CHAPTER 12.43

Zirconium

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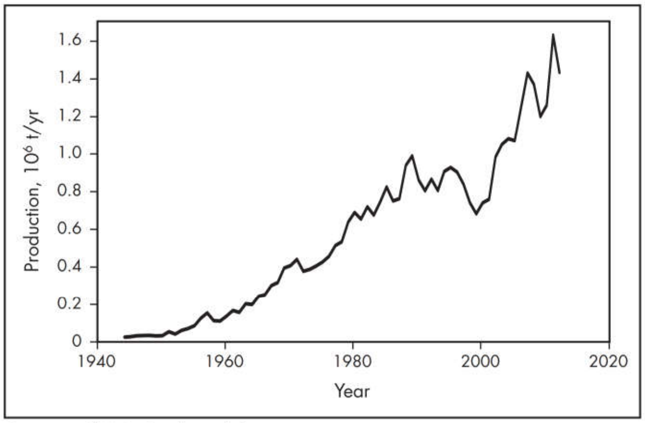
Zirconium is a silver-gray metal with a close-packed hexagonal crystal structure at room temperature. At 862°C, the crystal structure changes to a body-centered cubic structure. Both structures are very ductile, and the metal is easily machined, rolled, and extruded using conventional methods. Its principal alloys have outstanding resistance to corrosion in water and steam at high temperatures. Zirconium has a very low-capture cross section for thermal neutrons and is commonly used for fuel rod cladding and structural materials in nuclear power generation.

Zirconium naturally occurs as zircon ($ZrSiO_4$). It is found in zircon ore bodies and is a significant impurity in the titanium ore rutile. Zirconium ore contains between 1% and 4% hafnium as an impurity. Hafnium is highly resistant to hot water corrosion but exhibits a high-capture cross section for thermal neutrons and is commonly used for control rods in nuclear power generation.

Zirconium metal has two distinct industrial applications. Zirconium is exceptionally resistant to many common acids, alkalis, and seawater. Zirconium, used for its high corrosion resistance in nonnuclear applications, is manufactured with 1%–4% naturally occurring hafnium content, depending on the ore body. Nuclear-grade zirconium alloys (zircaloys) require that the hafnium content is reduced to less than 100 ppm from the naturally occurring ore levels. The cost of producing zirconium is higher than most common metals, limiting its use to specific applications.

PRODUCTION AND RESOURCES

Australia is the largest producer of zirconium concentrate, followed by South Africa and then China. This trend has not changed for the last 10 years. World production trends for zirconium concentrates are shown in Figure 1. Production statistics by country for 2017 are shown in Table 1. Current zirconium reserves are around 74 Mt (million metric tons). The largest reserves at 47 Mt are in Australia, followed by South Africa at 14 Mt.



Courtesy of U.S. Geological Survey

Figure 1 Zircon concentrate production trend

PRICE OF ZIRCON CONCENTRATES

The price trend for zircon concentrates for the 10-year period from 2007 to 2017 are shown in Table 2. The prices of zirconium concentrates rose dramatically during 2011; this was mainly caused by booming Chinese demand for zircon to meet the requirements of the ceramic and zirconium chemical sectors (Adams 2012). The subsequent decrease in world production and therefore price of zirconium mineral concentrates in 2013 was in response to weakened demand, particularly in China, because of a slowdown in housing construction.

ORE DEPOSITS

Zircon and the less common mineral, baddeleyite (ZrO_2), are found as accessory minerals in igneous rocks but rarely in economic concentrations. The world's largest primary deposits of zirconium are associated with alkaline igneous rocks. Baddeleyite is produced as a by-product from apatite and magnetite mining in Russia, Brazil, and South Africa.

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Table 1 Production and reserve statistics

Country	2017 Zirconium Concentrates, t	Zirconium Reserves, Mt ZrO_2
Australia	600,000	47
South Africa	400,000	14
China	140,000	0.5
Indonesia	120,000	Not applicable
Mozambique	75,000	1.8
Senegal	60,000	Not applicable
United States	50,000	0.5
India	40,000	3.4
Other countries	110,000	7.2
Total	**1,600,000**	**74**

Source: USGS 2007–2017

Table 2 Price of zircon concentrates*

Year	U.S. Domestic, $/t	U.S. Imported, $/t
2007	763	872
2008	788	773
2009	830	850
2010	850	860
2011	2,650	2,122
2012	2,650	2,533
2013	1,050	996
2014	1,050	1,106
2015	1,050	1,052
2016	1,025	877
2017	1,025	881

Source: USGS 2007–2017
*Prices are for domestic standard-grade bulk.

