surface coatings, dried, and separated into individual mineral components: rutile, leucoxene, ilmenite, zircon, xenotime, monazite, staurolite, garnet, kyanite, and sillimanite. These separation steps utilize differences in the specific gravity, induced magnetism, and electrical conductivity of the individual minerals grains to gradually recover each mineral in good purity.

The various mining operations produce a range of zircon products from high grades with very low levels of impurities to lower grades where the impurities vary with the nature of the orebody and the type of separation process used. These various grades supply a range of applications: foundry sands, refractories, abrasives, opacifiers, zirconium chemicals, zirconium metal, and welding rod coatings. A typical analysis of zircon for the metal industry is 66.6% (Zr + Hf) O_2 , 0.2% Al_2O_3 , 0.15% TiO_2 , 0.1% Fe_2O_3 , 0.1% P_2O_5 , 0.025% U, 0.020% Th.

Baddeleyite [12036-23-6], ZrO_2 , has been found in Brazil, South Africa, Sri Lanka, and Russia. Brazilian baddeleyite often occurs mixed with zircon. The mixture is known as caldasite and usually contains 65–80% zirconium oxide. South African baddeleyite is a byproduct of mining a volcanic orebody for copper and phosphate fertilizer. The baddeleyite concentrate

contains 96% zirconium oxide. Russian baddeleyite from the Kola Peninsula is a byproduct of open pit iron ore mining.

Eudialyte [12173-26-1], $(\text{Ca}, \text{Na}_2)_6(\text{Zr}, \text{Fe})(\text{Si}_3\text{O}_9)_2(\text{OH}, \text{Cl})_2$ has been found in Greenland, Norway, Brazil, Australia, Transvaal, and New Mexico. Some eudialytes contain 12–15% zirconium oxide, yttrium, and small amounts of niobium and rare earth metals.

Hafnium Content. All known zirconium minerals contain hafnium, usually in the range of 1.5–2.5% Hf/Zr + Hf, although higher hafnium contents have been found. There is a tendency for higher-hafnium ores to be also higher in uranium and thorium content. Hafnion, hafnium orthosilicate, with >95% Hf/Zr + Hf was found associated with a tantalum ore in Mozambique.

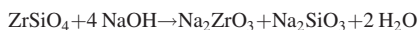
1.4. Production

Processing steps for the production of zirconium metal from zircon sand are shown in Figure 1.

1.4.1. Ore Cracking

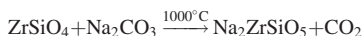
Zircon is a refractory mineral whose decomposition requires the use of high temperature and aggressive chemicals. Selection of a particular procedure depends on the subsequent product use or processing.

Caustic Fusion. Caustic fusion of zircon with a slight excess of sodium hydroxide at 650 °C (or sodium carbonate at 1000 °C) is the usual zircon decomposition process [8, 9]:



The cooled reaction mass is crushed and slurried in water. Water dissolves the sodium silicate and hydrolyzes the sodium zirconate to soluble sodium hydroxide and insoluble hydrous zirconia. The hydrous zirconia, recovered by filtration, can be fired to oxide, dissolved in mineral acid for further conversion to aqueous zirconium compounds, or dissolved in mineral acid for feeding to a hafnium extraction process.

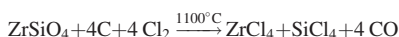
A variant of the caustic fusion process uses less caustic to produce an acid-soluble sodium zirconium silicate



The frit from this reaction is added to strong acid to yield a solution containing sodium and zirconium salts and silica gel:

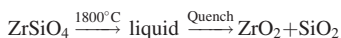


Chlorination. Fluidized-bed carbochlorination of milled zircon sand is the zircon decomposition process used by American and French zirconium metal producers. Chlorine is the fluidizing gas. The reaction is endothermic and supplemental energy is supplied, usually by induction heating of the interior graphite wall of the chlorinator.



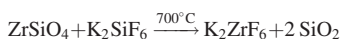
The product gases are cooled to 200 °C in a primary condenser that collects zirconium (and hafnium) tetrachloride as a powder. The remaining gas mixture is cooled to –20 °C in a secondary condenser, collecting silicon tetrachloride as a liquid which is subsequently purified and used to make fumed silica, fused quartz, and fused-quartz optical fiber.

Thermal Dissociation. Thermal dissociation of zircon in an arc plasma forms zirconium oxide in droplets of liquid silica. Rapid quenching, to minimize recombination, produces intimately mixed crystals of zirconium oxide in a bead of amorphous silicon oxide [10].



The mixture can be leached with sulfuric acid to yield a zirconium sulfate solution and insoluble silica, or leached with sodium hydroxide to yield a sodium silicate solution and insoluble zirconium oxide.

Fluorosilicate Fusion. The fusion of zircon and potassium hexafluorosilicate produces potassium hexafluorozirconate [11].



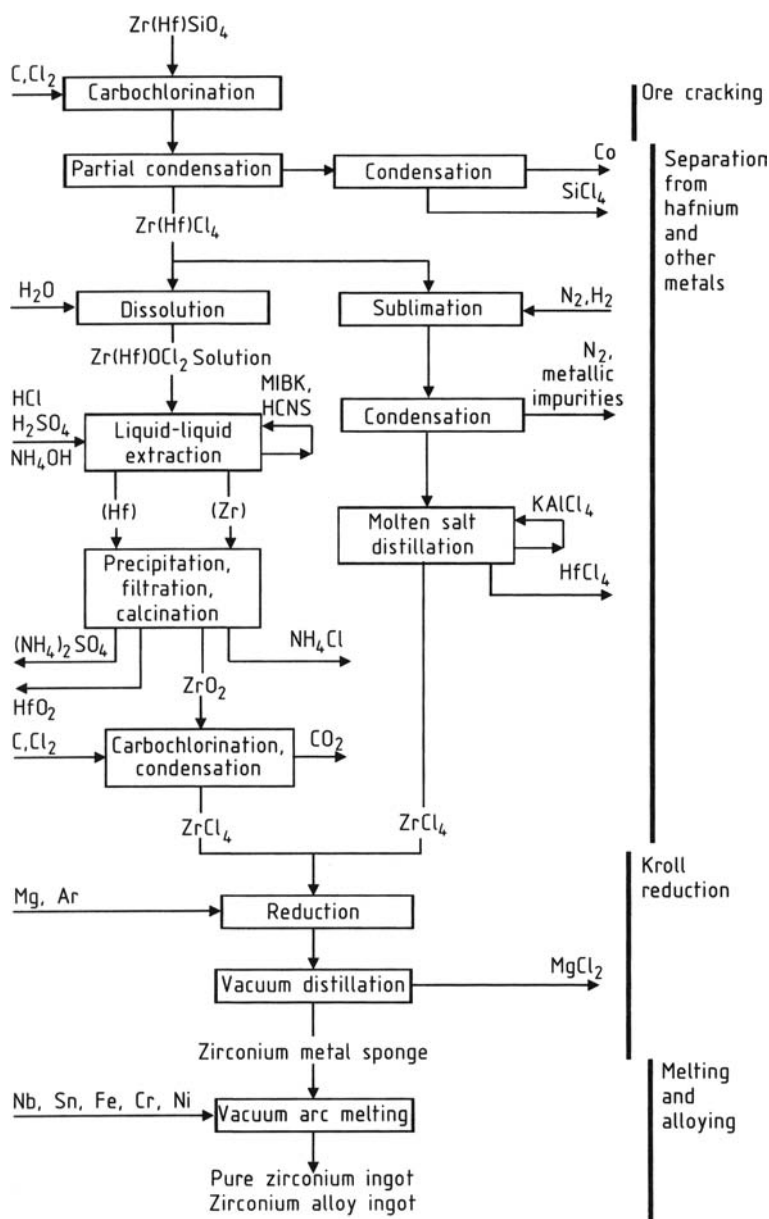


Figure 1. Flow diagram for production of zirconium

The fused mass is crushed, and then the fluoride salt is dissolved with acidified hot water. The hot solution is filtered to remove silica and cooled to crystallize potassium hexafluorozirconate.

Lime Fusion. Fusion of zircon with limestone or dolomite produces calcium zirconate

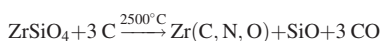
and calcium or magnesium silicate:



On cooling, the fused mass disintegrates into a very fine calcium silicate powder and coarse calcium zirconate crystals, which can be recovered

by mechanical means. The acid-soluble calcium zirconate can be converted into zirconium salts or zirconium oxide.

Carbiding. An intimate mix of zircon sand and coke is continually fed into an open-top electric arc furnace. Insufficient carbon is used for complete conversion to carbide, so that silicon monoxide is vaporized at the arc temperature [12]:



A crude zirconium carbonitride ingot grows under the electrode, surrounded by an unreacted mix, which acts as insulation for the steel furnace shell. When the furnace is full, it is moved to a cooling location. When cool, the ingot is separated from the unreacted charge, which is recycled. The product is a dense block, having a silver to golden-yellow fracture surface, depending on nitrogen content. The block is broken and crushed to ~75 mm chunks, which are subsequently chlorinated to zirconium tetrachloride. If the hot ingot is immediately removed from the furnace shell and unreacted charge, the ingot is oxidized to zirconium oxide containing ca. 5% silica.

High-Temperature Fusion. Direct electric arc smelting of baddeleyite or zircon is used to make fused zirconia or fused alumina–zirconia–silica (AZS). The silica is partially vaporized and recovered as fumed silica.

Baddeleyite is converted to zirconium sulfate by direct dissolution in concentrated sulfuric acid at ca. 200 °C. The recovery is low. Better recoveries are obtained by first heating the baddeleyite with lime to yield calcium zirconate, which reacts with sulfuric acid to give zirconium sulfate and gypsum.

1.4.2. Hafnium Separation

Zirconium and hafnium are chemically and metallurgically very similar, and for most uses of zirconium their separation is unnecessary. Their separation is conducted only to produce hafnium-free zirconium metal for the nuclear power industry. Of the many methods developed since the discovery of hafnium, four are used industrially: fluoride salt crystallization, methyl isobutyl

ketone extraction, tributyl phosphate extraction, and extractive distillation, in order of their development. In addition, ion exchange has been used for low-throughput, low-investment operations.

Fluoride Salt Crystallization. The first separation of zirconium and hafnium by repeated crystallization of potassium hexafluorozirconate from hot aqueous solution is credited to VON HEVESY [13]. The solution is acidified to minimize oxide–fluoride salt formation. At each step the salt crystals are depleted in hafnium. This multistep recrystallization procedure has been used for many years in the Ukraine [14].

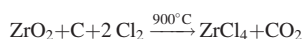
Methyl Isobutyl Ketone Extraction, developed at Oak Ridge National Laboratory and used by both American producers, is based on the preferred extraction of a hafnium dihydroxide thiocyanate complex from hydrochloric acid solution by methyl isobutyl ketone [15].

Zirconium–hafnium tetrachloride, produced by carbochlorination of zircon, is dissolved in water, with hydrolysis to form zirconium–hafnium dihydroxide chloride in a hydrochloric acid solution. This solution is contacted with methyl isobutyl ketone to extract iron as HFeCl_4 into the organic solvent. Then ammonium thiocyanate is added to the dihydroxide chloride solution, providing a mixed dihydroxide chloride/dihydroxide thiocyanate solution of zirconium and hafnium. This solution is countercurrently contacted with a methyl isobutyl ketone/thiocyanic acid solution to preferentially extract hafnium dihydroxide thiocyanate into the organic phase. This is conducted in a series of mixer-settlers or a series of packed or internally agitated columns. Hafnium is recovered from the ketone solution by scrubbing with dilute sulfuric acid.

Zirconium is recovered from the hydrochloric acid solution by heating the solution above 90 °C, adding precisely two moles of sulfuric acid to each five moles of zirconium, and then carefully raising the pH to 1.2–1.5 with dilute ammonium hydroxide. This precipitates a granular zirconium basic sulfate, $\text{Zr}_5\text{O}_8(\text{SO}_4)_2 \cdot x \text{H}_2\text{O}$ which is easily filtered and washed to remove aluminum and uranium impurities. The sulfate filter cake is repulped with dilute ammonium hydroxide to convert it to zirconium hydrous oxide, which is fired to give pure zirconium oxide [16].

