4 ZIRCONIUM MINERALS

Zirconium does not occur as a free element in nature due to its high reactivity. It occurs as zirconium oxide, baddeleyite and other more complex oxides [2, 6]. In terms of abundance, it is the 9th metal in the Earth's crust and the 18th element, with an abundance of 0.016 - 0.025% [2, 5, 16]. Zirconium is found in crystalline rocks such as chlorites, schist, gneiss, syenite, granite, iron ore beds, sandstone and ferruginous sands [1, 2, 3, 5]. Zirconium is also found in abundance in stars and has been identified in the sun and in meteorites. Lunar rock samples also show high levels of zirconium oxide in comparison with terrestrial rocks [7].

More than 40 zirconium minerals are known. These minerals can be placed into five groups [12, 28]:

1. *Zirconium orthosilicates*: included in this class are zircon and its metamict[2] varieties
2. *Zirconium dioxide*: baddeleyite and its altered varieties[3]
3. *Zircon silicates with sodium, calcium, iron and other elements*: the most important *zircon silicate* is eudialyte; eucolite, genttinsite and others are included
4. *Zirconium carbonates with sodium, calcium and other elements*: weloganite and others
5. *Others*: including zirconolite ($CaZrTi_2O_7$).

Among the high number of zirconium sources, zircon and baddeleyite are the most important. Zircon and baddeleyite contain varying amounts of radioactive U^{238} and Th^{232}, as impurities. The concentration of U and Th is 300 - 500 ppm in zircon and up to 1 000 ppm in baddeleyite [6]. Zircon is the predominant source of commercial zirconium minerals. It occurs in beach and river sands with other heavy minerals. Baddeleyite and eudialyte are also used. They are all obtained as by-products in the recovery of other minerals, such as rutile, ilmenite, monazite and garnet in river and beach sands [1, 2, 12].

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[2] Radiation damage occurs in zircon with U and Th as impurities owing to the radioactive decay of the latter

[3] Owing to U and Th radiation.

4.1 Zircon

Zircon is a naturally occurring zirconium silicate. It occurs in silica igneous rocks, particularly in granite, nepheline syenite and pegmatite. In metamorphic and sedimentary rocks, it occurs as an accessory mineral [2, 3, 12]. Zircon is found concentrated with other heavy minerals, such as rutile, ilmenite, monazite, leucoxene and garnet in river and beach sands. This is due to the high specific gravity of zircon, 4.6 - 4.8. In these deposits, iron and titanium appear to be the main contaminants [2, 3, 5, 14, 16]. Separation is effected through electrostatic, magnetic and gravitational techniques, through which levels of 99% purity can be achieved [2, 12].

Zircon sand is yellow in colour. Sometimes beautiful, crystal clear or vividly coloured zircon crystals are found, which are used as gems. Crystal clear zircon resembles diamond. Blue-green dichroitic zircons from Vietnam and topaz-coloured "hyacinth" stones from Ceylon are used as gemstones [5]. The variety of colours ranges from yellow, brown to red and the zircons may be colourless, green, rose-red, or violet [11]. Their appearance can be attributed, in part, to radioactive action [29].

Zircon is mined as a co-product of rutile, ilmenite and monazite. The mining of zircon and other heavy minerals is environmentally friendly. It involves the removal of light sands and mining is done with elevating scrapers and bulldozers. As heavy sands constitute only 4 - 7% of the whole deposit, the replacement of light sands can restore the original elevation of the sand and so the vegetation can be replaced [1, 3, 12]. Zircon extraction involves three stages – mining, wet concentration and dry separation [1].

The wet concentration process consists of two steps. In the first step, the raw material is subjected to magnetic separation. This process allows the separation of iron compounds. In the second step, the other contaminants are removed via solubility in hot sulphuric acid. It is preferable to grind the raw material beforehand [5].

4.1.1 Structure and properties of zircon

Zircon has a tetragonal structure, consisting of a chain of alternating, edge-sharing SiO_4 tetrahedra and ZrO_8 bisdisphenoids, also known as triangular dodecahedra or dodecadeltahedra. The bisdisphenoids have 8 vertices, 18 edges and 12 faces. This polyhedron consists of two interpenetrating, concentric tetrahedra [3, 8, 9, 10, 12, 15, 17, 30]. The name is derived from the fact that the structure consists of a sphenoid that has a wedge. A disphenoid is a tetrahedron with triangular faces [6, 17].