The main worldwide zircon ore deposits are heavy-mineral sands produced by the weathering and erosion of preexisting rocks and the concentration of zircon and other economically important heavy minerals, particularly in coastal environments. In coastal deposits, heavy-mineral enrichment occurs where sediment is repeatedly reworked by wind, waves, currents, and tidal processes. The resulting heavy-mineral sand deposits, called *placers* or *paleoplacers*, preferentially form at relatively low latitudes on passive continental margins and supply nearly all of the world's zircon.

Zircon makes up a relatively small percentage of the economic heavy minerals in most deposits and is produced primarily as a by-product of heavy-mineral sand mining for titanium minerals. Two styles of mineral sand deposits are found:

1. Strandline deposits are characterized by their relatively linear geometry.
2. Deposits found in the Wimmera region (WIM-style) of western Victoria, Australia, have a sheetlike geometry.

The strandline deposits tend to be coarse grained (>100 μm grain size), relatively rich, with grades in the range of 5%–20% heavy-mineral sands but are of relatively low tonnage. The WIM deposits are relatively fine grained (<100 μm grain size) with lower grades, in the range of 2%–5% heavy-mineral sands, but tonnages are generally at least one order of magnitude greater than that of the strandline deposits.

MINING

Mineral sands are mined using either wet or dry methods. Wet mining is by a dredge floating on the surface of a pond that is used to undercut the sand and pump the slurried sand to the wet processing plant usually situated in the pond behind the dredge. This method is generally used where access to water is not an issue. Dry mining uses large-scale earthmoving equipment (self-elevating scrapers, bulldozer traps, and front-end loaders) to excavate and transport the sand to the wet processing plant.

MINERAL PROCESSING

After mining, the ore is subjected to beneficiation process, which involves a wet primary concentration and a dry mineral separation. The primary concentration plant upgrades the run-of-mine ore by rejecting light gangue materials, such as quartz and shells, to produce a heavy-mineral concentrate (HMC) containing greater than 95% heavy mineral with minimum losses of valuable heavy minerals, such as ilmenite, rutile, and zircon. After separation of ilmenite and rutile by magnetic and high-tension (HT) separators, the rest of the HMC is subjected to zircon recovery processes.

In the wet processing plant, the heavy minerals are separated from the lighter gangue mineral, mainly quartz, by gravity methods, usually spirals and shaking tables. The light, rejected minerals in the processing plant (e.g., quartz, feldspar, mica, and clay minerals) are returned to the mined-out area of the mine, usually behind the dredge. The resulting HMC, containing up to 85%–98% heavy minerals, is composed mainly of ilmenite, zircon, rutile, and leucoxene, with smaller amounts of monazite, xenotime, and aluminum silicate minerals, such as garnet, kyanite, sillimanite, and staurolite.

In spiral separations, the slimes can affect the rheology of the slurry, preventing a clean separation of valuable mineral into the concentrate, thus increasing the loss of fine heavy-mineral particles into the tailings. As well, the mineral grains are often coated with iron oxides or clay minerals that can affect their magnetic and electrostatic properties, and so, the subsequent separations of the minerals. Desliming of the ore by attritioning and removing the fines with hydrocyclones help overcome these particular problems (Pownceby et al. 2105).

A clean separation of the heavy minerals is not achieved in a single spiral separation; consequently, several stages of separation (e.g., rougher, middlings, cleaner, recleaner, and scavenger stages) are required to obtain a final acceptable HMC. Developments in spiral separators have resulted in improved metallurgical performance, and changes in construction materials have increased unit capacities, simplified operation, and increased the recovery of fine heavy minerals. However, for the fine-grained WIM-style deposits, the heavy minerals may not be recovered with acceptable recoveries and grades using conventional processing equipment.

The individual heavy minerals in the HMC are separated in the dry processing plant. This is achieved by a combination of magnetic separations to recover ilmenite and associated magnetic products; and electrostatic separations to separate rutile, a conductor, from zircon, a nonconductor (Pownceby et al. 2105).

The advent of rare earth magnets has provided higher-strength permanent magnetic separators that are widely applied in the mineral sands industry. The performance of these separators depends on their field strength (gauss level) and their shape (field gradient). Several types of rare earth magnetic separators are used, including rare earth roll magnetic separators; rare earth drum magnetic separators, for both wet and dry separations; and matrix-type separators, such as wet high-intensity magnetic separators.

