Technical handbook on zirconium and zirconium compounds 2019
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References
1 — Introduction

1.1 Zirconium, zircon and zirconia definition

Zirconium is an amazing grayish-white metal with unique properties that make it highly important for a wide range of industrial, commercial and scientific applications. It is the 20th most abundant element in the Earth’s crust and commonly occurs in the mineral zircon (ZrSiO$_4$), in silicate form, and less frequently in the mineral baddeleyite (also known as natural zirconia, ZrO$_2$), in oxide form [1]. Zirconium was first discovered in Germany in 1789 by Martin H. Klaproth, who discovered the element by analysing zircon mineral samples. Jöns Jakob Berzelius isolated the metal for the first time in 1824, but it was not until 1925 that Anton Eduard van Arkel and Jan Hedrik de Boer developed the iodide or crystal bar process to produce high-purity zirconium, commercialising the metal soon after in 1930 [2].

Around 97% of zirconium compounds and zirconium metal produced worldwide are obtained from zircon recovered from heavy-minerals sands deposits (known as secondary placer type deposits), while the rest is obtained from primary igneous deposits such as baddeleyite mining (at present, the only commercially significant baddeleyite mining operation is located in northwestern Russia, near Murmansk) [3]. Zircon has a theoretical content of 67% zirconia and 32% silica, and it can typically contain a small percentage of hafnium in the range of 0.2 to 4% [2]. Directly after mining and production of a heavy mineral concentrate, zircon is separated, beneficiated and commercialised as zircon sand (zircon). In some cases, an intermediate zircon concentrate is exported to processing plants in China. Zircon sand is either used directly in certain applications (e.g. foundry sands) or processed to produce zirconium chemical compounds (e.g. Zirconia) or zirconium metal. Zirconia’s use has grown enormously in many fields despite its low availability in natural form (baddeleyite). This can be attributed mainly to the availability of synthetically produced zirconia, which, as explained by Iluka [4], can be produced from zircon sand through two different processes: fused zirconia or chemically derived zirconia from zirconium oxychloride.
In addition to zircon, heavy mineral sands also contain inclusions of other valuable minerals such as titanium minerals (ilmenite and rutile), alumina-silicates, magnetite, iron, and tin, as well as occasional inclusions of radioactive elements such as uranium and thorium in small amounts. The relative contents of these minerals varies from deposit to deposit; in some cases zircon is considered as a by-product and in other cases a co-product of titanium minerals production and there are also cases where zircon is the principal product and titanium minerals the co-products [1, 3].

1.2 Mineralogy and deposits

Zirconium can be found in up to twenty minerals around the Earth’s crust, most of which have no commercial importance due to their low zirconia (ZrO$_2$) content and uneconomic quantities [2]. Table 1.1 lists the seven most important zirconium minerals and their properties. Of these, zircon and Baddeleyite are the most commercially significant minerals.

Table 1.1: Zirconium bearing minerals (Elaborated with data from: [2])

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Chemical formula</th>
<th>Specific gravity</th>
<th>Hardness (Mohs’ scale)</th>
<th>ZrO$_2$ content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zircon</td>
<td>ZrSiO$_4$</td>
<td>4.2-4.86</td>
<td>7.5</td>
<td>63-67</td>
</tr>
<tr>
<td>Baddeleyite</td>
<td>ZrO$_2$</td>
<td>5.5-6</td>
<td>6.5</td>
<td>98-100</td>
</tr>
<tr>
<td>Eudialyte</td>
<td>(Na$<em>{0.5}$Fe$</em>{0.5}$)Zr(OH,Cl)(SiO$_3$)$_6$</td>
<td>2.9-3</td>
<td>5-5.5</td>
<td>1.2</td>
</tr>
<tr>
<td>Caldasite</td>
<td>Mixture of fibrous baddeleyite, zircon, altered zircon, and other minerals</td>
<td>-</td>
<td>-</td>
<td>60-75</td>
</tr>
<tr>
<td>Vlasovite</td>
<td>Na$_2$ZrSi$_2$O$_7$</td>
<td>2.97</td>
<td>6</td>
<td>29</td>
</tr>
<tr>
<td>Gittinsite</td>
<td>CaZrSi$_2$O$_7$</td>
<td>3.6</td>
<td>3.5-4</td>
<td>40.3</td>
</tr>
<tr>
<td>Zirkellite</td>
<td>(CaFe)(ZrTiTh)$_2$O$_8$</td>
<td>4.7</td>
<td>5.5</td>
<td>-</td>
</tr>
</tbody>
</table>

As explained by Elsner [5], zircon develops through early liquid magmatic crystallisation in albite-bearing acidic rocks such as granites, diorites, syenites and their pegmatites. All zircon found in other types of reserves and deposits can be traced back to zircon developed in this way. The map shown in Figure 1.1 elaborated by Town [2] with data from Bundesanstalt fur Geowissenschaften und Rohstoffe (BGR) [5], shows the geographical location and size of the major zirconium deposits found around the world. As can be seen from this map, zirconium deposits are concentrated in only thirteen countries, mostly in South Africa, Australia, China and the United States. Two types of zirconium deposits can be observed:

- Primary igneous deposits classified according to their magmatic or volcanic origin.
- Secondary placer deposits (i.e. heavy-mineral sands).

The large majority of deposits shown in Figure 1.1 are secondary placer deposits (i.e. heavy-mineral sands). This deposits originated when the zircon that was initially developed through early liquid magmatic crystallisation in acidic rocks was slowly eroded.
### 1.2 Mineralogy and deposits

**Figure 1.1:** Location, resources, and geological type of zirconium mineral deposits (elaborated with 1992 data from [2]); and 2017 production data per country (data extracted from [6]).