Zirconium and silicon atoms are linked by oxygen atoms. Although zircon has been formulated as $ZrSiO_4$ or $ZrO_2.SiO_2$, X-ray studies do not show significant differences between the oxygen atoms in the structure. This leads one to the conclusion that there are no separate groups of oxygen atoms and therefore the structure $ZrSiO_4$ is adequate. However, there is a remarkable formation of complex tetrahedron anions, $Si(O)_4$, surrounding zirconium cations. Another explanation that could justify the second formulation, $ZrO_2.SiO_2$, is the fact that at high temperatures the compound appears to be separated into two parts, ZrO_2 and SiO_2. In addition, with magnesia at 1 240°C zircon is completely converted to magnesium silicate and zirconia [5]. Figure 4.1 shows an atomic model of the structure of zircon crystals and Figure 4.2 a geometric design of zircon crystals. The green polyhedra represent the ZrO_8 bisdisphenoid structure and the SiO_4 tetrahedron is shown in blue.

The density of zircon varies according to its origin. Some authors have attributed these differences to the presence of an unknown component in the matrix. The density of zircon may be as low as 3.95 g/cm^3, but after beneficiation it is closer to 4.6 g/cm^3 on average. Light zircons contain free amorphous silica and amorphous zirconia. This transformation is attributed to radiation damage caused by α-rays. Heating restores the proper density [5].

The zirconium tetravalent ion in this compound is highly coordinated (8). Due to its structure, zircon is a very stable compound, both chemically and thermally [3, 4, 16, 31]. Zircon decomposes to ZrO_2 and SiO_2 under atmospheric conditions only above 1 690 °C [30]. This can also be achieved via plasma at high temperatures [3, 30].

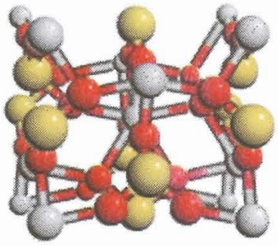

Figure 4.1: Atomic model of structure of zircon crystals

In general, zircon is unreactive to strong mineral acids, but is attacked by concentrated sulphuric acid at high temperature and pressure. Fluorides, such as hydrogen fluoride, potassium bifluoride and others, can convert zircon into complex zirconium fluoride and silica. Chlorination at high temperature in the presence of carbon gives zirconium tetrachloride [13]. Zircon's extreme stability with respect to strong mineral acids is the basis of the purification of zircon from various contaminants in its ores [5].

Finely divided zircon can be easily decomposed by fused alkali or alkali carbonates at their melting temperatures to orthosilicates and orthozirconates or metal zirconium silicates. At high temperatures, alkaline-earth metal oxides also react with zircon, giving the same products [5, 13].

The main producing countries are Australia, India, the USA and South Africa. World production in 1987 was about 800 000 tons per annum, with 55% coming from Australia [32].