In this extraction process, methyl isobutyl ketone and thiocyanate are recovered and reused, but considerable quantities of hydrochloric acid, sulfuric acid, and ammonia are consumed. Zirconium produced typically contains 35–90 mg Hf/kg and the hafnium contains 200–2000 mg Zr/kg, but any degree of separation can be attained, without further chemical consumption, by providing fewer or more contacting stages during separation.

The zirconium oxide and hafnium oxide are each chlorinated in fluidized beds to give their tetrachlorides. Chlorination of the oxides is faster than that of the silicates, and can be efficiently conducted at a lower temperature.



The zirconium tetrachloride is then purified by sublimation at 350–400 °C in a nitrogen atmosphere containing 1–5% hydrogen. The hot gases pass through a filter to remove entrained particles before being cooled to condense the zirconium tetrachloride. This sublimation reduces the levels of oxide, iron, phosphorus, and aluminum.

Tributyl Phosphate Extraction, developed concurrently in Britain, France, and the United States, was used commercially in the United States and is being used in India to obtain zirconium for the nuclear industry [17]. Hydrous zirconium–hafnium oxide from caustic fusion of zircon is dissolved in nitric acid. The nitric acid solution is countercurrently contacted with an organic solution of tributyl phosphate in kerosene. A zirconium tributyl phosphate complex is preferentially extracted into the kerosene, leaving hafnium and most metallic impurities in the aqueous phase. The zirconium is stripped from the kerosene solution with dilute sulfuric acid solution, precipitated, and fired to pure zirconium oxide.

Extractive Distillation. Hafnium tetrachloride is slightly more volatile than zirconium tetrachloride, and separation by fractional distillation would be feasible if the tetrachlorides could be handled as liquids. However, the tetrachlorides are either solid or gaseous, depending on temperature, unless kept under pressure while being heated to the triple point of zirconium

tetrachloride (435 °C, 2.0 MPa). However a distillation process was developed in which the liquid phase was molten potassium chloroaluminate, in which zirconium and hafnium tetrachloride are soluble without forming compounds that could impede the separation or the recovery of separated chloride [18].

The zirconium–hafnium tetrachloride from carbochlorination of zircon is first purified by sublimation. The purified tetrachloride is re-vaporized and the vapor is introduced into the distillation column, above the midpoint. The potassium chloroaluminate liquid, equilibrated with hafnium-rich tetrachloride, is fed into the top tray of the distillation column, which is at 350 °C. As the liquid cascades down the column, it is gradually stripped of the more volatile hafnium tetrachloride while acquiring zirconium tetrachloride from the rising vapor. The zirconium tetrachloride in the liquid melt reaching the bottom of the column contains <50 mg Hf/kg Zr.

In the boiler at the column bottom some of the zirconium tetrachloride is vaporized to provide the rising vapor in the column. From the boiler the liquid melt goes to a short, hotter column where it is stripped with nitrogen to remove the product zirconium tetrachloride.

The stripped liquid melt is returned to an absorber–condenser above the distillation column where it is equilibrated with hafnium-rich tetrachloride vapor, then returned to the top of the distillation column. Unabsorbed hafnium-rich tetrachloride vapor (HfCl₄ content 30–50%) is led to a condenser. The hafnium-rich tetrachloride is accumulated until it can be reprocessed in the distillation column in a separate campaign to recover pure hafnium tetrachloride (<1% ZrCl₄).

Control of the potassium to aluminum ratio in the melt is crucial. Excess potassium chloride preferentially bonds with hafnium tetrachloride, reducing its effective vapor pressure and thereby decreasing the separation efficiency. With a deficiency of potassium chloride, aluminum chloride is lost into the nitrogen stream in the stripper, contaminating the zirconium tetrachloride product.

This extractive distillation process has a higher yield than the liquid–liquid extraction processes, does not consume large quantities of chemicals, and eliminates the rechlorination step. It is very capital intensive.

Other Processes. Although zirconium is not easily reduced except by very strong reducing agents, it can be reduced more easily than hafnium. This has led to several separation procedures. The most significant [19] involved both molten metal (zinc base) and molten halide salts for good contact between the phases and for the close approach to equilibrium needed for good separation factors.

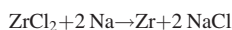
1.4.3. Reduction to Metal

Oxygen strengthens zirconium metal, decreasing its ductility and therefore its formability as a metal. To produce ductile zirconium metal, the zirconium compound to be reduced and the reducing agent should be as free of oxygen (and nitrogen and carbon) as possible. Anhydrous zirconium tetrachloride or tetrafluoride are usually used.

Kroll Process. Ductile zirconium metal is produced by reduction of pure zirconium tetrachloride with molten magnesium under an inert gas (helium or argon). The reduction retort is a long, vertical cylinder composed of two sections. The lower third is a stainless-steel-lined crucible which holds the magnesium ingots. The upper two-thirds has a central annular pipe slightly shorter than the retort wall. The space between the wall and the central pipe is filled with zirconium tetrachloride powder, then the two sections are welded together and a lid is bolted to the top. The assembled retort is warmed to 200 °C, evacuated and filled with argon several times to remove the last traces of air. The retort is lowered into a furnace with heating zones for each retort section. The lower section is then heated to 850 °C to melt the magnesium, and argon is bled from the warming retort to maintain atmospheric pressure (the retort is not a pressure vessel). Zirconium tetrachloride vapor passes down through the central pipe, which communicates with the lower section, and is reduced by the molten magnesium. At the end of the reduction, the lower crucible contains a thick suspension, or mud, of tiny zirconium metal beads in liquid magnesium, under a layer of liquid magnesium chloride. The retort is cooled and unloaded. The stainless steel liner is separated from the reduction mass and

the layer of magnesium chloride is mechanically removed from the zirconium–magnesium metallic regulus. Several reduction reguli are stacked and loaded into a distillation furnace for removal of magnesium and residual magnesium chloride. The distillation is conducted in a vacuum (<1 Pa), with the charge located in the upper end of the retort. The bell furnace around the top of the retort is heated in programmed steps, reaching 980 °C in ca. 30 h. As the charge heats, the magnesium chloride melts and drains away, and the magnesium metal slowly evaporates, condensing on the water-cooled retort wall. As the magnesium evaporates, the zirconium beads come into closer contact and begin to sinter together. The final sintered porous mass is known as zirconium sponge. The heating schedule is critical: If the magnesium receives heat faster than heat is removed by magnesium transpiration at the surface of the reguli, the reguli become soft and flow down out of the heated zone. After the retort is cooled and the sponge conditioned by slow, controlled exposure to air, the sponge regulus is removed from the retort. The regulus is broken into chunks by using a hydraulic chisel. The chunks are sorted into quality grades depending on color and relative location in the regulus. The chunks are crushed to less than 2 cm, and screened to remove –20 mesh fines, which are higher in impurities.

Other Reduction Processes. Ductile zirconium has been produced commercially in a two-step sodium reduction analogous to a titanium reduction process [20]. Zirconium tetrachloride vapor and liquid sodium are both slowly fed into an argon-filled stirred reactor containing granular sodium chloride to obtain a $\text{ZrCl}_2\text{--NaCl}$ mixture. This first step is very exothermic and the feed rate is controlled to allow excess heat to escape. The mixture is then transferred to a reactor by means of a screw conveyor. The reactor, already loaded with sodium, is sealed and heated to 800 °C:



The cooled mass was mechanically broken out of the reactor and leached with water to remove the sodium chloride from the zirconium. However, it was necessary to drip-melt the

zirconium, forming splat-cooled chunklets, to remove the last traces of salt.

The Russian practice is to reduce potassium hexafluorozirconate with calcium metal in a sealed bomb. In Canada, zirconium tetrafluoride was reduced with calcium metal in a sealed bomb.

Zirconium oxide can be reduced by calcium or magnesium. Finely divided metal powder is recovered by leaching with cold hydrochloric acid. The powder has 0.3–0.5% oxygen, and would not be ductile or malleable if melted into ingot. The powder particles are 1–8 μm in diameter and are very pyrophoric.

Electrolysis. Electrowinning and electrorefining of zirconium have been conducted but are not in commercial use. A pilot electrolysis system tested for zirconium was used commercially for hafnium [21]. A summary of the difficulties in developing an electrolysis process is given in [22].

1.4.4. Refining

From 1925 to 1945 the van Arkel and de Boer iodide process was the only consistent method for obtaining pure ductile zirconium metal. Now Kroll zirconium is used for most applications and iodide zirconium is used only when the highest purity is needed. In the iodide process, iodine vapor is reacted with Kroll zirconium sponge or calcium-reduced zirconium metal powder to produce zirconium tetraiodide [23, 24]. The tetraiodide vapor diffuses to a heated filament, usually zirconium wire, where the iodide is thermally dissociated, depositing zirconium and releasing iodine to repeat the cycle:



The reaction is conducted in an Inconel vessel at an absolute pressure of 40 Pa. The wire filament diameter grows as zirconium is deposited on the wire. Bars up to 40–50 mm in diameter can be grown.

Electron beam melting is not usually used to purify zirconium because the metal's vapor pressure at its melting point is higher than that of most impurities. Iron and aluminum levels can be reduced by electron beam melting. The metal vapor pressure results in considerable evapora-

tion loss in the high vacuum utilized in electron beam melting.

1.5. Fabrication

The procedures for melting zirconium sponge and for conversion of ingots to mill products are similar to those developed by the titanium industry, with the added requirement that high-neutron-cross-section materials, such as boron be rigorously excluded.

Melting. Zirconium sponge is pressed into compacts, cylindrical or hexagonal discs, which then are stacked and surface-welded together in an electron beam furnace to form an electrode. The discs may be pure sponge, or may contain alloying ingredients added in the midst of each disc during pressing, or may be recycled clean turnings of the same intended composition. The welded electrode is then melted in a vacuum arc furnace. An electric arc is struck between the electrode and a starter pad of zirconium chips in the bottom of a water-cooled cylindrical copper crucible. The electrode is not cooled and it slowly melts off in the arc, producing a molten pool in the cooled copper crucible. The pool edge freezes on contact with the cool crucible wall so that the remaining pool is separated from the crucible wall. As melting continues, the electrode is consumed and the ingot grows in the crucible, cooling and solidifying from the bottom and sides as the pool moves upward. The outer skin contains impurities that vaporize during melting, primarily magnesium and magnesium chloride, and any possible copper pickup from sliding the ingot out of the crucible. The first-melt ingot is surface machined to remove the outer skin. Since the molten pool was, at any one instant, only a small portion of the ingot, distribution of alloying ingredients in the ingot is not homogeneous after one melt. Two machined first-melt ingots are formed into a second electrode, first-melt bottom now at the top, which is again melted in a larger diameter copper crucible. A third melt assures complete homogeneity and dissolution of any inclusions. 750 mm diameter ingots of up to 9 t are produced.

Forming. Ingots are surface machined then heated to over 1000 $^\circ\text{C}$ and hot forged to 50–150 mm thick slabs, or to 200–400 mm diameter

rounds. At the conclusion of hot working, the surface oxide scale is removed by sandblasting and abrasive-wheel grinding. The underlying dark layer of oxygen-diffused metal is removed by pickling in dilute hydrofluoric–nitric acid solution [25].

Strip and sheet are formed by cold working the slabs in conventional rolling mills, including producing foil in a Sendzimir mill. The allowable cold deformation before annealing is 20–70%, depending on alloy toughness and the type of deformation process. Intermediate and final anneals are conducted in vacuum or inert-atmosphere furnaces.

For round products, the 200–400 mm rounds are cut to length, hot rotary forged to bar, cleaned, and swaged or drawn to rod or wire for welding use.

For hollow round products, short lengths of the rounds are drilled or trepanned to produce extrusion billets which are warm extruded to heavy wall tubeshells. Prior to extrusion the billets are coated with proprietary layers of glass, graphite, or copper. These coatings minimize oxidation of the surface and function as a lubricant during extrusion, but must be removed before subsequent cold working.