<table>
<thead>
<tr>
<th>Country</th>
<th>Top 11 Producers (2017)</th>
<th>GEOLOGIC DEPOSIT TYPE</th>
<th>1992 TOTAL RESOURCES [Tons]:</th>
<th>10^5 - 10^6</th>
<th>&lt;10^6</th>
<th>unreported</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>UNITED STATES</strong></td>
<td></td>
<td>Placer (●), Magmatic (■), Volcanic (▴)</td>
<td>10^6 - 10^7</td>
<td>100,000</td>
<td>100,000</td>
<td></td>
</tr>
<tr>
<td>1. Soledad Canyon</td>
<td></td>
<td></td>
<td></td>
<td>10^6 - 10^7</td>
<td>100,000</td>
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<tr>
<td>2. Kerr McGee Oak Grove</td>
<td></td>
<td></td>
<td></td>
<td>10^6 - 10^7</td>
<td>100,000</td>
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<td>3. Lakehurst</td>
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<td>4. Brunswick</td>
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<td>5. Tail Ridge Green Cove Springs</td>
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<td><strong>CANADA</strong></td>
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<td>6. Suncor Syncrude</td>
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<td>7. Thor Lake</td>
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<td>8. Strange Lake</td>
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<td>12. Poços de Caldas</td>
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<td>41. Bridge Hill</td>
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<td>44. Agnes Water</td>
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<td>51. Agnes Water</td>
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<td>52. Bayfield</td>
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<td>53. Brockman</td>
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</table>

by weather and water (weathering) over long geological periods. After weathering, zircon was transported by rivers to the sea shoreline, where it was concentrated through the combined action of maritime currents, wind and waves [2]. The relatively high specific gravity of zircon led to a uniform deposition of the material across the same coastline areas by the constant concentrating effect of wave actions [7]. In addition, zircon’s resistance to leaching and abrasion makes it resistant to erosion or dissolution by water. This natural concentration process occurs not only for zircon but also for other valuable minerals typically found in heavy-mineral sands such as rutile and ilmenite, leading to combined heavy-mineral grades of 10 - 20% in most placer deposits. However, exploitation of deposits with grades as low as 1% might be possible depending on the technical difficulty of extraction. Most placer deposits are younger than 2 million years of age (quaternary) [2].

Only a minority of zirconium (3%) is produced from non-placer primary igneous deposits [3], which can be locate in alkaline granite or granitic rocks, carbonatite alkali intrusions or altered volcanic tuffs, mostly of Precambrian age [2], with the only commercially significant magmatic deposit being the Kovdor baddeleyite mining operation in northwestern Russia.

1.3 Mining and processing

1.3.1 Zircon sands mining and concentrate production

Around 97% of zircon in the world is obtained from heavy-mineral sands mining [3]. This process consists of three main stages: mining, wet concentration and dry separation. Mining can be performed either by a wet mining process (employing floating dredges, typical for unconsolidated deposits), or by dry mining methods (employing scrapers, dozers and excavators, typical for cemented deposits) [8]. Dredging involves the processing of large amounts of solids to extract zircon and other valuable minerals from a water pond. As explained by Jones [8], dredging consists of a floating dredge cutting the ore under the surface of a pond and pumping the ore slurry to a wet concentrator floating in the same pond, as depicted in Figure 1.2.

Dry mining techniques are generally employed for hard and cemented deposits with
1.3 Mining and processing

Figure 1.3: Schematic view of a typical dry mining site. (Image extracted from [10]©).

high grade ore bodies. Figure 1.3 shows a schematic view of a typical dry mining site, while Figure 1.4 shows two possible process flows for this operation (although these may vary depending on the characteristics of each particular mining site). The first step is to clear the mine area from trees and other plants or rocks, followed by stripping and stockpiling the topsoil and subsoil separately from the underlying overburden material [9]. Overburden is stockpiled for replacement purposes at the end of the mine’s useful life. A typical dry mining operation consists mainly of depositing the ore into a hopper with the help of dozers, scrapers or excavators, as depicted in Figure 1.4, and transferring it to the primary separation process [9]. In here, waste material is screened out of the mix by the action of vibration and rotation separation devices, where large particles (over 150 mm) are screened out of the mix and mineral sand, silt and clay mixtures are washed away from rocks [9]. The resulting mineral sand, silt and clay slurry is then transferred to the wet concentrator.

The wet concentration process, which is employed to produce a high-grade heavy-mineral concentrate (85-95% HMC) [8], involves the use of a gravity circuit to separate the valuable heavy mineral sand from the non-valuable and lighter gangue that makes up most of the input slurry [9]. In this process, described in Figure 1.5, the input slurry is first passed through a series of hydrocyclones which remove very fine particles (usually of less than 63 µm, mostly clay), which are sent to a fines thickener where they mix with the quartz sand tails and are subsequently pumped to the mining void. An alternative route is to send the thickener underflow to a solar evaporation pond where dried clay can be recovered [8].

The underflow from the hydrocyclones is sent to a constant density (CD) tank which subsequently pumps it into the wet concentration process distributors above the primary spirals. Afterwards, the material is passed through the gravity separation circuit consisting of several spiral banks (between four and six stages: primary or rougher spiral stage, middlings stage, cleaner spiral stage, re-cleaner and scavenger stages) [8]. In this process, the heavy mineral is effectively separated from the lighter gangue minerals, mostly quartz sand. An optional magnetic separation step can be added at this point to separate magnetic ilmenite through the use of wet high intensity magnets.

The final heavy-mineral concentrate is stockpiled and drained before being transferred to
Various Dry Mining Process Flows
(Iluka operations are primarily dry mining)

Simple Mining Unit:
- Mobile
- Suitable for dunal sands with low clay and rock
- Low M&H cost therefore low cut-off grade (depending on strip ratio and asemblage)
- Low utilisation as range limited by tramming distance limitations of FEL/Dozer -> need to move at ~100m

Stationary Mining Unit:
- Design for high energy beneficiation (high clay and rock) with higher work index
- Autogenous mill / drum scrubber allows for higher HM recoveries
- Higher opex, often used in conjunction with ROM ore pad, and hence double handling

Figure 1.4: Examples of simple (above) and stationary (below) dry mining process flows (Image extracted from (10)©).
1.3 Mining and processing

Quartz Tails
Typical Concentrator Process Flows
Fines Thickener
UCC
Gravity Circuit Feed
Solar Evap Dam
Magnetic Separation
Ilmenite Tails
CD Tank
Tails Dam in mine void
Pre-Concentrator (mob)
Concentrate
Concentrators
• Multiple configurations
• Config dependent upon HM upgrade ratio and mineralogy
• Numerous tails handling and disposal options
• High utilisation and high VHM recovery required for maintaining capital efficiency and minimising mining costs

Figure 1.5: Wet concentration process flow (Image extracted from [10]©).
a secondary concentration process or mineral separation plant. Residual sand is pumped into the mining pit, while process water from cyclone stackers and the solar evaporation dam is recycled to a clean water dam where it can be used again in the wet concentration process [8, 9].