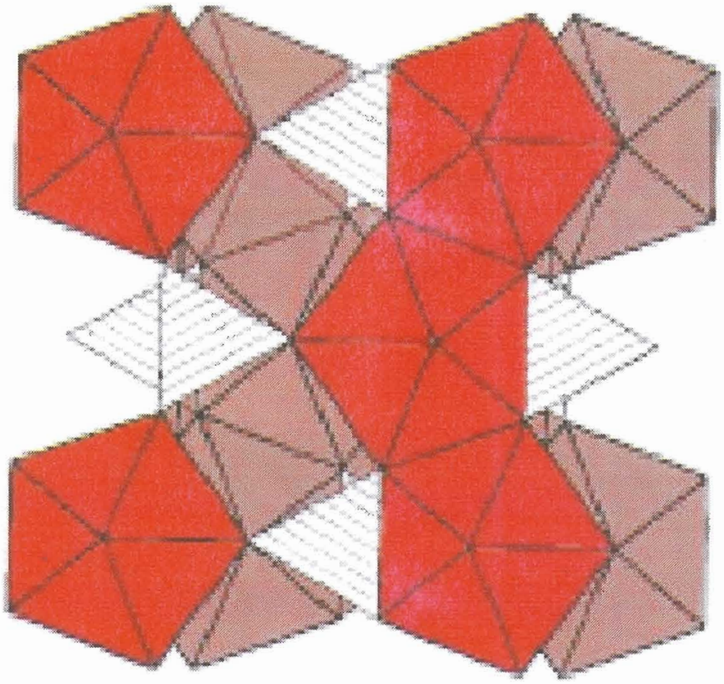

Figure 4.2: A geometric design of zircon crystals. The red polyhedra represent the ZrO_8 bisdisphenoid structure and shown in brown is the SiO_4 tetrahedron.

4.1.2 Some applications of zircon

Zircon on its own has a considerable number of applications, the most important being applications in foundries, refractory ceramics and as opacifiers.

a. Zircon as opacifier

Opacifiers are an important market for zircon in the ceramic industry. Zircon imparts high opacity and extreme whiteness to the glaze. It also improves colour stability and assists in the development of desirable properties on the fired glaze surface. Typically, zircon glaze uses 8 - 12% of milled zircon, depending on the degree of opacity required [33].

White pigments are widely used in ceramic glazes and enamels. The most powerful white pigment is titania. However, zircon is commonly used as an opacifier in the decorative ceramic industry, in tile glazes, and in porcelains and enamels [12, 16, 34, 35] owing to its higher thermal stability.

A black or white appearance depends on the behaviour of the matrix to incoming light. If the object absorbs all, or almost all, the incident light, then the object will appear to be black and opaque. A white object reflects most of the incoming beam, which enter the viewer's eye, giving a white shade [35].

Opacity is governed chiefly by the relative refractive indices of crystals and their media. Zircon has a high refractive index (1.92). Other factors that affect the quality of opacifiers are related to the number of independent light scatterers, and the size and shape of the particle crystals [34, 35].

To be used as an opacifier, zircon must be of a chemically high grade (ZrO_2+HfO_2>66%), with minimal amounts of iron (less than 0.05%) and titania (less than 0.1%). The grain size must be between 5 - 9 μ [33].

b. Zircon in refractories

Zircon is used as a refractory material in the glass and steel industries [12, 16]. In the glass industry, it can be used in association with alumina, which has high corrosion-resistance to molten glass. This is due to the low solubility of zirconium in molten silica [16, 33]. This corrosion resistance, the low defect potential and good manufacturing ability makes zircon-based refractories particularly suitable for the most exposed hot areas of a furnace [33]. In the steel industry, zircon is used in ladles and continuous casting nozzles [12].

Zircon is used fused or combined with alumina. This material has high resistance to corrosion by molten glass. The ceramic material has been used in contact zones, e.g. the sidewalls of glass smelters and refiners, and in furnaces [7, 12, 16, 33].

Zirconium silicate absorbs X-rays. For this reason it is added to glass television tubes to absorb the outgoing X-rays. It also toughens the glass [7, 12, 16].

c. Zircon in foundries

Zircon is used in foundries as the basic mould or as a facing for other mould materials, especially when high refractoriness is required to prevent metal penetration into the fused sand. This is the third most important market for zircon [33].

Nielsen and Chang [12] attributed zircon's usefulness in this application to its high thermal conductivity that allows higher cooling rates than other mould materials, as well as to zircon's high melting point and chemical stability.

In precision casting, zircon "flour" is used as a refractory paint in mouldings to provide heat resistance and reduce metal penetration into the mould [12, 33]. This is related to zircon's high melting point, low coefficient of thermal expansion and chemical stability.

The materials used in a foundry have an important impact on the production costs. Hence, the use of zircon sands in foundries is affected by the market prices of zircon. When prices are high, alternatives such as chromite, olivine and aluminosilicates are used [33].

4.2 Zirconia

Zirconia occurs naturally in monoclinic form as baddeleyite (also known as brazilite, zirkite or caldasite). The first deposit of relatively pure zirconia was discovered in Brazil by Hussak in 1892. E. Ritz was the first to exploit this deposit commercially [5, 13, 16, 36, 37]. According to Ryskewitch and Riecherson [5], the name "baddeleyite" was given to zirconia by L. Fletcher who discovered it before Hussak in samples from Ceylon. Joseph Baddeley collected the samples in which Fletcher found zirconia, in Sri Lanka, hence the name [37].