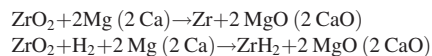
The extruded tubeshells are tube-reduced in pilger mills, with intermediate vacuum anneals, to produce thin-wall tube lengths. Zircaloy 2 or 4 (see Section 1.9) tubes are used as cladding for uranium oxide pellets for light-water nuclear fuel assemblies. This is the major use of zirconium metal.

Powder Metallurgy.

The Hydride–Dehydride Process. Malleable zirconium and high-zirconium alloy powders are obtained by the hydride–dehydride process. Zirconium is hydrided by heating to 800 °C and cooling in a pure hydrogen atmosphere. The product is brittle and easily ground to powder in an argon atmosphere chamber. The hydrogen is then removed by degassing in a vacuum above 650 °C. The metal powder is screened to obtain the desired particle-size distribution. The hydride powder can also be directly pressed and sintered, allowing for hydrogen outgassing.

Reduction Process. Zirconium oxide powder is mixed with a reducing agent (e.g., magnesium, calcium or calcium hydride granules). The mixture is heated in a retort under inert gas to

1100 °C. The reaction already starts at temperatures at around 250 °C. After the reduction is completed (approx. 2 h) the resulting products (zirconium, reduction agent oxide, and excess of reduction agent) are leached with HCl, washed, decanted, and dried. The Zr powder produced by the reduction process has a particle size of less than 45 µm (–325 mesh) and a purity of >98% [26]. For the production of zirconium hydride the Zirconium oxide / reducing agent mixture will be reduced within a hydrogen atmosphere.



Safe handling of Zr powder including drying, mixing, sieving, and milling is described in [27].

Welding. Zirconium can be welded in argon or helium atmospheres. If welding is not conducted in an inert-gas chamber, the welding fixtures or jigs must be so arranged that argon or helium gas flooding is sufficient to keep air completely away from the welding zone. Care must be taken to avoid oxygen or hydrogen pickup as these affect the ductility and corrosion behavior of the heat-affected zone. Electron beam welding is used for high-quality welds in repetitive situations, such as nuclear fuel assembly.

While zirconium can be welded to titanium, hafnium, niobium or tantalum, joining of zirconium with other metals (i.e., copper, iron, nickel) by fusion welding is not practical because of the formation of brittle intermetallic phases. To join these metals, methods must be used that avoid formation of liquid phases but use mechanical interlocking: friction welding or explosive bonding, which is used for cladding of zirconium lining onto ferrous alloys. Welding of zirconium to titanium, niobium, or tantalum destroys the corrosion resistance.

1.6. Hazards in Handling Zirconium Metal

Solid zirconium is not hazardous, but any high-surface-area form of zirconium metal (powder, dust, chips, foil, sponge) is hazardous because of its easy ignition in air and its exothermic reaction with many other elements and compounds.

Zirconium chemical equipment, if used under conditions not recommended, such as sulfuric

acid above 80% concentration or strong hydrochloric acid with ferric ion contamination, may suffer intergranular attack. This creates a highly pyrophoric surface layer, usually black, that is ignited easily when dry. The combination of γ -zirconium hydride and metallic particles has been suggested to be responsible for the pyrophoricity. Careful treatment in hot air or steam is recommended to stabilize this surface [28].

The ignition temperature of zirconium powder varies with particle size, method of production, and prior treatment. A powder <40 μ m prepared in inert atmosphere will immediately ignite upon exposure to air, unless it is first slowly exposed, such as by gradually back-filling the airlock of a glove box, allowing the heat of surface oxidation to dissipate.

Zirconium powder produced wet, such as by acid leaching of a reduction mass, is usually safe if the water content is >50 wt%. This prevents localized temperature excursions. The powder should not be allowed to settle and compact for long periods of time, especially when freshly prepared. Hydrogen is still slowly generated, and accumulated gas bubbles in a compact powder mass can insulate some grains from the water, allowing localized heating to ignition.

Drying of wet powder is most hazardous. While wet powder is harder to ignite than dry powder, it burns much more vigorously because of the available oxygen from the water and is more explosive because of the generation of hydrogen and steam. The most hazardous water content is 5–10%. Powder is dried as a thin layer on warm-water-heated trays in a vacuum drier.

Machining of zirconium generates fine chips which can be ignited easily. Hot chips are the usual ignition source. The best metal removal procedures consistent with keeping chip temperatures down are: using slow cutting speeds with heavy feeds, and using an ample flood of water-soluble cutting oil as a coolant. Accumulation of chips should be avoided. Chips should be removed as generated and stored in water-filled drums kept outside in an isolated area. Coarse chips, if not contaminated, possibly may be chopped, cleaned, and recycled. Fine chips should be disposed of by burning in an incinerator or an open pit, feeding the fire in small increments of 1–2 kg.

Many unexpected flash fires have been caused by improper handling of machining chips resulting in more than one incident of fatal flash burns.

Workers involved in handling, storing, cleaning, or disposal of machining chips or other zirconium fines should wear heat-reflectant clothing.

Zirconium fires can be controlled only by cutting off the supply of oxygen and other oxidants, such as water, carbon dioxide, carbon tetrachloride, iron oxide, and limestone. Small fires can be smothered with dry silica sand or dry table salt, or with argon or helium if the zirconium is enclosed in a container. Do not use water. Large fires are best left alone and allowed to burn out, keeping the surroundings from igniting.

Safe handling procedures for zirconium, including machining, grinding, welding, and descaling, are discussed in [29].

Solutions that corrode zirconium metal may react violently or explosively with zirconium powder. A solution of 83% concentrated H_2SO_4 and 17% KHSO_4 was added dropwise to 2 g of zirconium powder. Upon adding about 2 mL of the acid mixture, a violent explosion occurred.

1.7. Grades and Specifications

There are two parallel grading systems for zirconium: industrial (intended primarily for use as a construction material for equipment and piping in the chemical industry) and nuclear (intended for use as a construction material for fuel cladding and internal parts for nuclear power reactors). Some of these grades have little present usage.

The industrial grades are listed, showing first the ASTM designation, then any alternative designation:

R 60 701 (Zr 701)	an unalloyed zirconium of low hardness and containing low levels of the impurities iron and chromium
R 60 702 (Zr 702)	the usual unalloyed zirconium specified for general corrosion-resistant service
R 60 703 (Zr 703)	the least pure, available only as sponge metal, used primarily for alloying with other metals
R 60 704 (Zr 704)	an alloy containing tin and iron and used in chemical process applications where the higher strength of the alloy is needed and the corrosion resistance is sufficient
R 60 705 (Zr 705)	an alloy containing 2.5% niobium used where high strength is needed
R 60 706 (Zr 706)	a softer version of Zr 705 used specifically for severe forming applications

All of these grades may contain the usual 2% hafnium, or may be furnished hafnium-free. This does not affect the quality or usefulness in industrial applications.

Zirconium for use in nuclear service is supplied to meet individual company specifications (which usually use ASTM nuclear grades and specifications as a starting point). The nuclear grades are listed, showing first the ASTM designation, then any alternative designation:

R 60 001	unalloyed zirconium with a long list of controlled impurities to make it satisfactory for nuclear service.
R 60 802	Primarily iodide zirconium for the first reactor core (Zircaloy 2) an alloy containing 1.5 Sn, 0.15 Fe, 0.1 Cr, and 0.05 Ni used primarily in pressurized water reactors
R 60 804	(Zircaloy 4) an alloy containing 1.5 Sn, 0.2 Fe, 0.1 Cr used primarily in boiling water reactors
R 60 901	(Zr 2.5 Nb, 705) an alloy containing 2.5 Nb, used primarily for pressure tubes in the Canadian CANDU reactors

All of these grades are hafnium free, i.e., <100 mg Hf/kg Zr.

U.S. and Canadian specifications for zirconium products are listed in Table 3.

1.8. Uses

Zirconium is produced almost exclusively as the hafnium-free metal. Most of this metal is used in zirconium alloys containing low levels of tin or niobium, for structural parts in the core of water-moderated nuclear reactors. For this use, zirconium

has several desirable attributes: it is ductile, i.e., it can be formed. It has good strength up to 450 °C, i.e., it does not deform at reactor core temperature. Its alloys have hot-water and steam corrosion resistance, i.e., it lasts a long time in normal use. It has low thermal neutron cross section, i.e., neutrons are not absorbed, shutting down the nuclear reaction. Its ore is readily available.

Zirconium is used for building chemical process equipment for those applications where its corrosion resistance is needed. In hot sulfuric acid up to 65% concentration, zirconium is used in facilities which produce hydrogen peroxide, acrylic films and fiber, methyl methacrylate, and butyl alcohol. Zirconium is used in the cooler condenser on a nitric acid absorption column. The operation conditions are 200 °C and 1035 MPa. One condenser constructed with zirconium tubes and zirconium/304 L stainless steel explosion-bonded tubesheets contains over 18 km of zirconium tubing and has been in service since the mid 1970s. Zirconium is used in contact with ammonium carbamate in urea production, in production of acetic and formic acid, and in many hydrochloric acid environments. In these applications zirconium's corrosion resistance is excellent and the long life of the equipment has justified the use of zirconium.

Zirconium foil, 0.002 mm, is used as the ignition-flash material in photographic flash bulbs, just as zirconium powder used to be one ingredient in the old open "flash pans" of earlier photographers, but this usage is fading because of built-in electronic flashes in newer cameras.

Table 3. Specifications for zirconium and zirconium alloy products

Zirconium product	Industrial			Nuclear	
	ASTM	ASME	ASTM	DOE	AECL
Sponge	B 494		B 349		
Ingot	B 495		B 350	M10-1 T	MET 52
Forgings	B 493			M 2-9 T	
Bar (rod) and wire	B 550	SB 550	B 351	M 7-9 T	MET 62
Strip, sheet, and plate	B 551	SB 551	B 352	M 5-6 T	MET 59
Tubes, seamless and welded	B 523	SB 523	B 353	M 3-8 T	MET 92
Tubes, nuclear fuel cladding			B 811		MET 56
Pipe, seamless and welded	B 658	SB 658			
Welding fittings	B 653				
Bare welding rods		SFA 2.54*			
Castings	B 752				

* Also American Welding Society spec. A 2.54.

Zirconium powders, <45 μm (–325 mesh), find applications in various pyrotechnic areas. They are a source of heat for squibs and ignition devices for a variety of uses including automotive airbag inflators. For the production of highly reactive and quick fuse compositions in pyrotechnics for use in ammunition, explosives, airbags, and safety belt pretensioners. Zr powders are also used as alloying agent with other metals.

Zirconium and zirconium alloys with aluminum, iron, titanium, or vanadium are used for gettering in vacuum tubes [30], inert gases, and ultra-high-purity environments for the semiconductor industry [31]. Heated zirconium absorbs traces of oxygen, nitrogen, carbon monoxide, carbon dioxide, and water irreversibly. Hydrogen is reversibly adsorbed. The adsorbed materials diffuse into the bulk of the getter alloy, providing fresh surface for renewed adsorption. For ultra-pure inert gases, getters are used at the point of use to remove contaminants picked up from storage tanks or piping systems. Getters are used in gettering pumps for improving the quality of vacuum in ultra-high-vacuum systems.

Zirconium in the forms of clean, chopped machining chips, crushed sponge or magnesium-zirconium reguli turnings are often used in place of master alloys for zirconium additions to steel melts, super alloys, and nonferrous alloys.

1.9. Economic Aspects

Ores and Minerals. The four major producing countries for the world's current estimated annual production of 10^6 t of zirconium minerals are Australia 50%, Republic of South Africa 25%, United States 10%, and the Ukraine 6%. Australia and South Africa are the major exporting countries. Europe, Japan, China and the United States are major importers.

There are no zircon mines. Zircon is recovered as a byproduct of the extraction of the titanium-containing minerals rutile, ilmenite, and leucocoxene. The producers of these minerals adjust their output to follow paint-market demand for titanium oxide pigment. Therefore, the supply and the demand for zircon are rarely in phase and zircon prices have wide swings. During 1975–1995, zircon prices ranged from \$ 83 per tonne to over \$ 1100 per tonne in late 1989. The price during

1990–1995 averaged \$ 275–330 per tonne, varying with quality.