These separators are applied to concentrate and separate heavy minerals in different sections of the processing circuit. As an example, low-intensity magnetic separation and wet high-intensity magnetic separation may be used for separation of ilmenite from an HMC. High-intensity magnetic separations, however, are required to remove residual magnetic minerals from the resulting nonmagnetic product containing rutile and zircon. Wet magnetic separators are usually considered to be efficient for minerals with particle sizes larger than 75 µm.

Traditional electrostatic separations in mineral sand operations use combinations of HT roll and electrostatic plate separators. Heating the concentrate to 110°–130°C before the electrostatic separation improves the separation of zircon from other minerals. Substantial middling streams of conductors and nonconductors can be generated that require recirculation to different parts of the circuit (Pownceby et al. 2105). Flotation has been used for processing environmentally sensitive minerals, such as monazite, that are a health hazard when present as airborne dust during dry processing (Dunkin 1953; Subramanya 1960; Senior et al. 1996; Bruckard et al. 1999).

Impurity Removal from Zircon Concentrates

Zircon collected in the nonconductors fraction from electrostatic separations usually still contains small amounts of other nonconducting impurity minerals, such as monazite and aluminum silicates (e.g., kyanite), that must be removed. Monazite has a higher magnetic susceptibility than zircon and can be removed with a magnetic separation and centrifugal-type gravity concentrators, such as a Kelsey centrifugal jig (Jones and Foster 2010; Van der Westhuyzen et al. 2011; Capps and Waldram 1986).

Radioactivity in zircon concentrates is usually caused by uranium and thorium and/or their decay products contained in the crystal lattice, in mineral or fluid inclusions, in cracks and fissures in the zircon grains, or in other radioactive minerals such as monazite, xenotime, allanite, tantalite, betafite, thorianite, thorite that are present in the zircon concentrate. A global limit of 500 ppm U + Th or U + (0.4 × Th) <100 ppm usually applies to zircon concentrates. However, there are some countries that have different limits. The lower the level of uranium and thorium, the higher the marketing potential. In many treatment plants, the radioactive zircons, which are often weakly magnetic, are separated out during processing.

In many instances, the final zircon concentrate may contain zircon grains that are discolored and stained with coatings of iron oxide or clay minerals that prevent its use in many applications. Attritioning in water, acid, or alkaline solutions has been used to dissolve these impurities. However, more vigorous chemical treatments are required in many situations to meet market specifications. Table 3 provides an example of the quality specifications of a premium-grade zircon concentrate. Methods that are generally used include the following:

Table 3 Premium-grade quality specifications

Constituent	Weight %
$ZrO_2 + HfO_2$	Minimum 66
TiO_2	Maximum 0.15
Al_2O_3	Maximum 0.45
Fe_2O_3	Maximum 0.10
SiO_2	32.80
U + Th, ppm	Maximum 500

- In the hot acid leach process, hot zircon is treated with moderately concentrated sulfuric acid and reacted in a kiln, after which the product is attritioned, neutralized, and dried. A variant of this process employs a plug flow reactor in place of the rotary kiln.
- In the zircon upgrading process, the zircon is heated to ~400°C, after which it is quenched in dilute sulfuric acid.

MARKETING

Approximately 54% of zircon is used in finely ground form in the ceramics industry, 14% goes into the foundry industry, and 11%–14% into refractory applications. A growing portion of the zircon mined worldwide is used for the extraction of the metals zirconium and hafnium or their further processing to produce zirconium chemicals.

Zircon used in the ceramics industry has a wide range of applications. It is used as zircon sand directly from the mine and as a milled product in the form of zircon flour. Many milled zircon products, which vary in grain size and purity, are available commercially. The following are the most commonly used grades of opacifier used in the ceramics industry:

- Grade 9 µm (d_{50} = 1.5–2.0 µm) is widely use in ceramic glazes.
- Grade 6 µm (d_{50} = 1.2–1.5 µm) is used in ceramic glazes, as a cheaper substitute for the 5-µm material in sanitary ware, and for fully vitrified unglazed tiles.
- Grade 5 µm (d_{50} = 0.8–1.2 µm) is the highest-use product in fully vitrified unglazed tiles and sanitary ware. This grade tends to be the benchmark because of its high value-added-to-volume ratio of 4:5.

The application of zircon is determined by the particle size of the ground zircon. In addition to particle size, other physical properties are important in marketing zirconium concentrates. These are shown in Table 4.