The heavy mineral concentrate obtained from the wet concentration process might be subjected to attritioning in order to increase separation efficiency by cleaning the mineral surface prior to electrostatic separation. Additionally, the mineral concentrate might be subjected to a secondary concentration process in which fine quartz and other non-valuable minerals are removed to achieve heavy mineral grades of up to 98% [8, 9]. Following these steps, the concentrate is sent to a final mineral separation and zircon finishing process, where zircon is separated from ilmenite, rutile and leucoxene (HyTi), as well as from other non-valuable minerals, as shown in Figure 1.6. This process uses an array of screening, magnetic, electrostatic and gravity separation circuits to achieve zircon’s separation.

Ilmenite is separated through magnetic separation, while non-magnetic minerals are sent to a primary electrostatic separation circuit where non-conductor materials are separated from conductor minerals. The former are sent to a gravity separation circuit where zircon is separated due to its high specific gravity and subsequently sent to an additional electrostatic separation circuit to remove residual conductors [8]. Zircon’s last separation stage involves the use of an air table to remove fine quartz and residual kyanite. An optional configuration may involve zircon leaching to remove potential iron oxide coatings to improve the overall quality of the product. Conductor materials follow an additional electrostatic separation circuit where secondary ilmenite, rutile and leucoxene are obtained [8].

1.3.2 Zirconia and zirconium metal

There are many different methods employed to obtain zirconia from zircon sands by chemical decomposition. These methods, although distinct from each other, share three common features [11]: they all involve the decomposition of zircon by chemical, thermal or mechanical means; all products obtained from zircon decomposition are subsequently treated by solubility differentiation; and they all involve the isolation of zirconium compounds from residual impurities. A detailed exploration of all these methods is out of the scope of this report. However, a reference list of the most important methods is provided as follows [11]:

1. Thermal dissociation
2. Decomposition by fusion
   (a) Fusion with sodium hydroxide
   (b) Fusion with sodium carbonate
   (c) Fusion with calcium oxide and magnesium oxide
   (d) Fusion with potassium fluoro silicate
   (e) Fusion with calcium carbonate (or lime)
3. Chlorination
4. Carbidizing process
5. Other zirconia recovery methods
Figure 1.6: Final mineral separation and zircon finishing process (Image extracted from [10]©).
(a) Fusion with calcium sulphate  
(b) Mechanical zirconia processing  
(c) Hydrothermal decomposition  
(d) Anion-exchange process

Additionally, zirconia can be extracted from baddeleyite employing the following methods [11]:

6. Recovery of zirconia from baddeleyite  
   (a) Sulphate method  
   (b) Oxychloride crystallisation  
   (c) Precipitation with sulphur dioxide or sodium thiosulphate  
   (d) Precipitation as phosphate  
   (e) Purification as hydrated sulphate  
   (f) Double fluorides procedure  
   (g) Thermal decomposition of alkali chlorozirconates  
   (h) Sublimation of zirconium tetrafluoride  
   (i) Mechanical processing  
   (j) Sodium metaphosphate method

Furthermore, zirconium and hafnium can be separated with the following methods [11]:

7. Fluoride salt crystallisation  
8. Methyl isobutyl ketone extraction  
9. Tributyl phosphate extraction  
10. Extractive distillation

Reduction to metal can be achieved by the following procedures [11]:

11. Kroll process  
12. Sodium reduction zirconium tetrachloride  
13. Potassium hexafluorozirconate reduction with calcium metal  
14. Calcium or magnesium reduction  
15. Electrolysis

1.4 World production, reserves and market

1.4.1 Current production and reserves by country

Table 1.2 shows a breakdown of zirconium mine production (in thousand metric tonnes of zirconium concentrate) and reserves by country, based on data from the US Geological Survey [12–14]. Global production of zirconium concentrates in 2014 is estimated to be accounted for 1.54 million metric tonnes, lower than 2011 production of 1.62 million metric tonnes, but higher than 2010 and 2012 production.

In addition to the production and reserve figures shown in Table 1.2, the identified zirconium world resources in 2014 (i.e material that is potentially valuable and has reasonable prospects for eventual economic extraction) have been estimated to be around 78 million metric tonnes [1,12], distributed mainly among Australia (65%), South Africa (18%) and India (4%) [1].
1.4.2 Market behaviour and dynamic

Zircon sand production has historically experienced different periods of shortage and over-supply accompanied by price volatility. This is a normal phenomenon when considering that zircon is typically extracted as a by-product or co-product of mineral sands mining. This means that its production tends to be influenced not only by its direct demand, but also by the demand for other minerals contained in heavy mineral sands such as rutile and ilmenite [1, 2]. Examples of this occurred in 1981 when an economic recession and cutbacks in rutile and ilmenite production caused a shortage of zircon, or when strong demand for those minerals in the late 1950’s generated an oversupply of zircon [2]. The economics of mineral mining projects are typically evaluated through a unit cash cost measure, which considers the grade of the valuable mineral, scale of the project, mining method and associated costs [15]. Mineral sands mines exploit more than one mineral (e.g. ilmenite, rutile, zircon) and therefore the assemblage of the deposit (i.e. the weight of each of these minerals) needs to be considered when evaluating the revenue per tonne characteristics [15]. This is performed through the use of a revenue/cash cost ratio curve to evaluate the economic feasibility of particular deposits [15].