Consumption of zirconium ores continues its gradual growth. In 1975, world production of zircon was 455 000 t and by 1995 it had essentially doubled. Currently, the growth in demand for zirconium materials is being led by its use as an opacifier in glazed ceramic tile manufacture.

Metals. Less than 4% of the zirconium ores are used in the manufacture of zirconium metals. Since the incident at Three Mile Island, the meltdown at Chernobyl, and the ending of the cold war, the demand for commercial nuclear power and for military naval propulsion systems has diminished. It is estimated that in 1994 total world production was ca. 3600 t, compared to ca. 7300 t in 1982.

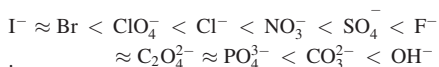
The United States has the largest production capacity with two producers: Teledyne Wah Chang in Albany, Oregon (nameplate capacity ca. 2700 t/a) and Western Zirconium in Ogden, Utah (nameplate capacity ca. 1360 t/a). In France, Compagnie Europeene du Zirconium (CEZUS), owned jointly by Pechiney, Framatome and Cogema, has a capacity of ca. 1800 t/a. The capacity of the Prinieprovsky plant in the Ukraine is estimated to be 2700 t/a of calcium-reduced reguli, which is crystal-bar refined at Glasnov, Russia. The Indian plant in Hyderabad has a nameplate capacity of 270 t; production is consumed internally. Japan is not presently producing zirconium sponge.

Prices in 1994 were \$ 20–28 per kilogram of sponge and \$ 45–110 per kilogram for cold-rolled sheet, strip, or foil.

2. Zirconium Compounds

In anhydrous halide-salt melts zirconium may exhibit valences of 4, 3, 2 or 1, but in aqueous solution its oxidation state is +4. Zirconium compounds have coordination numbers of 6, 7, or 8. The colorless ion is hydrolyzed in aqueous solution. Because of the ion's high charge and small radius, zirconium has a great tendency to hydrolyze and to form polymers. It is believed that most zirconium in aqueous solution is present as a tetramer $[\text{Zr}_4(\text{OH})_4]^{8+}$ [32]. Therefore, $\text{ZrOCl}_2 \cdot 8 \text{H}_2\text{O}$, by formula, is actually $[\text{Zr}_4(\text{OH})_4 \cdot 7 \text{H}_2\text{O}]_4\text{Cl}_8$. Hydrolysis and further

polymerization of these tetramer units occurs with time, by heating, or with decreasing acidity. True equilibrium may take days or weeks. The following anions are listed with respect to their ability to form complexes with zirconium:



2.1. Zirconium Silicate

Zirconium silicate, ZrSiO_4 , occurs in nature as the mineral zircon. It can be made by heating an intimate mix of zirconia and silica to just above 1500°C . The crystals are tetragonal with the zirconia and silica linked through shared oxygen atoms, forming edge-sharing alternating ZrO_8 triangular dodecahedra and SiO_4 tetrahedra [33]. Other, more complex silicates are also found in nature (see Section 1.5). Zirconium silicate is resistant to acids, aqua regia and cold alkali solutions. It is readily attacked by sodium oxide, by sodium hydroxide at 600°C , and by reaction with hot alkaline compounds (see Section 1.4.1). Above 800°C zircon is reduced by carbon, the basis for the carbochlorination process.

Uses. Zircon's mechanical strength, chemical stability and high melting point make it a desirable refractory. Total world production of zircon was $(770\text{--}960) \times 10^3$ t/a for 1990–1995. Of this ca. 35–40% is used in ceramic glazes and enamels, ca. 30–35% in refractories, 15–20% in foundry use, 8–12% in abrasives, and 8–12% in other uses including chemicals, metals and alloys, and glass constituents.

In the largest use, decorative ceramics, milled or micronized zircon is used as an opacifier for tile glazes and porcelain enamels. Zircon's high refractive index gives the glaze a white, opaque appearance.

Zircon is a popular refractory in the glass and steel industries. The glass industry uses fused zircon and AZS (alumina–zirconia–silica) refractories (\rightarrow Refractory Ceramics) which have a high corrosion resistance to molten glass. The AZS refractories are made by electric furnace fusion of alumina and zircon. The steel industry uses zircon in ladles and continuous casting nozzles. Refractory applications were once the

leading markets for zircon but they decreased significantly following the zircon shortage in the late 1980s. Other less-expensive refractories, such as alumina spinels were substituted.

Zircon is used in foundries as a basic mold material and as a facing on other mold materials. The high thermal conductivity of zircon gives higher cooling rates than other mold materials. Zircon's high melting point, low coefficient of thermal expansion, and chemical stability make it the preferred mold facing, particularly in precision casting.

Alloyed AZ (alumina–zirconia) abrasives (\rightarrow Abrasives) are made from 60–90% alumina–zirconia grains produced by fusing alumina with baddeleyite or zirconia derived from zircon, in electric arc furnaces. The addition of zirconia toughens the alumina, reducing its brittleness. The abrasives have particular application in the grinding of steel and steel alloys because of high strength, hardness, and surface crystal sharpness, resulting in fast grinding and long wheel life.

Zircon is added to glass for television tubes because of its X-ray absorption properties and its ability to toughen the glass.

2.2. Zirconium Oxide

Zirconium oxide [1314-23-4] occurs naturally as the mineral baddeleyite and is produced by calcining of other zirconium compounds. Three phases are stable at atmospheric pressure: cubic above 2370°C , tetragonal above 1170°C , and monoclinic below 1000°C . Transformation of the monoclinic phase to the tetragonal phase begins at ca. 1050°C and is complete at ca. 1170°C . The transformation is accompanied by a volume shrinkage of 3–5%. The transformation has a thermal hysteresis: on gradual cooling the tetragonal phase is stable to ca. 1000°C and only finishes conversion to monoclinic at ca. 800°C . With rapid quenching the tetragonal phase is metastable to room temperature.

The high-temperature cubic phases can be stabilized down to room temperature by the addition of magnesia, calcia, yttria, or rare earth oxides, whose presence creates vacancies in the zirconium anion lattice. These stabilized zirconium oxides contain from 3% yttria to 8% calcia. They have the same crystal structure from room temperature to melting, avoiding the catastrophic

mechanical failure suffered by pure zirconia ceramic parts on transforming from the tetragonal to monoclinic phase while cooling.

GARVIE [34] discovered that certain partially stabilized zirconias could be thermally cycled to precipitate metastable tetragonal zirconia within the grains of cubic zirconia. These materials had higher toughness than fully stabilized zirconias. The increased toughness of partially stabilized zirconia (PSZ) is the result of stress-induced martensitic transformation of the metastable tetragonal grains to the monoclinic form in the stress field of a propagating crack. This led to development of an entirely tetragonal zirconia, known as tetragonal zirconia polycrystal (TZP). The evolution of these materials and their growing application in structural ceramics can be followed in [35–40]. An introduction to zirconia ceramics is given in [41].

Zirconia also has a high-pressure (10 GPa) orthorhombic structure which can be stabilized to atmospheric pressure by addition of >12 mol% of niobia or tantalum or a mixture thereof [42]. No transformation toughening was found [43].

Stable lower oxides of zirconium are not known, although oxygen dissolved in the zirconium metal lattice has led to the identification of some superstructures as $\text{ZrO}_{0.3}$ [44]. Zirconium monoxide, ZrO , has been observed in mass spectrographic measurements [45]. The black oxide surface on zirconium metal after exposure to water at 350°C is a slightly substoichiometric $\text{ZrO}_{1.95}$.

Zirconia is very resistant to acids and alkalis, but slowly dissolves in concentrated hydrofluoric acid or hot concentrated sulfuric acid. Zirconia is resistant to many fluxes, molten glasses, or melts, silicate, phosphate, or borate, but is attacked by fluoride or alkaline melts. Zirconium oxide and alkaline oxides or caustics can be fired together to form solid-solution oxides, zirconate compounds, or a mixture of both.

Zirconium oxide is reduced by carbon, beginning at ca. 600°C . With excess carbon, in a vacuum furnace, the reaction proceeds rapidly to zirconium carbide at 1500°C . In the presence of chlorine the carbon reduction gives zirconium tetrachloride and carbon dioxide.

Uses. Zirconium oxide is used to coat the surface of titanium oxide pigment particles for some grades of exterior service paints. The coat-

ing minimizes ultraviolet excitation of the titania, which would interact with the organic paint binder, shortening the service life. Zirconia has been used in place of titania as the pigment of white camouflage paints for use in snow environments because zirconia more closely simulates snow in the infrared and microwave spectra. Over 300 t of single-crystal cubic zirconia are grown each year to provide low-cost gems for the jewelry trade [46]. Stabilized zirconia is being used in everyday applications, such as fishing rod ferrules, knives, unbreakable shirt buttons, and golf putter heads.

While stabilized zirconias are insulators at room temperature, at elevated temperatures the vacancies in the anion lattice allow O^{2-} ions to diffuse and the zirconia becomes a solid electrolyte with applications in oxygen sensors and high-temperature fuel cells. Some stabilized zirconias can be used as resistors or susceptors. Inductively heated yttria-stabilized zirconia cylinders are used as heat sources to melt quartz boules for the drawing of quartz optical fibers.

Zirconia is a constituent of lead zirconate titanate (PZT) used in piezoelectric ceramics (\rightarrow Ceramics, Electronic) for applications as gas furnace and barbecue igniters, microphone and phonograph crystals, ultrasonic transducers for medical ultrasound imaging, for agitation in cleaning tanks, and for underwater sonar. With the further addition of lanthanum (PLZT), ferroelectric optically active transparent ceramics have become available (\rightarrow Ceramics, Electronic) [47].

2.3. Hydrous Zirconium Oxide

Neutralization of an aqueous zirconium solution causes hydrolysis and condensation of the zirconium cations, forming a white gel called zirconium hydroxide but generally considered to be a hydrous oxide. The freshly precipitated amorphous gel is generally considered to be a network of tetramer units $[\text{Zr}_4(\text{OH})_8 \cdot 16 \text{H}_2\text{O}]^{8+}$ linked through hydroxyl groups; it is easily dissolved by dilute or weak acids. As the gel ages some of the hydroxyl links are converted to oxo links, and the gel's reactivity decreases. Upon heating to 500°C the gel yields monoclinic or metastable tetragonal oxide, or a mixture of these. The specific structure obtained has been attributed to the precursor zirconium salt [48], pH of the liquid

in final contact with the condensed gel [49], electronegativity and pH [50], slow or rapid condensation from sol to gel, ageing, the presence during gelling of sulfate, sodium, potassium, or ammonium ions, and particle size [51].

Hydrous zirconium oxide in controlled particle size is prepared by hydrolysis of sodium zirconate [52].

Hydrous zirconium oxide sol is used in sol-gel processes to produce stabilized zirconias in spherical or fibrous form, and to form an oxidation-protective film on stainless steels.

2.4. Zirconium Chlorides

The fully chlorinated form of zirconium is zirconium tetrachloride. The tetrachloride is normally produced by carbochlorination of zircon or zirconia [53] (see Section 1.4.1) or by reacting zirconium metal with chlorine or hydrogen chloride. Chlorinated hydrocarbons, particularly carbon tetrachloride, chloroform, or hexachloroethane, are useful laboratory chlorinating agents. Zirconium tetrachloride can be formed by reacting ferrozirconium or silicozirconium with iron (II) chloride at elevated temperature [54].

Zirconium tetrachloride vapor is a tetrahedral monomer which crystallizes below 331 °C in a AB₄ type structure with ZrCl₆ octahedra coupled to each other by two edges to form a zig-zag chain. Each zirconium has four bridging chlorine ligands and two terminal chlorines which are mutually *cis* [55]. Some physical properties of zirconium tetrachloride are shown in Table 4.

Zirconium tetrachloride reacts rapidly with water, vapor or liquid, to exchange two chlorines for oxygen. Any handling of zirconium tetrachloride must be in moisture-free atmospheres to avoid degradation. Zirconium tetrachloride powder fed into water hydrolyzes to form a solution

of zirconium hydroxide chloride and free hydrochloric acid. Zirconium tetrachloride vapor reacts with steam to yield zirconium oxide, and reacts with water to yield either an oxide slurry or hydroxide chloride solution.