The average content of zirconia in baddeleyite is 80%. Some sources yield baddeleyite with 90% or more of zirconia [5, 13]. Ores of this kind can be used immediately in many applications without pre-treatment. The major problem with natural sources of baddeleyite is that they are scarce and are limited in terms of availability.

There are various deposits of baddeleyite in different countries, but their commercial importance depends on the purity of the deposits. Their radioactivity is an important factor in the quality of the deposits. Crude forms of baddeleyite are found in Brazil and Sri Lanka. The main commercial sources are found in the Kola Peninsula in Russia and in Phalaborwa, South Africa [15, 16, 32, 37].

Baddeleyite is beneficiated by the gravity separation of heavy minerals. Thereafter, the product is acid-leached and magnetically separated to obtain a commercial-grade product containing 96% to 99.5% of ZrO_2+HfO_2. The product typically contains HfO_2 at levels of 1.5-1.7% [37].

Baddeleyite occurs with forsterite, apatite and magnetite. In these zones, baddeleyite may constitute up to 0.15% [38].

Although the production of baddeleyite is confined to South Africa and Russia, much zirconia is produced in many countries, from zircon sands. In 1995, 31 000 tons were produced worldwide, with South Africa producing 18 000 tonnes [39].

4.2.1 Properties of zirconia

Zirconia is the most stable oxide of zirconium. Zirconium oxide is a high refractory material. In its pure form it is a white powder with a melting point of 2 710 ± 35 °C. Stabilised zirconia has a lower melting point, and with 15% of calcia or magnesia it can melt at 2 500 °C. The boiling point is calculated to be approximately 3 730 °C, using values of the vapour pressure of zirconia [5, 33].

Zirconia is hard, strong and chemically inert, with a high melting point, a low coefficient of friction and low specific heat. It is an excellent thermal insulator and is biocompatible [32]. As a result of its intrinsic proprieties, zirconia is a most important zirconium chemical. It is applied in various fields of science and technology.

Zirconia is polymorphic. It exists in three crystalline forms: monoclinic, which is the stable form up to 1 170 °C; tetragonal, which is stable between 1 170 °C and 2 370 °C; and cubic, which is stable above 2 370 °C [4, 38]. Cubic zirconia is widely used as a diamond substitute for decorative and industrial applications [4, 5]. Collins established that the cubic structure of zirconia is of the fluorite type. Ruff and collaborators established the nature of these modifications (Figure 4.3) [5].

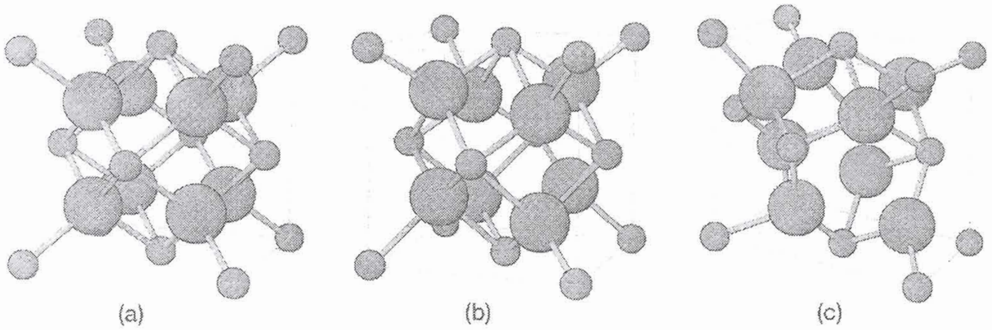

Figure 4.3: Schematic representation of polymorphic forms of zirconia: (a) cubic, (b) tetragonal, and (c) monoclinic

The transformation of the monoclinic structure to the tetragonal structure is followed by a volume contraction of about 9%. In fact, the monoclinic form has an average density of 5.31 while that of the tetragonal modification is 5.72, and that of the cubic modification is 6.09 [5].