REFINING

Unlike most metals that utilize smelting to refine the raw ore, zirconium ore refining is accomplished using chemical processes. Zirconium ore contains significant quantities of silicon, hafnium, iron, and aluminum.

Separation

Raw zirconium ore is dissolved and chemically processed to remove the silicon, iron, and aluminum, resulting in an aqueous solution of zirconium. Zirconium is then separated from the hafnium using a liquid–liquid separation process, where the zirconium resides in the aqueous phase and the hafnium in the organic phase that floats atop the aqueous phase. The resultant zirconium solution is precipitated as a zirconium sulfate, which is subsequently roasted in a rotary kiln to convert the sulfate to an oxide. The result is a very pure, finely divided ZrO_2 powder.

Table 4 Physical properties and applications

	Application			
Physical Properties	**Ceramics**	**Abrasives**	**Refractory**	**Foundry**
AFS*				X
Grain size distribution		X	X	X
Low loss on ignition	X	X	X	X
pH	X		X	X
Apparent density			X	
Low demand for acid				X
Color	X			X
Grain shape		X	X	X
Calcination	X			X
High tensile strength				X
High melting point	X		X	X
Great hardness		X		

Source: Pirkle and Podmeyer 1992

* American Foundry Society value for characterizing the grain fineness of foundry sand.

Chlorination

The manufacture of zirconium from ore is essentially identical to the manufacture of titanium. The commercial process predominantly used is the Kroll process, developed by William J. Kroll for manufacture of zirconium through carbochlorination of the ZrO_2 followed by subsequent reduction of the resultant zirconium tetrachloride ($ZrCl_4$) with magnesium to form pure zirconium metal and magnesium chloride salt. ZrO_2 powder is combined with a fine powdered petroleum coke (essentially pure carbon) and heated in a fluidized-bed reactor with pure chlorine as the fluidizing gas. $ZrCl_4$ vapor is condensed to pure zirconium tetrachloride powder. Unlike titanium, zirconium tetrachloride (and hafnium tetrachloride, as well) does not exhibit a stable liquid phase at ambient conditions and condenses from the vapor phase directly to a solid particle, as shown in the following reaction.

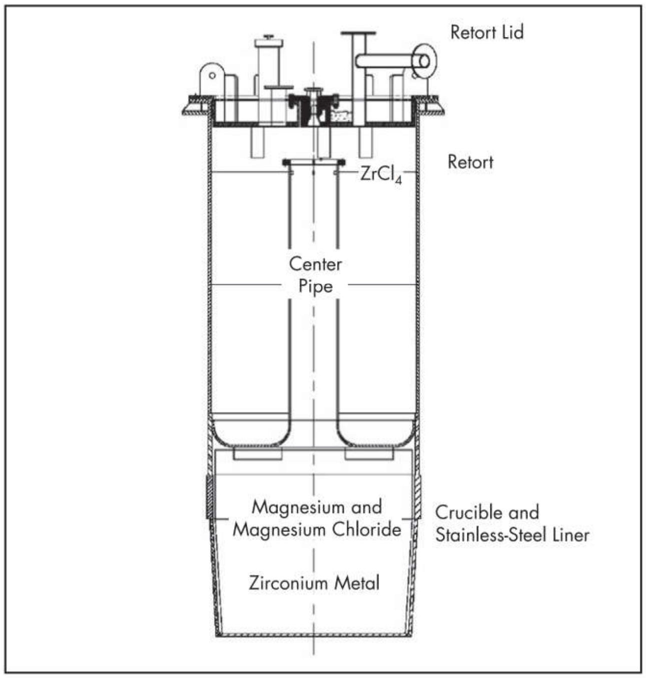
$$ZrO_2(s) + C(s) + 2Cl_2(g) + \text{heat} = ZrCl_4(g) + CO(g) + CO_2(g) \qquad \textbf{(EQ 1)}$$

Reduction

Processing of zirconium from a tetrachloride to a metal is similar to titanium and hafnium processing. Zirconium tetrachloride vapor is reacted with pure magnesium to form pure zirconium metal and magnesium chloride salt ($MgCl_2$), following the reaction:

$$ZrCl_4(g) + 2Mg(l) = Zr(s) + 2MgCl_2(l) + \text{heat} \qquad \textbf{(EQ 2)}$$

The processing of zirconium ore through the $ZrCl_4$ stage is typically accomplished in air, and the materials routinely are in contact with air. $ZrCl_4$ is hygroscopic, absorbing moisture (humidity) and creating a dilute hydrochloric acid (HCl) on its surface. Although the water is not necessarily a quality issue, the bound water can create a safety issue in subsequent processing.