Zirconium tetrachloride is used to form zirconium nitride coatings, to react electrochemically to form zirconia in high-temperature fuel cells, to react with alcohols to form alkoxides, and to produce zirconium organometallic compounds. Zirconium tetrachloride is reduced by molten alkali and alkaline earth metals, yielding zirconium metal.

Zirconium tetrachloride reacts reversibly with ammonium chloride, alkali metal chlorides, and alkaline earth chlorides to form hexachlorozirconates [56, 57]. Zirconium tetrachloride forms addition compounds with aluminum and iron trichlorides and phosphorus pentachloride, but FeZrCl₆ dissociates to FeCl₂ and ZrCl₄ above 350 °C.

Lower valent zirconium chlorides including zirconium trichloride [10241-03-9], dichloride [13762-26-0], monochloride [14989-34-5], and zirconium chloride cluster phases Zr₆Zl₁₂ and Zr₆Cl₁₅ are produced by reduction of zirconium tetrachloride with zirconium metal or with zirconium monochloride in sealed tantalum containers. The reactions are slow, usually requiring weeks at 300 to 800 °C [58–60]. Zirconium monochloride reacts reversibly with hydrogen at 340 °C in a sealed tube to form ZrClH_x ($x \leq 1$) [61].

2.5. Zirconium Hydroxide Chlorides

Zirconium hydroxide dichloride [22196-48-1], empirically Zr(OH)₂Cl₂ · 7 H₂O, has been known by several names: zirconyl chloride, zirconium oxychloride, zirconium oxide dichloride, all commonly identified as ZrOCl₂ · 8 H₂O.

Table 4. Physical properties of zirconium tetrahalides

Property	ZrF ₄	ZrCl ₄	ZrBr ₄	ZrI ₄
Color	white	white	white	orange-yellow
Density, kg/m ³	4430	2800	3980	4850
Sublimation temp (101.3 kPa)	903	331	357	431
Melting point, K	923	437	450	499
Critical temperature, K	932	503.5	532	686
Critical pressure, MPa		5.7	4.3	4.1
Crystal structure	monoclinic	monoclinic	cubic	cubic
CAS registry no.	[7783-64-4]	[10026-11-6]	[13777-25-8]	[13986-26-0]

Structurally the hydroxide dichloride is really $[\text{Zr}_4(\text{OH})_8 \cdot 16 \text{H}_2\text{O}]\text{Cl}_8 \cdot 12 \text{H}_2\text{O}$ [62].

Zirconium hydroxide dichloride solution is formed by dissolving hydrous zirconium oxide or zirconium carbonate in hot hydrochloric acid, or by hydrolysis of zirconium tetrachloride in water. The solubility in hot water is quite high and the solubility is decreased by cooling and by adding hydrochloric acid. Excellent recoveries are obtained by crystallization ending with a 6 N hydrochloric acid mother liquor. This crystallization procedure also leaves most impurities dissolved in the mother liquor. Crystallization may be repeated to obtain very pure crystals.

Zirconium hydroxide dichloride crystals dissolve in their hydration water on gentle heating, and readily lose the hydrates outside the tetramer unit. With continued heating both water and hydrogen chloride are evolved until zirconium oxide remains [63, 64].

Zirconium hydroxide monochloride $[\text{Zr}_4(\text{OH})_{12} \cdot 16 \text{H}_2\text{O}]\text{Cl}_4$ is formed in solution by reacting equimolar portions of zirconium hydroxide dichloride and hydrous zirconium oxide or zirconium basic carbonate, or by the action of hydrogen peroxide upon zirconium hydroxide dichloride [65].

Anhydrous zirconium oxide chlorides have been prepared: the reaction of zirconium dioxide with zirconium monochloride at 980 °C produced ZrClO_y ($y < 0.42$) [66]. The reaction of zirconium tetrachloride powder in carbon tetrachloride with dichlorine oxide at -30 °C yielded ZrOCl_2 , which dissociated to ZrCl_4 and ZrO_2 above 200 °C [67].

2.6. Zirconium Bromides

Zirconium tetrabromide, ZrBr_4 , can be prepared by heating zirconium metal or carbide above 400 °C in a stream of bromine, or similarly a fine mixture of zirconium oxide and carbon at 900 °C. Its behavior is similar to zirconium tetrachloride but, because of its higher cost, the tetrabromide is of little commercial interest. Some physical properties are shown in Table 4.

Zirconium tribromide [24621-18-9], zirconium dibromide [24621-17-8], zirconium monobromide [31483-18-8], and zirconium monobromide hydride [60921-40-6] can be made by the

same procedures used for their chloride analogues [68].

2.7. Zirconium Iodides

Zirconium tetraiodide, ZrI_4 , is important because of its use in the van Arkel-de Boer refining process (see Section 1.4.4). The tetraiodide cannot be produced by heating fine zirconium oxide and carbon in iodine vapor, but is produced by heating zirconium metal to 300 °C in iodine. A temperature of ca. 1000 °C is required for a reasonably rapid reaction of iodine with zirconium carbide, carbonitride, or nitride. Zirconium tetraiodide is oxidized by dry air at about 200 °C. Some physical properties are shown in Table 4.

Lower-valence iodides have been made by reduction of zirconium tetraiodide with zirconium in sealed tantalum tubes or with zirconium or aluminum in aluminum iodide solvent [69]. Compounds formed include zirconium triiodide [13779-87-8], zirconium diiodide [15513-85-6] (both α monoclinic and β orthorhombic form), zirconium clusters Zr_6I_{12} [66908-75-6], and zirconium monoiodide [14728-76-8] [70].

2.8. Zirconium Fluorides

There are several methods for the production of zirconium tetrafluoride, ZrF_4 . Anhydrous zirconium tetrafluoride is produced in good purity by mixing hydrogen fluoride gas and zirconium tetrachloride vapor at 350 °C [71]. The hydrofluorination of zirconium oxide proceeds rapidly at 25 °C, followed by a purifying sublimation in dry hydrogen fluoride at 825 °C [72]. Zirconium tetrafluoride monohydrate is precipitated by adding strong hydrofluoric acid to a concentrated zirconium nitrate/nitric acid solution. The filtered crystals are washed with nitric acid, dried, and dehydrated with hydrogen fluoride at 450 °C [73]. Zirconium metal or zirconium hydride can be fluorinated with hydrogen fluoride but unless the reaction is conducted above 800 °C, the tetrafluoride products coat the metal, impeding the reaction. Zirconium oxides mixed with ammonium hydrogen difluoride and heated to 200 °C yield ammonium heptafluorozirconate [17250-81-6], $(\text{NH}_4)_3\text{ZrF}_7$, which on heating to 500 °C gives off ammonium fluoride. Some

physical properties of zirconium tetrafluoride are shown in Table 4.

Zirconium tetrafluoride is hydrolyzed in water to a hydroxide fluoride $\text{Zr}_4(\text{OH})_6\text{F}_{10} \cdot 3 \text{H}_2\text{O}$ with limited solubility. With increasing hydrofluoric acid concentration, $\text{ZrF}_4 \cdot 3 \text{H}_2\text{O}$ crystallizes at 30–35 wt% HF, $\text{HZrF}_5 \cdot 4 \text{H}_2\text{O}$ at 30–35 wt% HF, and $\text{H}_2\text{ZrF}_6 \cdot 2 \text{H}_2\text{O}$ at 40–60 wt% HF. In strong nitric or sulfuric acid containing excess hydrofluoric acid, the monohydrate crystallizes. Heating these hydrates produces ZrOF_2 at 300 °C.

Very high purity anhydrous zirconium tetrafluoride is a major constituent of some fluoride glasses, particularly ZBLAN, being developed because their transparency for near UV to mid IR (0.3–6 μm) was projected to be better than that of quartz optical fiber.

Potassium hexafluorozirconate production by fluorosilicate fusion is described in Section 1.6. This compound has been used to introduce zirconium into molten aluminum and magnesium as a grain refiner.

As mentioned in Section 1.7, zirconium metal is customarily pickled in dilute hydrofluoric acid/nitric acid solution. To minimize fluoride waste discharge the pickling solution is regenerated by adding sodium fluoride to precipitate sodium fluorozirconates. The particular salt precipitated varies with the sodium fluoride concentration: $\text{NaZrF}_5 \cdot \text{H}_2\text{O}$ is precipitated when the sodium fluoride concentration is less than 0.21%, and Na_2ZrF_6 is precipitated if the sodium fluoride concentration is between 0.21 and 0.4%. At higher sodium fluoride concentration $\text{Na}_5\text{Zr}_2\text{F}_{13}$ and Na_3ZrF_7 precipitate.

Zirconium tetrafluoride forms many double fluoride compounds in different proportions with alkali fluorides, alkaline earth fluorides, and others as diverse as stannous hexafluorozirconate and zirconium hexafluorogermanate, both proposed for caries prophylaxis.

2.9. Zirconium Sulfates

The sulfates of zirconium are classified as anionic, normal, or basic, depending on the sulfate to zirconium ratio. For anionic complexes this ratio is >2 . Normal sulfates have a ratio of exactly two, and basic sulfates have less than two sulfates per zirconium. Basic sulfates made by hydrolysis

of neutral sulfates usually have a ratio >1 , while basic sulfates precipitated by adding sulfate ions to hot dilute solutions of zirconium hydroxide chloride have a ratio <1 , usually 0.4–0.7.

Zirconium sulfate solutions can be generated by the action of strong sulfuric acid on hydrous zirconium oxide, zirconium oxide, zirconium carbonitride, zirconium metal, or basic zirconium sulfate. Normal zirconium sulfate [7446-31-3], $\text{Zr}(\text{SO}_4)_2 \cdot 4 \text{H}_2\text{O}$, also known as zirconium orthosulfate, can be crystallized from the above solution, or from a zirconium hydroxide chloride solution by adding sulfuric acid up to a concentration of 45% and allowing the solution to cool below 60 °C. A better purification is obtained during the crystallization if the solution contains some chloride ion.

Ammonium zirconium sulfates can be prepared by heating zirconium oxide with ammonium sulfate at 400 °C [74] or by precipitation from a zirconium sulfate solution [75]. A crude sodium zirconium sulfate can be prepared by adding sulfuric acid to sodium zirconate. Structure and composition of many sulfate variants are discussed in [32, 76, 77].

Basic zirconium sulfates containing less than one sulfate per zirconium are precipitated from hot acidic solutions of zirconium hydroxide chloride by adding 0.4–0.6 mol of sulfate per zirconium. The stoichiometric formula is $\text{Zr}_5\text{O}_{(10-x)}(\text{SO}_4)_x$ ($x = 1.8\text{--}3.5$). The most common basic sulfate is $\text{Zr}_5\text{O}_7(\text{SO}_4)_3 \cdot n \text{H}_2\text{O}$.

Normal zirconium sulfate is used for leather tanning, as a catalyst, to coat titanium oxide pigment powder, and for conversion to other zirconium chemicals. The basic sulfate is converted into other zirconium chemicals, many retaining the particle size developed during the controlled precipitation of the basic sulfate.

2.10. Zirconium Carbonates

Basic zirconium carbonate [37356-18-6] is produced by adding basic zirconium sulfate to a sodium carbonate solution, and filtering the insoluble basic carbonate. The empirical formula is $\text{ZrO}_2 \cdot \text{CO}_2 \cdot x \text{H}_2\text{O}$ but the zirconium to carbonate ratio varies considerably.

The basic carbonate is reacted with organic acids to make soluble zirconium salts, such as the citrate, oxalate, and acetate, free of chloride and sulfate ions. The carbonate is used to make a

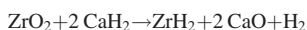
zirconium–aluminum–glycine complex, an active ingredient of antiperspirant formulations.

Zirconium basic carbonate is added to potassium carbonate or ammonium carbonate solutions to make water-soluble double carbonates. At room temperature, these solutions hydrolyze so slowly that they are considered to be stable for a month, but on heating carbon dioxide evolves and insoluble hydrous zirconium oxide forms. Ammonium zirconium carbonate [22829-17-0], empirically $(\text{NH}_4)_3[\text{Zr}_2\text{O}(\text{OH})_3(\text{CO}_3)_3]$, is used extensively in bonding starch onto coated paper [78], and in controlling pitch deposition in pulp and papermaking systems [79].