1.5 Industry structure and consumption patterns

The steep zircon production increase observed after the year 2000, as shown in 1.7, coincided with a considerable growth of Chinese demand for zircon sand. Figure 1.8 illustrates the global zircon production pattern by country for the years 2004-2013. During this period, Australia continued to be the main producing country.

Figure 1.9 illustrates the evolution on the share of end-use sectors of global zircon consumption. Over the last few year, the consumption of zircon in chemicals and foundries has been gaining market share to ceramics. Figure 1.10 shows a simplified

---

**Table 1.2:** World Zr production 2010-2016 and current world Zr reserves (Elaborated with data from [6, 13, 14]). 2016 data are estimates only.

<table>
<thead>
<tr>
<th></th>
<th>Zr mine production (x10^6 kg)</th>
<th>Zr reserves (x10^6 kg of ZrO₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Australia</td>
<td>540</td>
<td>762</td>
</tr>
<tr>
<td>South Africa</td>
<td>381</td>
<td>383</td>
</tr>
<tr>
<td>China</td>
<td>140</td>
<td>150</td>
</tr>
<tr>
<td>Indonesia</td>
<td>50</td>
<td>130</td>
</tr>
<tr>
<td>Mozambique</td>
<td>37</td>
<td>44</td>
</tr>
<tr>
<td>India</td>
<td>38</td>
<td>39</td>
</tr>
<tr>
<td>United States</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Other</td>
<td>84</td>
<td>110</td>
</tr>
<tr>
<td>Total</td>
<td>1,270</td>
<td>1,620</td>
</tr>
</tbody>
</table>
version of the global zircon industry and its biggest end-use markets in 2013. This diagram shows the mass flows of zircon, from mining to end-use sector, as well as some key intermediate processing steps. The width of the lines represents the amount of mass following each particular flow. Zirconia is derived from zircon either by a chemical route that involves leaching and decomposition, or via a fusion process. Similarly, zirconium metal is obtained either from zircon or zirconia. A more detailed image of the zircon industry is given in Figure 1.11.
1.5 Industry structure and consumption patterns

**Figure 1.8:** Global zircon production pattern by country from 2004 to 2013 (Elaborated with data from [6,14]).

**Figure 1.9:** Global zircon consumption pattern by sector from 2004 to 2013 (Elaborated with data from [6,14]).
Figure 1.10: Simplified structure of the global zircon industry by sector of consumption in 2013 (Elaborated with data from (14, 18)). Values are presented in thousands of metric tonnes of zircon equivalent.
1.5 Industry structure and consumption patterns

TZ Minerals International Pty Ltd © 2013 “Zircon Annual Review 2013”

Figure 1.11: Detailed structure of the zircon industry (Courtesy of TZMI).
Zirconium is a metallic element located in Group IVB of the periodic table, with an atomic weight of 91.22 and atomic number 40. As shown in Figure 1.10, it is mostly used in its silicate form as zircon, and less frequently in its pure form as zirconium metal and in oxide form as zirconia. Despite this, there is a great diversity of zirconium compounds that have found their way into academic literature and, to a lesser extent, into industrial applications. This section presents the physical, mechanical and nuclear properties of the element zirconium, in addition to the physical properties of some commonly used zirconium compounds, including zirconia and zircon.

Providing a complete list of zirconium compounds and their properties is a challenging task that is out of the scope of this report. Therefore, the list of properties and compounds shown here is not exhaustive. However, the information presented in this section is intended as a quick property reference for some of the most important commercial forms of the material: zirconium, zircon and zirconia.
2.1 Zirconium

2.1.1 Physical and Mechanical

The physical and mechanical properties of zirconium are given in Table 2.1.

Table 2.1: Zirconium Physical and Mechanical Properties (Elaborated with data from (19), (20), (21), (22) and (23)).

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Thermal properties</strong></td>
<td></td>
</tr>
<tr>
<td>Atomic number</td>
<td>40</td>
</tr>
<tr>
<td>Atomic weight</td>
<td>91.22</td>
</tr>
<tr>
<td>Standard state</td>
<td>Solid at 298K (25°C)</td>
</tr>
<tr>
<td>CAS Registry ID</td>
<td>7440-67-7</td>
</tr>
<tr>
<td>Group in Periodic Table</td>
<td>IVB</td>
</tr>
<tr>
<td>Colour</td>
<td>Silvery white</td>
</tr>
<tr>
<td>Classification</td>
<td>Metallic</td>
</tr>
<tr>
<td>Oxidation numbers</td>
<td>+4, +3, +2, 0, -2</td>
</tr>
<tr>
<td>Density 20°C (g/cm³)</td>
<td>6.45</td>
</tr>
<tr>
<td>Molar volume</td>
<td>14.02 cm³</td>
</tr>
<tr>
<td>Melting point</td>
<td>1852 ± 10°C</td>
</tr>
<tr>
<td>Boiling point</td>
<td>4409°C</td>
</tr>
<tr>
<td>Allotropic transition HCP to BCC</td>
<td>862 ± 5°C</td>
</tr>
<tr>
<td>Thermal expansion</td>
<td>6.39x10⁻⁶ / °C</td>
</tr>
<tr>
<td>Linear coefficient</td>
<td>5.64x10⁻⁶ / °C ⊥ c-axis</td>
</tr>
<tr>
<td></td>
<td>5.64x10⁻⁶ / °C random</td>
</tr>
<tr>
<td></td>
<td>[all at 20°C]</td>
</tr>
</tbody>
</table>