The volume contraction makes it difficult to produce ceramic pieces by firing zirconia directly. The phase transformation can be avoided by adding small amounts of other oxides forming a solid solution with zirconia. These oxides must have a cubic structure. They cause a slight stress in the zirconia lattice, forcing it to retain the cubic structure on cooling. The discovery of the way to control this transformation had a pivotal effect on zirconia applications [40]. The atomic radius of the oxides must be of approximately the same in order to make it possible for them to enter into the zirconia lattice structure. Those solutions have important properties: at low temperatures they are good insulators and above 900 °C they exhibit high electrical conductivity. These properties can be considered the antecedent to incandescent light [5].

Zirconia is a typical amphoteric oxide: it acts as a base with strong mineral acids and as an acid with strong bases. In both cases it forms comparatively stable salts. Generally, salts with strong acids and hydrofluoric acid are soluble in water. Solutions of zirconium salts diluted in water can suffer from hydrolysis, forming hydroxy or oxy salts. That can be shown by zirconium chloride [5, 13]:

$$ZrCl_4 + H_2O \rightarrow ZrOCl_{2\,(aq)} + 2HCl$$

$$ZrOCl_{2\,(aq)} \rightarrow Zr(OH)OCl_{(aq)} + HCl, \text{ etc.}$$

Scheme 4.1: Hydrolysis reaction of zirconium tetrachloride in water [5, 13]

Zirconia is soluble in alkali melts, such as sodium or potassium, forming alkali-meta-zirconates. It is not reducible by alkali metals under normal conditions, but is reducible at the high temperatures at which those metals become volatile. With alkaline earth metals, including beryllium and magnesium, zirconia reacts at elevated temperatures, resulting in the reduction of zirconia to metal. Aluminium can also reduce zirconia. Silicone can reduce zirconia only at temperatures above 1 800-°C. Zirconia reacts with carbon at 1 250 – 1 300 °C to form zirconium carbide, bypassing metallic zirconium [5].

Zirconia has an impressive combination of properties, including great hardness, high strength, a high melting point and biocompatibility. In association with calcia, magnesia, yttria and rare earth oxides, zirconia[4] competes with metals and alloys in some applications, especially where

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[4] Stabilised zirconia, by doping with these oxides.

high-temperature performance, and resistance to erosion and corrosion are required [4, 31, 38, 40].

Zircon, as stated, is the major and cheaper source of zirconia and is very stable, both chemically and thermally. To extract zirconia from zircon requires aggressive chemical and thermal conditions, or very high temperatures to break the bonds between the two oxides (ZrO_2 and SiO_2). Several methods of producing zirconia from zircon sands have been investigated [3, 4].

4.2.2 Applications of zirconia

Most of the applications of zirconia are associated with its high chemical and thermal stability. Zirconia is applied to the surface of other materials, in refractories, as a coating for structural ceramic materials to provide thermal and corrosive protection. The nozzles and inner surfaces of wall furnaces can have zirconia coatings. Zirconia can be used to replace fireclay and similar aluminosilicates if they are unable to achieve the required refractoriness or corrosion stability [12].

Zirconia is a ceramic material and ceramic materials have been called “the material of the future” since they are derived from sand. Sand composes about 25% of the Earth’s crust. In comparison, all metals together compose only 1% of the Earth’s crust. For our purpose, a ceramic material can be defined as a non-metallic and inorganic material and, in most case; these materials have been treated at high temperature during their manufacture [11].

a. Zirconia in paints and pigments

Zirconia is used in the paint industry to coat the surface of titania pigment particles for specific exterior paint applications. It minimises ultraviolet excitation of the titanium atoms, which would otherwise react with the organic binders in the paint and thus reduce the lifetime of the paint [12].

Zirconia is also used to replace titania as a pigment in the camouflage paints used in snow environments because it more closely camouflages snow in the infrared and microwave spectra [12].

Zirconia is used as a pigment for stoneware in the ceramic industry. (Stoneware is high-fired, coarse vitreous clay ware.) Such pigments are inexpensive and have low toxicity. In these industries an estimated 6 000 tons of zirconia are used per year [16].

b. Zirconia in jewellery

Single crystals of zirconia with a cubic structure are used in jewellery as low-cost gemstones. For this application, more than 300 tons of single crystals are grown every year worldwide [7, 12].