2.11. Zirconium Hydride

Zirconium hydride [7704-99-6], ZrH_2 , is prepared by the reversible absorption of hydrogen into heated zirconium, usually sponge or ingot slices. The metal is heated above 600 °C in an inert atmosphere or vacuum to dissolve the surface oxide film, then hydrogen is introduced. At 600 °C, hydrogen dissolves into the α -phase metal up to 6 atom%, when β -Zr appears — hydrogen is a β -phase stabilizer, lowering the transformation temperature from 863 °C to 550 °C. At 40 atom% the solubility in β -Zr is exceeded and δ -phase hydride appears. At 60–64 atom% only δ -phase exists. Above 64 atom% the tetragonal ϵ -phase is stable [80]. To obtain fully hydrided ZrH_2 the charge is cooled to 300 °C in full hydrogen atmosphere.

The reduction of zirconium oxide with calcium hydride yields a fine (2–5 μm particles) hydride powder for use in pyrotechnics, such as fuses or fireworks:



Extreme care must be used in dissolving the calcium oxide to recover the hydride powder.

Hydriding of zirconium sponge or ingot is the first step in producing coarse zirconium powder for powder metallurgy applications. Hydrided metal begins to lose its ductility above 40 atom% hydrogen, and above 60 atom% the hydrided metal is quite brittle and suitable for crushing, which is conducted in an inert atmosphere. During hydriding, the metal density decreases with increasing hydrogen content, going from 6.5 to 5.6 when fully hydrided.

Zirconium hydride loses hydrogen upon heating. For complete dehydriding the powder must be heated under vacuum (e.g., 700 °C until the vacuum falls to 10^{-3} Pa). Dehydriding is faster at higher temperatures but the powder begins to sinter.

Zirconium hydride contains about the same number of hydrogen atoms per volume as room-temperature water, and some alloys, such as ZrNi and ZrCr_2 can hold even more [81]. Zirconium hydride has been used in the nuclear industry as a moderator for thermal neutrons in compact, high-temperature reactors. Zirconium hydride is of interest for hydrogen storage and nickel-base hydrogen battery applications.

Zirconium hydride is inert to air and water at room temperature. It ignites in air at 340 °C or lower, depending on powder size. Zirconium hydride is resistant to corrosion by carbon dioxide up to 315 °C.

Zirconium hydride, <45 μm (–325 mesh), mixed with oxidizing agents is used in compositions for flares, fuses, and combustion charges in pyrotechnics. It is also used as a binding or brazing component for grinding agents, carbides, ceramics, and metals in abrasive wheels and polishing disks. Zirconium hydride powder is applicable as hydrogen source for the foaming of metals (e.g. aluminum foam).

Zirconium hydride heated with carbon yields the hexagonal zirconium carbohydride, $\text{ZrC} \cdot \text{ZrH}_{1.46}$ [82]. Zirconium monochloride reversibly absorbs hydrogen up to ZrClH [83].

2.12. Zirconium Carbide

Zirconium carbide [12020-14-3], ZrC , is a hard, brittle metallic carbide. It is an electrical conductor and does not hydrolyze in water. It is an interstitial carbide with the carbon atoms occupying the octahedral interstices of the zirconium lattice; at 2000 °C, carbon is soluble in liquid zirconium up to 38.5 atom%. Zirconium carbide is a single phase within the concentration range of 38.5–49.4 atom% carbon with a congruent composition of 44 atom% carbon at the melting point of 3445 °C [8, 85].

Zirconium carbide can be produced from zircon by reduction with coke in electric arc furnaces [86]. An intimate mix of fine zirconium oxide and carbon black heated in vacuum or

hydrogen in an induction-heated graphite crucible at 1600 °C yields a porous, light zirconium carbide. Milling and refiring above 2200 °C gives a dense powder. Zirconium tetrachloride and methane in a hydrogen atmosphere are heated to 1200 °C to deposit zirconium carbide films on tool bits. Pure zirconium metal powder and fine graphite powder react exothermically, once ignited, to form zirconium carbide, usually to form a composite with an excess of one reagent.

2.13. Zirconium Nitrides

Zirconium nitride [25658-42-8], ZrN , is a golden-colored, hard, brittle metallic nitride. It is thermally and chemically stable, and has low resistivity. As with the carbide, it is an interstitial compound with a NaCl cubic structure. At 2000 °C, nitrogen is soluble in liquid zirconium up to 39 atom% nitrogen. Zirconium nitride is a single phase within the concentration range of 39–50 atom% nitrogen [87, 88]. While 3253 K is the accepted melting point of zirconium nitride, the melting temperature of 3970 K as measured in a positive pressure of nitrogen [89] is compatible with a thermodynamic study of the Zr–N system.

Zirconium nitride has been made by heating zirconium or zirconium hydride powder in nitrogen at 1000 °C, and by heating a zirconium oxide/carbon mixture in a nitrogen atmosphere. The reaction of zirconium tetrachloride with ammonia or nitrogen and hydrogen has been used to produce nitride powder and to deposit coherent films on substrates at 1000–1200 °C. Very limited quantities of nitride have been made by the very exothermic reaction of lithium nitride and zirconium tetrachloride powders [90].

Metastable Zr_3N_4 has been made by dual ion beam deposition [91] and by reacting zirconium tetraiodide with ammonia at 500 °C and heating the product to Zr_3N_4 at 700 °C [92]. On further heating to 1000 °C ZrN is formed. Thin films of Zr_3N_4 have been grown by passing ammonia and tetrakis(diethylamido)zirconium over substrates at 200–400 °C [93].

Zirconium nitride has been used as a wear-resistant coating on steel drill bits and cemented-carbide tool bits, as decorative coating, as a protective coating on steel vessels handling molten metal, and as solar energy collector surface film.

2.14. Zirconium Borides

While three zirconium borides, ZrB , ZrB_2 and ZrB_{12} , are found in the zirconium–boron system, only the diboride is chemically and thermally stable. Zirconium diboride [12045-64-6] is a gray refractory solid with a hexagonal crystal structure and a very high melting point of 3245 °C. Technical-quality zirconium diboride can be prepared by reacting zircon, boron oxide, and carbon in a submerged-electrode arc furnace [94]. Purer diboride can be produced by co-reduction of zirconium tetrachloride and boron trichloride with hydrogen or aluminum in a chloride bath. Zirconium diboride films can be produced by subliming zirconium tetrahydridoborate at 25 °C in a vacuum and passing the vapor over a substrate heated to 250 °C.

Zirconium diboride has high hardness, good oxidation resistance, and excellent thermal-shock resistance. It has been used as a diffusion barrier in semiconductors, as a container for molten metals, and as a burnable absorber in nuclear reactor cores.

2.15. Zirconium Tetrahydridoborate

Zirconium tetrahydridoborate [12370-59-1], $\text{Zr}(\text{BH}_4)_4$, is prepared by reaction of zirconium tetrachloride with lithium tetrahydridoborate in diethyl ether, followed by double distillation at 20 °C [95]. It has a tetrahedral structure with three hydrogen atoms bridging the zirconium atom and each boron atom. Zirconium tetrahydridoborate is one of the most volatile zirconium compounds known: *mp* 29 °C; *bp* 118 °C; vapor pressure 2 kPa at 25 °C. Its decomposition near 250 °C forms the basis for a low-temperature method of depositing zirconium boride films. Zirconium tetrahydridoborate catalyzes the polymerization of unsaturated hydrocarbons. It reacts with aliphatic alcohols to form zirconium and boron alkoxides [96]. Zirconium tetrahydroborate inflames on contact with dry air.

2.16. Zirconium Tungstate

Zirconium tungstate is precipitated as a white gel by simultaneous addition of dilute solutions of

sodium tungstate and zirconium hydroxide dichloride to vigorously stirred water. After acidification the slurry is refluxed. The dried and fired product is ZrW_2O_8 [97]. Other studies indicate that ZrW_2O_8 formed by the reaction of a mixture of ZrO_2 and WO_3 which is held between 1100 and 1400 °C for at least 24 h melts incongruently at 1257 °C and dissociates below 1105 °C [98]. ZrW_2O_8 is an unusual compound which contracts equally in each dimension when it is heated over the temperature range 1–1050 K [99].

2.17. Zirconium Phosphate

Insoluble, amorphous zirconium phosphate is obtained when a zirconium salt is added to an excess of phosphoric acid. If the original salt was solid rather than in solution, the resulting phosphate will have a similar physical size and shape: i.e., beads, granules, fibers. Refluxing the precipitate in strong phosphoric acid gives a crystalline product of constant composition, $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$. Zirconium bis(monohydrogenphosphate) with one water of hydration is known as α -zirconium phosphate. Below 80 °C a second water of hydration is added to form γ -zirconium phosphate. On heating α -zirconium phosphate, the water is lost between 300 and 650 °C, leaving β -zirconium phosphate. Conversion to zirconium pyrophosphate, ZrP_2O_7 , occurs between 800 and 920 °C [100].

Zirconium bis(monohydrogenphosphate) has ion exchange properties and, because of its structure and bonding between layers, can also act as an intercalation compound [101]. Zirconium phosphate shows excellent catalytic activity for the selective condensation of acetone to mesityl oxide, and when palladium is deposited on the phosphate surface the combination is an effective catalyst for the direct synthesis of methyl isobutyl ketone from acetone and hydrogen [102].

The addition of univalent ions Li, Na, K and compensating trivalent ions In, Y, Eu into ZrP_2O_7 produces a solid electrolyte [103]. Ultra-low thermal expansion ceramics have been developed in the $\text{Na}_2\text{O}-\text{ZrO}_2-\text{P}_2\text{O}_5-\text{SiO}_2$ system [104], while the addition of vanadium to sodium zirconium pyrophosphate: $\text{Na}_2\text{PrP}_{2-x}\text{V}_x\text{O}_7$ yields a ceramic which shrinks when heated above 60 °C [105].

2.18. Zirconium Nitrates

Zirconium hydroxide dinitrate [20213-65-4], $\text{Zr}(\text{OH})_2(\text{NO}_3)_2$, is formed by dissolving hydrous zirconium oxide in nitric acid or by dissolving zirconium hydroxide dichloride in nitric acid and distilling off the chlorine.

Zirconium tetranitrate [12372-57-5], $\text{Zr}(\text{NO}_3)_4 \cdot 5 \text{H}_2\text{O}$, can be precipitated from strong nitric acid at low temperature, less than 15 °C [106].

2.19. Zirconium Carboxylates

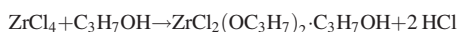
Zirconium hydroxide carboxylates form upon adding carboxylate salts to a solution of zirconium dihydroxide chloride, or carboxylic acids to zirconium basic carbonate. The general formula is $\text{Zr}(\text{OH})_{4-n}(\text{OOR})_n$, where n is 1–3 usually.

When zirconium basic carbonate paste is slowly stirred into a mineral spirit solution of octanoic acid, a solution of zirconium dihydroxide octanoate is produced which is of use in oil-based paints as a dryer catalyst.

Short-chain carboxylates may be soluble, i.e., zirconium dihydroxide diacetate. Longer aliphatic chain carboxylates (zirconium soaps) are water insoluble [107].

2.20. Zirconium Alkoxides

Zirconium alkoxides are prepared by adding zirconium tetrachloride to anhydrous alcohols [108]:



If there is no steric hindrance, all four chlorines can be exchanged if ammonia is added to combine with the hydrogen chloride.

Alkoxides of different alcohols can be formed by alcohol exchange. This can be facilitated by removal of the more volatile alcohol, or a lower-boiling azeotrope with an inert solvent, such as benzene. The conversion of zirconium tetramethoxide by refluxing with tertiary butanol proceeds only to zirconium methoxide tri-*tert*-butoxide because of steric factors. The following order was found in the interchange of alkoxy groups:



The reaction of *tert*-butanol with zirconium tetrahydridoborate yielded a double alkoxide complex of zirconium *tert*-butoxide with bis (*tert*-butoxy) borane [96].

Zirconium alkoxides hydrolyze quite easily. This provides a route to high-purity, high-surface-area zirconium oxide.