Courtesy of Westinghouse Electric Company

Figure 2 Zirconium reduction retort

The zirconium tetrachloride is loaded into a large steel container called a retort. The retort is typically a very-large-diameter cylinder with a large-diameter center pipe protruding through the retort bottom and extending to near the retort top. Zirconium forms a eutectic compound with iron at the Zr/Mg reaction temperature, preventing the use of mild steel containment for the reaction products. Pure magnesium metal pigs are therefore loaded into a liquid-tight, cylindrical, stainless-steel liner inserted within a mild steel crucible, which is then welded to the bottom of the retort. A welded pressure-tight joint between the crucible and retort is required because the retort/crucible assembly is heated to 1,000°C and held for approximately 48 hours. A lid is then affixed to the top of the retort. The entire assembly is checked to ensure that it is leak tight. The entire assembly, as depicted in Figure 2, is then evacuated to remove all air and then backfilled to atmosphere with high-purity argon.

Magnesium and zirconium both readily react to form oxides and nitrides, thereby requiring an atmosphere with no residual air. Because the magnesium and $ZrCl_4$ have been in contact with air and the $ZrCl_4$ is hygroscopic, the feed materials hold a quantity of trapped moisture. While under vacuum, the assembly is heated to just below the $ZrCl_4$ sublimation temperature of 331°C to drive off any absorbed water vapor. Any water vapor allowed to remain in the assembly could react with the magnesium as it melts, creating magnesium oxide (MgO) and hydrogen gas. As the temperature increases, the vapor expands, building pressure within the assembly, which must be vented. The vented hydrogen vapors can react explosively with air. Therefore, all residual water must be removed along with the air.

The temperature of the top zone (top half) of the reduction furnace is controlled to sublime the $ZrCl_4$, typically no greater than 500°C. The bottom zone (bottom half) is heated above the melting point of magnesium (649°C) and held until most of the magnesium is molten and a vapor of magnesium is present. The sublimed $ZrCl_4$ vapor travels from the retort, down the center pipe, reacting with the molten magnesium and magnesium vapor, forming very finely divided zirconium particles ~10 µm in size in a bath of molten magnesium and magnesium chloride salt. Fine zirconium particles settle through the molten magnesium/magnesium chloride bath to the bottom of the crucible. The density of the magnesium is slightly lower than the molten magnesium salt, and the magnesium floats on top of the magnesium chloride salt, which continues the reaction.

The reaction of $ZrCl_4$ and magnesium is exothermic. The excess heat of reaction, within the retort and crucible assembly, can result in an acceleration of the sublimation of the $ZrCl_4$, causing a rapid increase in reaction rate. Reaction kinetics must be controlled to prevent this runaway reaction, resulting in a relatively lengthy reaction time.

After the complete consumption of the zirconium tetrachloride, the entire run is allowed to cool to room temperature at 1 atm of argon pressure. Because nitrogen reacts with hot zirconium, the only acceptable inert gases are helium and argon. When the entire run has cooled, the weld connection between the retort (top) and the crucible (bottom) is milled apart. The empty retort is washed and prepared for subsequent loading. The crucible now contains a regulus of zirconium metal on the bottom and solid magnesium chloride salt on top. The magnesium chloride is removed and processed as a coproduct. The zirconium metal regulus is a semisolid mass of very fine zirconium particles entrained in solidified magnesium metal and magnesium chloride salt mixture. Because magnesium chloride is highly hygroscopic, exposure of the zirconium regulus to the humidity in the air must be limited.