Continued on next page
<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal conductivity</td>
<td>22.7 W m$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>Specific heat</td>
<td>0.2759 J/g$^\circ$C [at 25$^\circ$C]</td>
</tr>
<tr>
<td>Molar heat capacity</td>
<td>$Zr(\alpha)C_p = 6.83 + 1.12\times10^{-3}T$</td>
</tr>
<tr>
<td></td>
<td>$-0.87\times10^5T^{-2}(298 - 1135K)$</td>
</tr>
<tr>
<td></td>
<td>$Zr(\beta)C_p = 7.27(1135 - 1400K)$</td>
</tr>
<tr>
<td>Heat content</td>
<td>$Zr(\alpha)H_T - H_{298}(298 - 1135K) = $</td>
</tr>
<tr>
<td></td>
<td>$6.83T + (0.56\times10^{-3}T^2) + (0.87\times10^5T^{-1}) - 2378$</td>
</tr>
<tr>
<td></td>
<td>$Zr(\beta)H_T - H_{298}(1135 - 1400K) = 7.27T - 1163$</td>
</tr>
<tr>
<td>Entropy</td>
<td>38.89 ± 0.16 J/mole-deg [at 298 K]</td>
</tr>
<tr>
<td>Heat of fusion</td>
<td>23 kJ/mole</td>
</tr>
<tr>
<td>Heat of vaporisation</td>
<td>$\Delta H_0 = 595,153 \pm 1465$ J/mole</td>
</tr>
<tr>
<td>Vapour pressure</td>
<td>$\log P$ (atm) $= \frac{-31.066}{T} + 7.3351$</td>
</tr>
<tr>
<td></td>
<td>$-2.415\times10^{-4}T(1949 - 2054K)$</td>
</tr>
<tr>
<td>Thermal neutron absorption cross section</td>
<td>0.180 ± 0.004 barns/atom</td>
</tr>
</tbody>
</table>

**Electrical properties**

| Electrical resistivity                        | High-purity crystal bar -44.1             |
|                                               | Regular crystal bar -45                   |
|                                               | Mg reduced, melted -54                    |
|                                               | [microhm-cm at 20°C]                      |
| Temperature coefficient of resistivity        | $43.5\times10^{-4}$°C (0 - 200°C)         |
|                                               | $29.3\times10^{-4}$°C (0 - 800°C)         |
| Pressure coefficient of resistivity           | Pressure (R at pressure / (kg/cm$^2$) R at 0 pressure) |
|                                               | 0 / 1                                    |
|                                               | 40,000 / 0.9914                          |
|                                               | 80,000 / 0.9836                          |
### Material Properties

#### Table 2.1 – continued from previous page

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Superconductivity</strong></td>
<td>$T_c = 0.546 - 0.680K$</td>
</tr>
<tr>
<td><strong>Electrochemical equivalent</strong></td>
<td>0.2363 mg/coulomb for valence of four</td>
</tr>
<tr>
<td><strong>Thermoelectric power</strong></td>
<td>$Zr$ versus constantan (0 - 600°C)</td>
</tr>
<tr>
<td></td>
<td>$\frac{dE}{dt} = 0.05725 - 109.4t \times 10^{-8} \text{mv/°C}$</td>
</tr>
<tr>
<td></td>
<td>$Zr$ versus alumel (0 - 600°C)</td>
</tr>
<tr>
<td></td>
<td>$\frac{dE}{dt} = 0.02881 - 336t \times 10^{-7} \text{mv/°C}$</td>
</tr>
<tr>
<td><strong>Optical and thermionic properties</strong></td>
<td></td>
</tr>
<tr>
<td>Emissivity coefficients</td>
<td>0.46($\alpha$)-0.50($\beta$) (5410 Å)</td>
</tr>
<tr>
<td></td>
<td>0.43($\alpha$)-0.48($\beta$) (6520 Å)</td>
</tr>
<tr>
<td></td>
<td>0.49($\alpha$)-0.51(liq) (6500 Å)</td>
</tr>
<tr>
<td>Photoelectric threshold</td>
<td>3200 Å</td>
</tr>
<tr>
<td>Work function</td>
<td>4.1 volts to 3.7 volts</td>
</tr>
<tr>
<td><strong>Magnetic properties</strong></td>
<td>200 K $1.28 \times 10^{-6}$ cgs</td>
</tr>
<tr>
<td></td>
<td>400 K $1.32 \times 10^{-6}$ cgs</td>
</tr>
<tr>
<td></td>
<td>600 K $1.41 \times 10^{-6}$ cgs</td>
</tr>
<tr>
<td><strong>Mechanical properties</strong></td>
<td>68 GPa</td>
</tr>
<tr>
<td>Young’s modulus</td>
<td>68 GPa</td>
</tr>
<tr>
<td>Rigidity modulus</td>
<td>33 GPa</td>
</tr>
<tr>
<td>Poisson’s ration</td>
<td>0.32 - 0.35</td>
</tr>
<tr>
<td>Hardness</td>
<td>As low as 60-70 Brinell and Vickers or 20-30 $R_B$ for highest purity Zr</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>As low as 0.17 GPa for high purity annealed</td>
</tr>
</tbody>
</table>
2.2 Zirconium Compounds

2.1.2 Nuclear

The stable isotopes of zirconium are listed in Table 2.2 together with data on natural abundance, atomic mass and thermal neutron capture cross-section. A very low neutron absorption capacity can be observed, making zirconium a suitable material for nuclear reactors, as suggested by [24].

<table>
<thead>
<tr>
<th>Isotope</th>
<th>% Natural abundance</th>
<th>Atomic mass</th>
<th>Neutron capture cross-section (barns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{90/40}$Zr</td>
<td>51.46</td>
<td>89.9043</td>
<td>0.1</td>
</tr>
<tr>
<td>$^{91}$Zr</td>
<td>11.23</td>
<td>90.9053</td>
<td>1.0</td>
</tr>
<tr>
<td>$^{92}$Zr</td>
<td>17.11</td>
<td>91.9046</td>
<td>0.2</td>
</tr>
<tr>
<td>$^{94}$Zr</td>
<td>17.40</td>
<td>93.9061</td>
<td>0.1</td>
</tr>
<tr>
<td>$^{96}$Zr</td>
<td>2.80</td>
<td>95.9082</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Table 2.2: Stable Isotopes of zirconium (Elaborated with data from [24])

2.2 Zirconium Compounds

2.2.1 Silicates - Zircon Physical Properties

As explained by [24], zirconium silicates exist in a wide number of minerals, the most important being zircon ($ZrSiO_4$ - Figure 2.1), which is a very hard, highly refractive, birefringent and refractory material. Zircon remains stable below 1673°C [25], but it can be dissociated to form $ZrO_2 + SiO_2$ if forced beyond that temperature. The dissociated compounds can recombine again under slow cooling. Zircon is mostly unreactive to acids at low temperatures, however, it can be attacked by sulphuric acid at high temperatures and pressures [24]. Some important physical properties of zirconium silicates are given in Table 2.3.