3. Analysis

Analysis for zirconium in ore, soil, vegetation in compounds, and as a minor alloying constituent involves bringing the zirconium into solution, then precipitating with mandelic acid [109] and firing the precipitate to oxide. For the determination of zirconium in air samples, plasma emission spectroscopy is used.

Methods to determine the hafnium associated with the zirconium include atomic absorption spectroscopy, emission spectroscopy, mass spectroscopy, X-ray spectroscopy, and neutron activation.

Most impurities in zirconium and zirconium compounds are determined by emission spectroscopy, with arc-spark [110] or plasma excitation [111, 112]. Atomic absorption is also used to determine a variety of impurities [113].

Carbon and sulfur in zirconium are measured by combustion followed by chromatographic or IR determination of the oxides [114]. Hydrogen is determined by thermal conductivity after hot-vacuum extraction, or by fusion of zirconium with a transition metal in an inert atmosphere and subsequent separation by gas chromatography [115, 116].

Simultaneous determination of oxygen and nitrogen is accomplished by fusion of zirconium with a transition metal in the presence of carbon in an inert atmosphere and subsequent separation by gas chromatography [117, 118]. Nitrogen can be determined by the Kjeldahl technique [114].

Phosphorus may be determined by visible spectrophotometry using molybdenum blue [114] but can be determined more rapidly by phosphine evolution and flame emission spectroscopy.

Chloride at low level is determined indirectly by precipitation with silver nitrate and determination of the silver by X-ray or atomic absorption spectroscopy. Fluoride and higher levels of chloride can be measured by selective ion electrode techniques [119, 120].

4. Toxicology

Zirconium and its compounds are generally of low toxicity. However, the strongly acidic compounds, such as zirconium tetrabromide, zirconium tetrachloride, zirconium tetrafluoride, zirconium tetraiodide, zirconium tetranitrate and zirconium sulfate are strongly corrosive to eyes, lungs, skin, mouth, esophagus, and stomach. Exposure to these compounds should be avoided, not because they contain zirconium, but because of the acidic nature of their hydrolysis products generated upon contact with animal or plant tissue.

Inhalation of zirconium materials in the workplace has not resulted in significant toxicity in 40 years of considerable exposure if reasonable care was used. One case of pulmonary fibrosis, believed to have been induced by heavy and continued exposure to zirconium oxide dust while preparing slurries for lens polishing, developed after a 15-year latency period [121]. Severe respiratory tract irritation from inhaling zirconium acetoacetate disappeared after exposure ceased [122]. In 1978 the FDA banned the production of antiperspirant aerosols containing zirconium because of concern about possible lung granulomas.

Inhalation laboratory tests with insoluble zirconium oxide varied. Some showed no effect, some caused fibrosis. Russian tests with the insoluble compounds zirconium boride [123] and zirconium hydride [124] both showed fibrogenic action in the lungs of albino rats. Aerosols of soluble zirconium dihydroxide chloride and zirconium dihydroxide nitrate each caused intense irritation of upper breathing passages similar to the action of strong acid. The animals died within 30–40 min. Sodium zirconium lactate caused lung granulomatosis in rabbits [125], and it is indicated that a complex of zirconium chlorhydrate and aluminum chlorhydrate also induces granulomatous lung changes [126].

Antiperspirants and poison ivy remedies containing zirconium have caused skin granulomas as a delayed hypersensitivity reaction in a few users [127].

Toxicity tests on laboratory animals showed that the acute toxicity of inorganic zirconium salts is very low when administered orally. Administered intraperitoneally, both organic and

Table 5. Toxicity data (rat) for some zirconium compounds [129]

Compound	Oral LD ₅₀ , mg/kg	Inhalation LCLo, mg/m ³
Dihydroxide chloride	3500	500 for 30 min
Dihydroxide nitrate	2290	500 for 30 min
Sulfate	3500	
Tetrachloride	1688	3124 ppm HCl for 1 hour
Acetate	4100	

inorganic compounds were 2–20 times more toxic.

An excellent summary of zirconium toxicology through 1975 is available [128]. Toxicity data for some zirconium compounds is shown in Table 5.

The OSHA exposure limit for zirconium and zirconium compounds as airborne particulate is 5 mg/m³ TWA and 10 mg/m³ STEL, as zirconium. In Germany, the MAK is 5 mg/m³ as zirconium. In Russia, MAK is 6 mg/m³ as zirconium.

5. Storage and Transportation

High-surface-area zirconium metal, such as sponge or powder is a combustible solid which should be kept dry and stored away from sources of ignition and oxidizers.

The Department of Transportation has classified all dry zirconium powder as “spontaneously combustible”, hazard class 4.2, with identification number UN 2008. The powders are subdivided into packing group I, II, or III, as evaluated by their burning rate in a standardized testing procedure. Group I is for very fine zirconium powder which is a pyrophoric material. Group I powder may not be shipped by air.

Some zirconium powder, usually fuse powder, is recovered wet and shipped wet. This powder is classified as a flammable solid, hazard class 4.1, UN 1358.

Zirconium hydride is classified as a flammable solid, hazard class 4.1, UN 1437.

Zirconium nitrate is classified as an oxidizer, hazard class 5.1, UN 2728.

Zirconium sulfate is classified as corrosive, hazard class 8, NA 9163.

Zirconium tetrachloride is classified as corrosive, hazard class 8, UN 2503.

References

- 1 A.E. van Arkel, J.H. de Boer, *Z. Anorg. Allg. Chem.* **148** (1925) 345–350.
- 2 J.H. De Boer, J. D. Fast, *Z. Anorg. Allg. Chem.* **153** (1926) 18.
- 3 W.J. Kroll, *J. Franklin Inst.* **260** (1955) 169–192.
- 4 O. Botstein, A. Rabinkin, M. Talianker, *Scr. Metall.* **15** (1981) 151–155.
- 5 T.L. Yau in C.S. Young, J.C. Durham (eds): *Industrial Applications of Titanium and Zirconium*: Fourth Conference STP 917. American Society for Testing and Materials. Philadelphia 1986, pp. 57–68.
- 6 T.L. Yau, R.T. Webster in: *Metals Handbook*, 9th ed., vol. 13, Corrosion, ASM International, Metals Park, Ohio, 1987, pp. 707–721.
- 7 B. Mason: *Principles of Geochemistry*, 3rd ed., Wiley & Sons, New York 1966, p. 45.
- 8 H.L. Gilbert, C.Q. Morrison, A. Jones, A.W. Henderson, *Bur. Mines Invest.* **5091** (1954) .
- 9 H.S. Choi, *Can. Min. Metall. Bull. Trans.* **67** (1965) 65–70.
- 10 P.H. Wilks, *Chem. Eng. Prog.* **68** (1974) .
- 11 Kawecki Chemical, US 2 653 855, 1953 (H.C. Kawecki).
- 12 A.J. Hudson, A.C. Haskell, Jr., *Electr. Furn. Conf. Proc.* **1958**, 211–220.
- 13 G. von Hevesy, *Chem. Rev.* **2** (1925) 1.
- 14 N.P. Sajin, E.A. Pepelyaeva, *Proc. Int. Conf. Peaceful Uses At. Energy. 8th* 1956, pp. 559–562.
- 15 J.M. Googin in F.R. Bruce, J.M. Fletcher, H.H. Hyman (eds.): *Progress in Nuclear Energy Series 3*, Process Chemistry, vol. 2, Pergamon Press, Oxford 1958, pp. 194–209.
- 16 R.H. Nielsen, R.L. Govro, *Bur. Mines, Invest.* **5214**, (1956) .
- 17 N.P.H. Padmanabhan, T. Sreenivas, N.K. Rao, *High Temp. Mater. Process* **9** (1990) no. 2–4, 217–247.
- 18 L. Moulin, P. Thouvenin, P. Brun in D. G. Franklin, R.B. Adamson (eds.): “Zirconium in the Nuclear Industry: Sixth International Symposium”, *ASTM Spec. Tech. Publ.* **824** (1984) 37–44.
- 19 J.A. Megy, H. Freun, *Metall. Trans. B* **10 B** (1979) 413–421.
- 20 F.W. Starratt, *J. Met.* **II** (1959) 441–443.
- 21 A.P. Lamaze, D. Charquet in K.C. Liddell, D.R. Sadoway, R.G. Bautista (eds.): *Refractory Metals: Extraction, Processing and Applications*, The Minerals, Metals & Materials Society, Warrendale, PA, 1990, pp. 231–253.
- 22 S.N. Flengas, G.J. Kipouros, P. Tumidajski, *Met. Mater. Processes* **2** (1990) no. 3, 151–177.
- 23 Z.M. Shapiro in B. Lustman, F. Kerze, Jr. (eds.): *The Metallurgy of Zirconium*, McGraw-Hill, New York 1955, pp. 135–215.
- 24 R.F. Rolston: *Iodide Metals and Metal Iodides*. The Electrochemical Society, New York 1961.
- 25 ASTM Specification B614: Descaling and Cleaning Zirconium and Zirconium Alloy Surfaces.