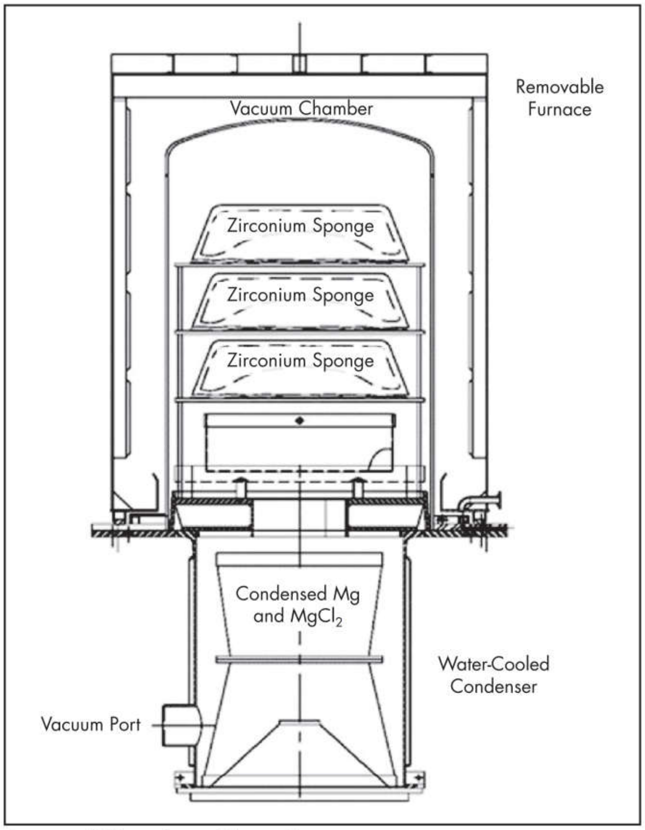
Vacuum Distillation

After removal of the zirconium sponge mass from the crucible, multiple zirconium reguluses are loaded into a vacuum furnace for vacuum distillation. A high vacuum is maintained while the zirconium reguluses are heated to temperatures above the vapor transition temperature for both magnesium and magnesium chloride. A water-cooled section of the furnace recondenses the vaporized magnesium and magnesium vapors. Figure 3 shows a schematic of a vacuum distillation vessel.

The size and density of the zirconium regulus limits the movement of the vapors from the interior of the regulus to the surface. As a result, the vacuum distillation process requires extended time at temperature. At the end of the distillation process, the temperature within the distillation furnace is raised to sinter the fine particles of zirconium into a semisolid mass. The zirconium reguluses are subsequently cooled to room temperature in an inert atmosphere. After distillation, the pores in the metal that previously contained the magnesium and magnesium chloride are now voids. The zirconium regulus now has the appearance of a metal sponge.

Newly formed zirconium metal has a high affinity for oxygen and, to a lesser extent, nitrogen. When freshly produced zirconium is initially exposed to air, the surface zirconium particles react rapidly with the air. The reaction is very exothermic, and extreme care must be exercised during air exposure and initial handling of the zirconium regulus to prevent ignition.

Zirconium burns extremely hot. Typically, a zirconium fire brightly glows, emitting very little smoke. Burning zirconium is highly reactive with water, forming $ZrO_2(s)$ and hydrogen gas. Therefore, zirconium fires should never be attacked with water or water-based extinguishers. Dry sand or fine table salt should be used. The sand or salt forms a crust that limits the exposure to air, eliminating the oxidizer. Zirconium fires should be buried and allowed to cool completely prior to cleanup.



Courtesy of Westinghouse Electric Company

Figure 3 Vacuum distillation furnace

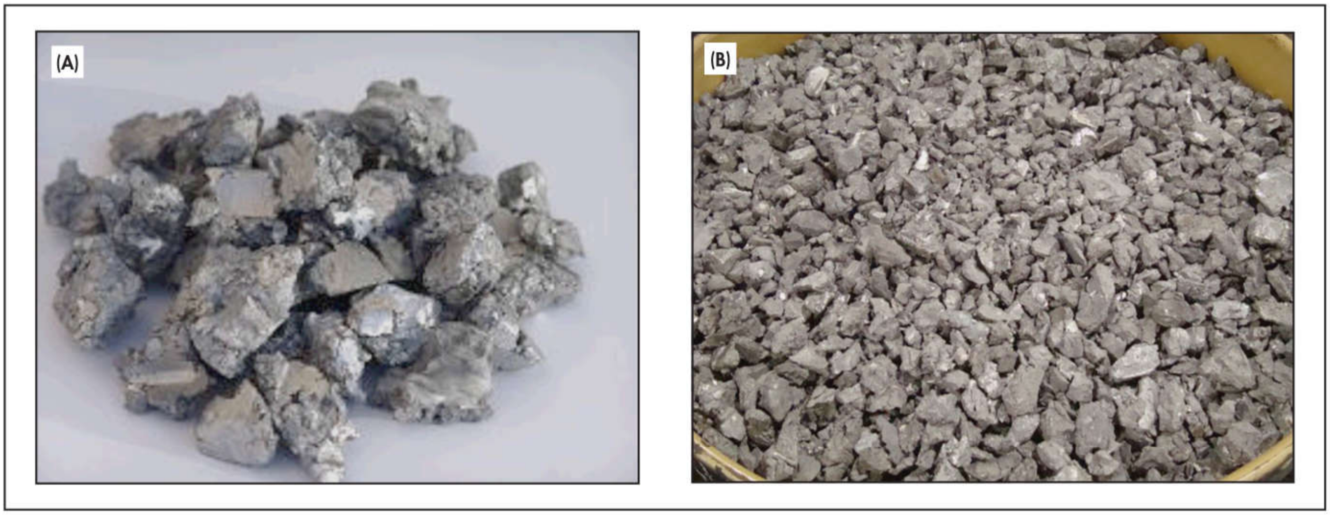
Before further processing, the entire surface of the regulus is visually inspected for rejectable materials. Rejectable materials are, for example, excessive residual metal chlorides and burned material. A mechanical press is usually used to break the large sponge mass into smaller pieces. These pieces are further shredded into sizes compatible with subsequent use (Figure 4).