Zircon is commonly commercialised in sand and milled sand form. The specifications for such products can vary depending on the intended applications. A thorough review of zircon concentrates specifications can be found in the work of [5] and [26], who have compiled the guaranteed specifications for a wide range of commercial zircon sands.

Figure 2.1: Chemical structure of zircon
2.2.2 Oxides - Zirconia Physical Properties

The most commercially important oxide formed by zirconium is zirconia ($\text{ZrO}_2$). This compound can either be produced from zircon or obtained naturally from the mineral baddeleyite (which is mostly composed of zirconia contaminated with zircon, silica and other iron, aluminium and titanium oxides). In addition to natural zirconia, other types of zirconia have been developed by stabilising the material at one of its various phases through the addition of various oxides. Each phase may possess distinct properties and hence the interest to use the material at different phases for different applications. As explained by [27], common oxides used to stabilise zirconia include yttria ($\text{Y}_2\text{O}_3$), ceria ($\text{CeO}_2$), magnesia ($\text{MgO}$) and lime ($\text{CaO}$). In this way, different types of zirconia may be formed, including Tetragonal Zirconia Polycrystals (TZP), Partially Stabilised Zirconia (PSZ), Fully Stabilised Zirconia (FSZ), Transformation Toughened Ceramics (TTC), Zirconia Toughened Alumina (ZTA), and Transformation Toughened Zirconia (TTZ). Some important physical properties of zirconia in its basic natural form are given in Table 2.4.

Although it would be difficult to review the properties of all zirconia compounds available in the market, [27] has compiled a list of properties for various zirconia products, as shown in Table 2.5.

2.2.3 Borides, Carbides, Silicides and Nitrides - Physical Properties

The physical properties of some representative zirconium borides, carbides, silicides, and nitrides are given in Table 2.6.

2.2.4 Halides - Physical Properties

The physical properties of some zirconium halides are given in Table 2.7.
Table 2.3: Physical Properties of Zr Silicates (Elaborated with data from [28] and [24])

<table>
<thead>
<tr>
<th>Property</th>
<th>ZrSiO$_4$</th>
<th>Complex silicates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point ($^\circ$C)</td>
<td>2100-2300</td>
<td>Na$_2$ZrSi$_2$O$_7$, 1470</td>
</tr>
<tr>
<td></td>
<td>(Zr sand)</td>
<td>Rb$_2$ZrSi$_2$O$_7$, ≥ 1350</td>
</tr>
<tr>
<td>Transition temperature ($^\circ$C)</td>
<td>Na$_2$ZrSi$_2$O$_7$, 1470</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Na$_2$Zr$_2$Si$_2$O$_9$, 1120</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Na$_2$Zr$_2$Si$_2$O$_9$, 850</td>
<td></td>
</tr>
<tr>
<td>Heat capacity (J deg$^{-1}$ mole$^{-1}$)</td>
<td>4.1868 * [31.48 + (3.92*10$^{-3}$)$T$</td>
<td>NaH$_2$SiO$_4$, 300</td>
</tr>
<tr>
<td></td>
<td>−(8.08*10$^5$)$T^{-2}$] (at 25-1500 $^\circ$C)</td>
<td></td>
</tr>
<tr>
<td>Specific gravity</td>
<td>4.7 (a$^2$)</td>
<td>Rb$_2$ZrSi$_2$O$_7$, 3.84</td>
</tr>
<tr>
<td></td>
<td>3.9 - 4 (y$^2$)</td>
<td></td>
</tr>
<tr>
<td>Resistivity (ohm·cm)</td>
<td>9.9*10$^{11}$ (at 200$^\circ$C)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.2*10$^{10}$ (at 450$^\circ$C)</td>
<td></td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>12 (at 17-22$^\circ$C)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.51 (at 450$^\circ$C)</td>
<td></td>
</tr>
<tr>
<td>Zr-O bond length (Å)</td>
<td>2.15, 2.29</td>
<td></td>
</tr>
<tr>
<td>Hardness (Mohs)</td>
<td>7.0 - 7.5</td>
<td>(Zr sand)</td>
</tr>
<tr>
<td>Coefficient of linear expansion (cm/cm$^\circ$C)</td>
<td>7.2*10$^{-6}$ (Zr sand) at 93.3-1093.3$^\circ$C</td>
<td></td>
</tr>
</tbody>
</table>
**Table 2.4:** Physical Properties of ZrO\(_2\) (Elaborated with data from (24))

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point (°C)</td>
<td>2397</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>4275</td>
</tr>
<tr>
<td><strong>Density:</strong></td>
<td></td>
</tr>
<tr>
<td>Monoclinic</td>
<td>5.85</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>6.16</td>
</tr>
<tr>
<td><strong>Unit cell parameters (Å):</strong></td>
<td></td>
</tr>
<tr>
<td>Monoclinic</td>
<td>a=5.169 b=5.232 c=5.341 β = 80°45'</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>a=5.085 c=5.166</td>
</tr>
<tr>
<td>Cubic</td>
<td>a=5.1</td>
</tr>
<tr>
<td><strong>Heat of formation (kJ mole(^{-1}))</strong></td>
<td>-1098.2</td>
</tr>
<tr>
<td><strong>Heat capacity (J deg(^{-1}) mole(^{-1}))</strong></td>
<td>4.1868 * [11.62 + 10.46(\times)10(^{-3})T - 1.777(\times)10(^5)T(^{-2})]</td>
</tr>
<tr>
<td><strong>Refractive index:</strong></td>
<td></td>
</tr>
<tr>
<td>Monoclinic</td>
<td>2.15</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>&gt;2.15</td>
</tr>
<tr>
<td><strong>Magnetic susceptibility (g(^{-1}))</strong></td>
<td>-0.112(\times)10(^{-6})</td>
</tr>
<tr>
<td><strong>Coefficient of thermal expansion (deg(^{-1})):</strong></td>
<td></td>
</tr>
<tr>
<td>Monoclinic (at 20°C)</td>
<td>7(\times)10(^{-6})</td>
</tr>
<tr>
<td>Tetragonal (at 20°C)</td>
<td>12.8(\times)10(^{-6})</td>
</tr>
<tr>
<td><strong>Transition temperature (monoclinic-tetragonal, °C)</strong></td>
<td>1205</td>
</tr>
<tr>
<td><strong>Heat of transition (kJ mole(^{-1}))</strong></td>
<td>5.95</td>
</tr>
</tbody>
</table>
### Table 2.5: Physical and Mechanical Properties of Various Types of doped zirconias (Elaborated with data from [27])