- 26 Chemetall, WO 20057906, 2005 (M. Bick, B. Sermond, G. Wilfing).
- 27 Chemetall's "Precautionary Handling Advice for Zirconium, Zirconium hydride, Titanium, Titanium hydride, and Zr/Ni alloys in powder form," Chemetall GmbH, Jan. 2009, http://www.specialmetals.chemetall.com/pdf/A750DF8DEC190B2BC1256E-FA0073AEDA_0.pdf
- 28 T.L. Yau in R.T. Webster, C.S. Young (eds.): "Industrial Application of Titanium and Zirconium: Third Conference", *ASTM Spec. Tech. Publ.* **830** (1984) 124.
- 29 J.H. Schemel: "ASTM Manual on Zirconium and Hafnium," *ASTM Spec. Tech. Publ.* (1977).
- 30 R.I. Jaffee in Z.M. Shapiro in B. Lustman, F. Kerze, Jr. (eds.): *The Metallurgy of Zirconium*, McGraw-Hill, New York 1955, pp. 26–29.
- 31 D.A. Lorimer, E.J. Baker, M. Succi, D.K. Weber, *Solid State Technol.* **33** (1990) 77–79.
- 32 A. Clearfield, *Rev. Pure Appl. Chem.* **14** (1964) 91–108.
- 33 J.A. Speer in P.A. Ribbe (ed.): *Orthosilicates*, 2nd ed., Mineralogical Society of America, Washington D. C. 1982.
- 34 R.C. Garvie, R.H. Hannink, R.T. Pascoe, *Nature (London)* **258** (1975) 703–704.
- 35 R.C. Garvie in A.E. Alper (ed.): *High Temperature Oxides*, part II. Academic Press, New York 1970, pp. 117–166.
- 36 A.H. Heuer, L.W. Hobbs (eds.): *Science and Technology of Zirconia*, American Ceramic Society, Columbus, Ohio, 1981.
- 37 N. Claussen, M. Ruhle, A.H. Heuer (eds.): *Science and Technology of Zirconia II*. American Ceramic Society, Columbus, Ohio 1984.
- 38 S. Somiya, N. Yamamoto, H. Yanagida (eds.): *Science and Technology of Zirconia III*, American Ceramic Society, Westerville, Ohio, 1988.
- 39 S. Meriani, C. Palmonari (eds.): *Zirconia '88—Advances in Zirconia Science and Technology*. Elsevier Appl. Sci., London 1989.
- 40 S.P.S. Badwal, M.J. Bannister, R.H.J. Hannink (eds.): *Science and Technology V*, Technomic Publishing Co., Lancaster 1993.
- 41 R. Stevens: *Zirconia and Zirconia Ceramics*, 2nd ed., Magnesium Elektron, Manchester, UK, 1986.
- 42 A. Pissenberger, G. Gritzner, *J. Mater. Sci. Lett* **14** (1995) 1580–1582.
- 43 G. Gritzner, C. Puchner, J. Dusza, *J. Eur. Ceram. Soc.* **15** (1995) 45–49.
- 44 Y. Sugizaki et al., *J. Phys. Soc. Japan*, **54** (1985) 2543–2551.
- 45 R.J. Ackerman, E.G. Rauh, C.A. Alexander, *High Temp. Sci.* **7** (1975) 304–316.
- 46 J.F. Menckus, *J. Crystl. Growth* **128** (1993) 13–14.
- 47 G.H. Haertling, C.E. Land, *Am. Ceram. Soc. Bull.* **49** (1970) 411.
- 48 R. Srinivason, B.H. Davis, *Catal. Lett.* **14** (1992) 165–170.
- 49 G.T. Mamott et al. *J. Mater. Sci.* **26** (1991) 4054–4061.
- 50 M. Henry, J.P. Jolivet, J. Livage, *Struct. Bonding (Berlin)* **77** (1992) 153–206.
- 51 R.C. Garvie, *J. Phys. Chem.* **69** (1968) 1238–1243.
- 52 Societe Europeen des Produits Refractaires, US 5 149 510, 1992 (J. Recasens, D. Urffer, P. Ferlanda).
- 53 W.W. Stephens, H.L. Gilbert, *J. Met.* **194** (1952) 733–737.
- 54 Electro Metallurgical Co., US 2 433 253, 1948 (W.J. Kroll, F.E. Bacon).
- 55 B. Krebs, *Angew. Chem. Int. Ed. Engl.* **8** (1969) 146–147.
- 56 M. Ohashi, S. Yamaoka, Y. Morimoto, M. Hattori, *Bull. Chem. Soc. Jpn.* **60** (1987) 2387–2390.
- 57 S.N. Flengas, P. Pint, *Can. Met.* **8** (1969) 151–166.
- 58 A.W. Strauss, J.D. Corbett, *Inorg. Chem.* **9** (1970) 1373–1376.
- 59 D.G. Adolphson, J.D. Corbett, *Inorg. Chem.* **15** (1976) 1820–1823.
- 60 J.D. Corbett, *Pure Appl. Chem.* **56** (1984) 1527–1543.
- 61 H.S. Marek, J.D. Corbett, R.L. Daake, *J. Less Common Metals* **89** (1983) 243–249.
- 62 A. Clearfield, P.A. Vaughan, *ACTA Crystallogr.* **9** (1956) 555–558.
- 63 K.I. Arsenin, L.A. Malinko, I.A. Sheka, I. Ya Pishcai, *Russ. J. Inorg. Chem. (Engl. Transl.)* **35** (1990) 1327–1331.
- 64 M.D. Atherton, H. Sutcliffe, *J. Less Common Met.* **138** (1988) 63–70.
- 65 Teledyne, WO 94/12435, 1993 (J.A. Sommers).
- 66 L.M. Seaverson, J.D. Corbett, *Inorg. Chem.* **22** (1983) 3202–3210.
- 67 K. Dehnicke, J. Weidlein, *Angew. Chem. Int. Ed. Engl.* **5** (1966) 1041.
- 68 R.L. Daake, J.D. Corbett, *Inorg. Chem.* **16** (1977) 2029–2033.
- 69 E.M. Larsen, J.S. Wrazel, L.G. Hoard, *Inorg. Chem.* **21** (1982) 2619–2624.
- 70 D.H. Guthrie, J.D. Corbett, *Inorg. Chem.* **21** (1982) 3290–3295.
- 71 Teledyne, WO 89/1087, 1989 (J. A. Sommers).
- 72 M. Robinson, K.C. Fuller, *Mater. Res. Bull.* **22** (1987) 1725–1732.
- 73 W.J.S. Craigie, E.G. Joe, G. M. Ritchey, *Can. Met. Q.* **9** (1970) 485–492.
- 74 National Lead, US 2 525 474, 1950 (W.B. Blumenthal).
- 75 ICI Australia, WO 86/06362, 1986 (K. Ngian, A.J. Hartshoren, D.H. Jenkins).
- 76 I.J. Bear, W.G. Mumme, *Rev. Pure Appl. Chem.* **21** (1971) 189–211.
- 77 P.J. Squattrito, P.R. Rudolf, A. Clearfield, *Inorg. Chem.* **25** (1987) 4240–4244.
- 78 Hopton Technologies, US 5 472 485, 1995 (V.E. Pandian, C.V. Calcar, R.W. Wolff).
- 79 Nalco Chemical, US 5 230 774, 1993 (C.S. Greer, N.P. James).
- 80 T.B. Massalski (ed.): *Binary Alloy Phase Diagrams*, 2nd ed., ASM International, Materials Park, Ohio, 1990, pp. 2078–2080.
- 81 W.M. Mueller, J.P. Blackledge, G.G. Libowitz: *Metal Hydrides*, Academic Press, New York 1968, pp. 241–321.
- 82 J. Rexer, D.T. Peterson: *Nuclear Metallurgy, International Symposium on Compounds of Interest in Nuclear*

- Reactor Technology*, vol. X, AIME, New York 1964, p. 327.
- 83 A.W. Struss, J.P. Corbett, *Inorg. Chem.* **16** (1977) 360.
- 84 R.V. Sara, *J. Am. Ceram. Soc.* **48** (1965) 243–247.
- 85 E. Rudy: *Compendium of Phase Diagram Data*, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio, 1969.
- 86 Norton Co., US 3 161 470, 1958 (J. J. Scott).
- 87 T. Ogawa, *J. Alloys and Compounds* **203** (1994) 221–227.
- 88 W.E. Wang, D.R. Olander, *J. Alloys and Compounds* **224** (1995) 153–158.
- 89 M.A. Eronyan, R.G. Avarbe, *Inorg. Mater. (Engl. Transl.)* **10** (1974) 1850.
- 90 E.G. Gillan, R.B. Kaner, *Inorg. Chem.* **33** (1994) 5693–5700.
- 91 B.O. Johansson, H.T.G. Hentzell, J.M.E. Harper, J.J. Cuomo, *J. Mater. Res.* **1** (1986) 442–451.
- 92 R. Juza, A. Rabenau, I. Nitschke, *Z. Anorg. Allgem. Chem.* **332** (1964) 1–4.
- 93 R. Fix, R.G. Gordon, D.M. Hoffman, *Chem. Mater.* **3** (1991) 1138–1148.
- 94 J.C. McMullen, W.D. McKee Jr., *Am. Ceram. Soc. Bull.* **44** (1965) 448–491.
- 95 B.D. James, B.E. Smith, *Synth. React. Inorg. Met. Org. Chem.* **4** (1974) 461–465.
- 96 L.A. Petrova, A.P. Borisov, V.D. Makhaev, *Sov. J. Coord. Chem. (Engl. Transl.)* **18** (1992) 425–428.
- 97 A. Clearfield, R. H. Blessing, *J. Inorg. Nucl. Chem.* **36** (1974) 1174–1176.
- 98 L.L.Y. Chang, M.G. Scroger, B. Phillips, *J. Am. Ceram. Soc.* **50** (1967) 211–215.
- 99 T.A. Mary et al., *Science* **272** (1996) 90–92.
- 100 A. Clearfield, J.A. Stynes, *J. Inorg. Nucl. Chem.* **26** (1964) 117–129.
- 101 U. Costantino in A. Clearfield (ed.): *Inorganic Ion Exchange Materials*, CRC Press, Boca Raton 1982.
- 102 Y. Watanabe, Y. Matsumura, Y. Izumi, Y. Mizutani, *Bull. Chem. Soc. Jpn.* **47** (1974) 2922–2925.
- 103 R. Sacks, Y. Avigal, E. Banks, *J. Electrochem. Soc.* **129** (1982) 726–729.
- 104 J. Alamo, R. Roy, *J. Am. Ceram. Soc.* **67** (1984) C 78–82.
- 105 V. Korthuis et al. *Chem. Mater.* **7** (1995) 412–417.
- 106 W.B. Blumenthal: *The Chemical Behavior of Zirconium*, D. Van Nostrand, Princeton 1958, p. 286.
- 107 W.B. Blumenthal: *The Chemical Behavior of Zirconium*, D. Van Nostrand, Princeton 1958, p. 319.
- 108 D.C. Bradley, R.C. Mehrota, D.P. Gaur: *Metal Alkoxides*, Academic Press, London 1978, pp. 10–41.
- 109 R.B. Hahn, E.S. Baginski, *Anal. Chim. Acta* **14** (1965) 45–47.
- 110 R. Brayer, R. O'Connell, A. Powell, R.H. Gale, *Appl. Spectrosc.* **15** (1961) 10–13.
- 111 G.L. Beck, O.T. Farmer, *J. Anal. Spectrom.* **3** (1988) 771–773.
- 112 G.L. Beck, J.P. Fraley, Teledyne Wah Chang procedure ASP-OES-1 Rev. 0, 1988.
- 113 J. Schlewitz, M. Shields, *At. Absorpt. Newsl.* **10** (1971) 39–43.
- 114 R. VanSanten, J. Schlewitz, G. Beck, R. Walsh in F.D. Snell, L.S. Ettre (eds.): *Encyclopedia of Industrial Chemical Analysis*, vol. 14, Wiley-Interscience, New York 1971, pp. 103–148.
- 115 R. K. McGeary in: *A Symposium on Zirconium and Zirconium Alloys*, American Society for Metals, Cleveland 1953, pp. 168–175.
- 116 W.G. Guldner, *Talanta* **8** (1961) 191–202.
- 117 W.G. Smiley, *Anal. Chem.* **27** (1955) 1098–1102.
- 118 P. Ebling, G.W. Howard, *Anal. Chem.* **32** (1960) 1610–1613.
- 119 J. Surak, D. Fisher, C. Burros, L. Bate, *Anal. Chem.* **32** (1960) 117–119.
- 120 J. Lingane, *Anal. Chem.* **39** (1967) 881.
- 121 T. Bartter et al. *Arch. Intern. Med.* **151** (1991) 1197–1201.
- 122 M.Y. Longley et al.: *A Toxic Hazard Study of Selected Missile Propellants*, Technical Documentary Report no. ARML-TDR-64–28 Biomedical Lab., Aerospace Med. Res. Lab. Wright-Patterson Air Force Base, Ohio, 1964.
- 123 I.T. Brakhova: *Environmental Hazards of Metals. Toxicity of Powdered Metals and Compounds*, translated from the Russian (original pub. 1971) by S.L. Slep, Consultants Bureau, New York, NY, 1975.
- 124 I.T. Brakhova, G.A. Shkupko, *Gig. Sanit.* **37** (1972) 36–39.
- 125 J.T. Prior, G.A. Cronk, D.D. Ziegler, *Arch. Environ. Health* **1** (1960) 297–300.
- 126 “Aerosol Drug and Cosmetic Products Containing Zirconium. Proposed Determination,” *Fed. Regist.* **40** (1975) 24327–24344.
- 127 W.B. Shelley, H.J. Jurley Jr. in M. Sauter (ed.): *Immunological Diseases*, 2nd ed., Little, Brown & Co., Boston 1971, pp. 722–734.
- 128 I.C. Smith, B.L. Carson: *Trace Metals in the Environment*, vol. 3, Zirconium, Ann Arbor Science Publ., Ann Arbor 1978, pp. 173–371.
- 129 U.S. Registry of Toxic Effects of Chemical Substances.

Further Reading

- P. Enghag: *Encyclopedia of the Elements*, Wiley-VCH, Weinheim 2004.
- R. K. Jyothi: *Studies on Liquid-Liquid Extraction of Tetravalent Zirconium and Hafnium*, VDM Verlag Dr. Müller, Saarbrücken 2010.
- R. J. Lewis: *Hazardous Chemicals*, 6th ed., Wiley, Hoboken, NJ 2008.
- I. Marek (ed.): *New Aspects of Zirconium Containing Organic Compounds*, Springer, Berlin 2005.
- R. H. Nielsen, J. H. Schlewitz, H. Nielsen: *Zirconium and Zirconium Compounds*, *Kirk Othmer Encyclopedia of Chemical Technology*, 5th edition, vol. 26, p. 621–664, John Wiley & Sons, Hoboken, 2007, online: DOI: 10.1002/0471238961.26091803.a01.pub2 (January 2007)
- R. W. Revie, H. H. Uhlig: *Corrosion and Corrosion Control*, 4th ed., Wiley-Interscience, Hoboken, NJ 2008.
- S. Zhuiykov: *Electrochemistry of Zirconia Gas Sensors*, CRC Press, Boca Raton, FL 2008.