To prevent fires, the mechanical shredding is usually performed in a sealed unit under a cover of argon gas. After shredding, the entire quantity of sponge is 100% visually inspected to remove any rejectable materials. The most common reject is burned sponge. Burned sponge contains a high proportion of ZrO_2 and zirconium nitride (ZrN) compounds. The ZrO_2 can result in elevated oxygen in the sponge, limiting its use. The presence of ZrN is a significant quality detractor because it has a very high melting point and limited solubility in molten zirconium. ZrN particles in sponge can result in hard nitride defects in products, causing failed final components.

After crushing and visual inspection, a sample is melted into a small ingot for chemical analysis. Because the sponge regulus is not uniform in chemistry across its entire volume, it is imperative that a representative sample of the entire crushed sponge mass is used for the evaluation ingot. Zirconium sponge has no direct applications as a finished product. Zirconium sponge can be used as an alloy addition in other metal systems such as aluminum, titanium, or steel.

MELTING

Melting of zirconium must be performed in furnaces isolated from exposure to air because zirconium reacts rapidly with air



Courtesy of Westinghouse Electric Company

Figure 4 Zirconium sponge

to form ZrO_2. Zirconium readily dissolves or is contaminated by all refractory materials. Consequently, zirconium melting is typically performed in water-cooled copper containment. Four typical furnace types are used to melt zirconium:

1. Vacuum arc remelting (VAR)
2. Electron beam melting (EBM)
3. Plasma arc melting (PAM)
4. Vacuum induction melting (VIM)

VAR and EBM are performed under a high vacuum, whereas PAM is performed in an atmosphere of argon and/or helium. Furnace type is selected for a specific material outcome.

Vacuum Arc Remelting

VAR is a consumable electrode melt that is very similar to arc welding. An electrode of alloyed zirconium is loaded into a water-cooled copper crucible with a gap between the outside of the electrode and the inside of the crucible. An arc is struck between the electrode and copper crucible bottom. A high-current, low-voltage arc melts the bottom of the electrode, which drips into the copper crucible, forming a solidifying ingot. At the end of the melt, the electrode has been consumed, creating a solidified ingot.

The entire electrode/ingot is never molten at the same time; therefore, the homogeneity of the input material along the entire length of the electrode is critical to produce a homogeneous final ingot. VAR is a high-throughput melt technique resulting in ingots up to 86 cm in diameter and weighing up to 9,072 kg.

The melting technique provides for exposure of the molten metal droplets to high vacuum, causing vacuum purification of the metal. The high power melt also results in a deep molten pool that mixes the alloy, resulting in good composition control. The melt rate is typically 14–41 kg/min. Because of the rapid melt rate, the purification from a single melt can be limited. Standard nuclear alloys require three consecutive melts. The primary melt electrode is very long but small in diameter. Each subsequent melt becomes shorter but increases in diameter. VAR melting is the predominant method for most zirconium manufacture.

Electron Beam Melting

EBM furnaces are of two types: drip melt and hearth melt. EBM takes place in a high-vacuum chamber. Under a high vacuum, high-energy beams of electrons are directed onto the zirconium metal. The beams are created by stripping electrons from a filament within an electron beam generator.

The electron beam operates at very high voltage and low current. EBM furnaces generate a significant quantity of high-energy X-rays. The furnaces typically are double walled with viewing systems of leaded glass, or they utilize cameras to prevent X-ray exposure.

In a drip melt furnace, the melt stock is suspended directly over a copper crucible. The electron beams impinge on the melt stock and the molten pool simultaneously, dripping the melt stock into the molten pool. The copper crucible has a moveable copper puller inserted into the bottom of the crucible. As metal is dripped in the top, the puller is slowly removed from the bottom, withdrawing a solidified ingot.