<table>
<thead>
<tr>
<th>Property</th>
<th>Y-TZP</th>
<th>Ce-TZP</th>
<th>ZTA</th>
<th>Mg-PSZ</th>
<th>TZ-3Y20A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g·cm⁻³)</td>
<td>6.05</td>
<td>6.15</td>
<td>4.15</td>
<td>5.75</td>
<td></td>
</tr>
<tr>
<td>Hardness ((Hv_{50}))</td>
<td>1350</td>
<td>900</td>
<td>1600</td>
<td>1020</td>
<td>1470</td>
</tr>
<tr>
<td>Bending strength (MPa)</td>
<td>1000</td>
<td>350</td>
<td>500</td>
<td>800</td>
<td>2400</td>
</tr>
<tr>
<td>Compressive strength (MPa)</td>
<td>2000</td>
<td>-</td>
<td>-</td>
<td>2000</td>
<td>-</td>
</tr>
<tr>
<td>Young’s modulus (GPa)</td>
<td>205</td>
<td>215</td>
<td>380</td>
<td>205</td>
<td>260</td>
</tr>
<tr>
<td>Poisson’s ratio</td>
<td>0.3</td>
<td>-</td>
<td>-</td>
<td>0.23</td>
<td>-</td>
</tr>
<tr>
<td>Fracture toughness ((MPa·m^{\frac{1}{2}}))</td>
<td>9.5</td>
<td>15-20</td>
<td>4-5</td>
<td>8-15</td>
<td>6</td>
</tr>
<tr>
<td>Thermal expansion coefficient at 20°C ((\times10^{-6} · °C^{-1}))</td>
<td>10</td>
<td>8</td>
<td>8</td>
<td>10</td>
<td>9.4</td>
</tr>
<tr>
<td>Thermal conductivity ((W·m^{-1}·K^{-1}))</td>
<td>2</td>
<td>2</td>
<td>23</td>
<td>1.8</td>
<td>3</td>
</tr>
</tbody>
</table>

### Table 2.6: Physical Properties of Zr Borides, Carbides, Silicides and Nitrides (Elaborated with data from [24])

<table>
<thead>
<tr>
<th>Property</th>
<th>ZrB₂</th>
<th>ZrC</th>
<th>ZrSi</th>
<th>ZrN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point ((^°C))</td>
<td>3050</td>
<td>3500</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Heat capacity, 25°C ((J·deg^{-1}·mole^{-1}))</td>
<td>48.27</td>
<td>36.67</td>
<td>-</td>
<td>40.44</td>
</tr>
<tr>
<td>Heat of formation ((kJ·mole^{-1}))</td>
<td>-301.86</td>
<td>-196.77</td>
<td>-123.09</td>
<td>-336.74</td>
</tr>
<tr>
<td>Density</td>
<td>6.1</td>
<td>6.7</td>
<td>5.56</td>
<td>7.18</td>
</tr>
<tr>
<td>Coefficient of thermal expansion (\times10^6) (deg⁻¹)</td>
<td>5.5</td>
<td>7.5</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 2.7: Physical Properties of Zr Halides (Elaborated with data from [24])

<table>
<thead>
<tr>
<th>Property</th>
<th>ZrF₄</th>
<th>ZrCl₄</th>
<th>ZrBr₄</th>
<th>ZrI₄</th>
<th>ZrCl₃</th>
<th>ZrBr₃</th>
<th>ZrI₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point (°C)</td>
<td>932</td>
<td>438</td>
<td>450</td>
<td>500</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vapour pressure, log p(mm) = A-(B/T)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>12.5</td>
<td>Solid, A = 11.7</td>
<td>12.268</td>
<td>10.59</td>
<td>11.632</td>
<td>8.367</td>
<td></td>
</tr>
<tr>
<td>Liquid, A = 9.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>11,400</td>
<td>Solid, B = 5700</td>
<td>5945</td>
<td>5730</td>
<td>6246</td>
<td>4671</td>
<td></td>
</tr>
<tr>
<td>Liquid, B = 3500</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heat of sublimation (kJ mole⁻¹)</td>
<td>α = 205.36</td>
<td>100.48</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>β = 230.27</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heat of formation, 25°C (kJ mole⁻¹)</td>
<td>-1913.36</td>
<td>-981.81</td>
<td>-760.32</td>
<td>-485.25</td>
<td>-720.12</td>
<td>-632.21</td>
<td>-431.24</td>
</tr>
<tr>
<td>Entropy of formation (J deg⁻¹ mole⁻¹)</td>
<td>339.80</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Free energy of formation, 25°C (kJ mole⁻¹)</td>
<td>-893.46</td>
<td>-722.22</td>
<td>-488.18</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>4.5</td>
<td>2.803</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Magnetic moment, 19.85°C (BM)</td>
<td></td>
<td></td>
<td>0.4</td>
<td>0.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean bond length, M-X (Å)</td>
<td>2.1</td>
<td>2.33</td>
<td>2.44</td>
<td>2.55</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Zircon consumption by end-use market for the year 2011 is shown in Figure 3.1. Although consumption patterns may change from year to year, this information is useful to understand the current main uses of zircon mineral and the overall downstream structure of the zircon industry. Ceramics are by far the largest end-use sector (55%), followed by foundry applications, chemical applications, refractory uses, glass, and other minor applications. This section discusses these applications in more detail.