Cubic zirconium dioxide is a synthetic stone used as diamond simulant. It can be given different colours, depending on the dopants applied in cubic zirconia production. The dopants are used to induce cubic crystallisation. Well known among zirconia gemstones is the so-called white zirconia, a colourless modification of zirconia. With cerium, red, orange and yellow gems can be obtained. Yellow, amber and brown gems are obtained with copper, iron, nickel, praseodymium and titanium oxides. Erbium, europium and holmium oxides produce pink gems. Chromium, thulium and vanadium oxides produce olive green, while cobalt, manganese and neodymium oxides produce lilac and violet gemstones. Other colours such as sapphire blue and emerald green can be produced under specific conditions [41].

c. Zirconia in electronics

Stabilised zirconia (SZ) is used as a solid electrolyte at elevated temperatures in oxygen sensors and high-temperature fuel cells. This is due to the voids in the lattice structure that allow oxygen ions to diffuse through them at high temperatures. At room temperature, stabilised zirconia is an insulator. Some kinds of stabilised zirconia are used in resistors and susceptors. Yttria-stabilised zirconia cylinders, inductively heated, are used as heat sources to melt quartz bowls for the drawing of quartz optical fibres [12].

Zirconia is used in oxygen-sensing devices. The electrochemical cell is made in such a way that one side has a known fugacity and the other the unknown fugacity. When the oxygen is adsorbed at that surface of the sensor, a drop in the electrochemical potential develops and a voltage is generated. This voltage is related to the fugacity [27].

Zirconia can replace titanium in lead titanate, forming a solid solution that has piezoelectric properties. The desired composition is 53:47 (Zr:Ti). Lead titanate and lead zirconate (PZT) solution doped shows electro-optical properties. PZT piezoelectric ceramics are used in gas furnaces and barbeque igniters, microphones, phonograph crystals, in ultrasonic transducers for agitation in cleaning tanks and in underwater sonar. Lanthanum is one of the dopants that produce material with good electro-optical properties and high optical transparency. This class of materials is called PLZT (lead lanthanum zirconate titanate). A useful composition is a Zr:Ti ratio of 65:35 and 8 - 9% mol of lanthanum [12, 27].

d. Zirconia in the medical field

Nowadays, ceramic materials are competing with the common metal-polyethylene or metal-metal joint prosthesis devices in orthopaedic surgery, because they reduce strongly the amount of wear debris [11, 42]. Ceramic materials present excellent biocompatibility. They have high mechanical resistance, high wetability and high stability [11].

Alumina was very popular in this field in the 1980s. It was used in hip joints in femoral ball heads. Although alumina is chemically more stable than zirconia, critical fracture problems led to its falling into disuse. Zirconia is twice as strong and mechanically harder than alumina. For this reason, zirconia has been used as a replacement for alumina to solve the critical fracture problem. In this use, zirconia shows high biocompatibility and high resistance to scratching [11, 43, 44]. Phase transformation in zirconia ceramics may, however, cause fracture and roughness in the surface of prostheses [45].

Zirconia is used in the treatment of dermatitis [26]. Zirconia lead oxide and titania are used in the piezoelectric ceramic systems that are used in ultrasonic transducers for medical ultrasound imaging [12].

e. Zirconia in other applications

In its stabilised form, zirconia is used in fishing rods, ferrules, knives, unbreakable shirt buttons and golf putter heads [12].

Partially stabilised zirconia ceramics are considered to be advanced ceramics and as such have been commercialised since 1970. According to the amounts of stabilising agent added, these zirconia ceramics exhibit different properties in response to stress under different loading conditions. They are applied in wiredrawing technology, for thermal shock conditions, in combustion engines (cylinder lines), valve seats and bypass valve guides [16].

Zirconia is used in ceramic oxygen generators (COGs). A COG is an electrochemical device that employs an oxygen-ion-conducting electrolyte, such as stabilised zirconia, to generate oxygen electrochemically from air and other gases, such as carbon dioxide and water vapour. This technology is under consideration for use on Mars [46].