In the hearth melt furnace, solid or granular loose material is fed into a water-cooled hearth. The electron beams impinge on the metal in the hearth, melting the new material into the existing molten hearth. Once the hearth is adequately filled, the metal is allowed to overflow into a copper crucible with a puller. The electron beams heat the top of the withdrawing ingot to allow for a continuous ingot withdrawal.

EBM is much slower than VAR. The molten pool is relatively shallow, and the homogeneity of the electron beam melts is not as good as the VAR technique. The extremely high energy of the beam, the high vacuum, and the slow melt rate evaporate most of the highly volatile elements from the molten pool, which then deposit on the EBM chamber walls. EBM is typically used for purification melts. Alloy control is very difficult in EBM furnaces because large quantities of alloy must be added to compensate for the evaporation. The shape of the crucible is essentially unlimited in two dimensions. A semifinished shape can be made with the hearth/withdrawal system.

Plasma Arc Melting

PAM takes place in an inert atmosphere. The PAM furnace is typically a vacuum chamber with an inert gas system. When the furnace is closed, the vacuum system evacuates all of the air. The furnace is then back filled with either argon or helium. The hearth melting takes place exactly like EBM, with the exception of the heat source. In PAM, high-throughput plasma torches provide the energy for melting. Input material is fed into the hearth; the metal is melted and cast into an ingot by the hearth overflow system.

PAM is performed with a partial or full atmospheric pressure, significantly reducing the alloy loss caused by evaporation. With a PAM system, chemical composition control is much better than with an EBM system. As in EBM, the molten pool is relatively shallow. Additionally, because the melt takes place at a higher pressure, the refinement of the zirconium is limited in PAM.

Zirconium sponge contains small quantities of residual Mg and $MgCl_2$. VAR and EBM eliminate the high vapor pressure material through evaporation; PAM does not appreciably remove the volatile materials. Residual magnesium chloride in the final cast ingot results in microscopic longitudinal defects, known as *stringers*, in the fabricated product, which are detrimental to performance of the final components. The PAM furnace also uses a large quantity of inert gas, which can be very expensive. Expensive gas recovery systems are typical in PAM furnace operations.

Other Melting Methods

Most applications for zirconium are fabricated products. Several other techniques are infrequently used to melt zirconium that may or may not be fabricated.

Vacuum Induction Melting

VIM can be used to initially melt input materials of zirconium sponge, recycle, and alloy to form a primary melt ingot for subsequent VAR. VIM can also be utilized to create a volume of molten alloyed zirconium that can be used to pour castings.

VIM is performed by melting a volume of zirconium inputs in a water-cooled, segmented copper crucible. Zirconium readily dissolves all common refractories. A solidified layer of zirconium (called a *skull*) forms on the surface of the water-cooled copper. The balance of the molten material is therefore contained within a zirconium shell of the same composition. When the entire charge of input material is molten, the crucible is tilted, pouring the metal into the previously placed mold. The crucible and mold are contained within a vacuum chamber, preventing contamination with air.

Vacuum Arc Skull Melting

Vacuum arc skull melting is a hybrid of the VAR process where an electrode is melted in a water-cooled copper crucible to form a molten pool. When the appropriate amount of metal has been melted, the crucible is tilted to pour into a previously placed mold. The quantity of metal is relatively small because the arc-melted material is constantly being cooled by the water-cooled crucible during the melting process.

APPLICATIONS

Typically, zirconium metal is melted into ingots that can be fabricated into forms that can be used in industrial applications. The standard commercial alloy compositions are unalloyed zirconium ASTM grade 702 and ASTM grade 705, which is a Zr-2.5% Nb alloy (ASTM B350/B350M-11 [2016]). Two ASTM nuclear grades are common:

1. Zr-2 (Zr-1% Sn, 0.15% Fe, 0.1% Cr, 0.07% Ni)
2. Zr-4 (Zr-1% Sn, 0.2% Fe, 0.1% Cr)

Several other trademarked alloys are gaining wide nuclear industry use as Zr-Sn-Nb-Fe alloys.

CONCLUSION

Zirconium is a metal with several desirable attributes of water corrosion resistance and moderate ease of fabrication. However, as discussed, the costs associated with its production limits zirconium to specific niche applications. The production of zirconium metal from raw ore is expensive and requires significant care to produce an acceptable final product. Although zirconium is more expensive and difficult to fabricate, it is the best metal for certain highly critical applications.

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