3.1 Foundry sands and coatings

Zircon is widely used in the foundry industry, mostly in the form of sand and flour (milled sand) for casting and refractory applications. A breakdown of zircon’s foundry uses is shown in Figure 3.1 [4].

The properties that make zircon a suitable material for these applications include [4, 5, 11, 26, 30, 31]:

- Low acidity: its pH varies between neutral to slightly acid.
- Clean and round grains that allow the material to be easily bonded together.
- Consistent fineness and ability to form fine grains (sizing - when used as zircon flour).
- High ability to bind with all organic and inorganic sand binders.
- Low thermal expansion coefficient and high spatial stability at increased temperatures.
- High melting point (2,100 - 2,300°C).
- High thermal conductivity.
- Chemical stability at high temperatures.
- Low wettability by molten metal.
- Good recyclability.

The aforementioned properties have allowed the wide application of zircon as a moulding
Figure 3.1: Global zircon consumption by end-use market 2011 (Elaborated with data from [26,29]).
base material for Sand Casting and Investment Casting, in addition to its use as mould coating in Die Casting and in refractory paints and washes to reduce the wettability of other foundry sands. The advantages of using zircon sand and zircon flour in these foundry processes can be summarised as follows:

- zircon’s low wettability, consistent grain fineness and ability to form fine grains allows the creation of high precision castings with good surface finish, prevents the mineral from sticking to the cast metal and avoids metal penetration into the mould.
- Its high thermal conductivity allows higher cooling rates than other mould materials, which also results in a better surface finish.
- The higher dimensional accuracy and better surface finish accomplished through the use of zircon minimises post-casting operations such as machining and cleaning of the cast part.
- zircon’s low wettability by molten metal increases the recoverable sand and hence the recyclability of the material.
- Its chemical stability ensures uniform results when using recycled sand.

3.2 Refractories

The properties that make zircon a valuable material for the Foundry industry also make it an attractive choice for the refractory industry, which is one of its core applications. Zircon consumption in the Refractory industry is mainly divided into three product categories, as shown in Figure 3.1 [4].

As explained by Selby [30], refractories are materials that are designed to maintain strength, dimensional stability and chemical resistance at high temperature. These are typically made from alumina, magnesia, clays, binders and zircon or zirconia. In addition to the properties enlisted in §3.1, there are a few extra characteristics that make zircon and zirconia suitable materials for Refractory applications: [2, 31, 32]:

- Low solubility in molten silica and molten metal.
- Chemical inertness.
- Resistance to corrosion and erosion.
- Low defect potential.

These properties allow zircon and zirconia to be used in a wide range of refractory functions, including refractory mortar, firebricks or refractory linings for glass and metal furnaces [5], as well as fibres, nozzles, slide gates, valves and grouts. Zircon bricks for glass furnaces contain typically 30-40 % zircon, while nozzles, slide gates, filters, and ceramic linings normally employ zirconia up to 94%wt [30]. Some of the key benefits achieved by zircon and zirconia in refractory applications can be summarised as follows:

- The addition of zircon and zirconia to refractory materials increases thermal shock resistance [32].
- The low thermal conductivity of zircon translates into very low heat losses.
- When fused or combined with alumina and silica (AZS), zirconia provides high-corrosion resistance to molten glass due to the low solubility of zirconium in molten silica [11, 31].
• Its corrosion resistance together with its low defect potential and good manufacturing ability makes zircon based refractories particularly suitable for the most exposed hot areas of a furnace [31].

3.3 Ceramics

The most important market for zircon is the Ceramics industry. Within this sector, zircon is mostly employed as a raw material in the production of ceramic bodies, glazes, enamels, frits and pigments applied to traditional ceramics, which includes wall and floor ceramic tiles, porcelain tiles, sanitaryware, washbasins, tableware, special porcelains and industrial tiles, among others [5, 33]. Around 85% of the total zircon used by the ceramics industry corresponds to tile production, as shown in 3.1 [4]. The remaining fraction is distributed between other traditional ceramics like tableware and sanitaryware. Zircon is also used as a raw material in the production of fused and chemically derived zirconia, which is commonly employed in advanced ceramic applications such as such as electroceramics, structural ceramics, pump components and biocompatible devices, as well as advanced technical ceramics such as oxygen sensors and solid oxide fuel cells.

3.3.1 Traditional ceramics

Zircon as a whitener and opacifier

Zircon has varied applications as a whiteness and opacity enhancer in traditional ceramics. It can be used directly on ceramic compositions to improve the whiteness and opacity of the entire ceramic body, used in engobes to produce a white and opaque layer that hides the colour of the body, as a raw material in ceramic glazes to increase their opacity, or in frit compositions used to produce glossy, opaque, white glazes [33]. In the case of porcelain tile bodies, whiteness increases with zircon content [33]. When used in glazes, zircon enhances resistance to abrasion and chemical attack. In frit production, zircon is first added as a raw material into the batch composition and then added during the melting process in a glassy phase [33]. Zircon devitrifies when the frit-based glaze is fired, opacifying the glaze [33].

During ceramic tile manufacturing, zircon is mostly used in the form of flour – to introduce zirconium to frit compositions – or as micronized zircon to produce glazes, engobes and ceramic body compositions [33]. Zircon sand is occasionally employed to improve abrasion resistance of glazed surfaces, particularly for floor tiles [33]. When used as micronized zircon to opacify glazes, engobes and bodies, smaller zircon particle sizes lead to increased opacity [33] and higher price.

The properties that make zircon a suitable opacifier material include [4]:

• High refractive index (1.96).
• High number of independent light scatterers with small and round crystals.

Fine zircon grains are capable of scattering visible light, making the ceramics appear white and opaque [34]. In order for zircon to be an effective opacifier, its refractive index (1.96) must be higher than that of the glass matrix where it is contained (1.5), which results in reflection and refraction of light [4].
An additional property that makes zircon attractive for ceramic manufacturing is its high hardness (7.5 on Mohs scale), which helps to resist scratching and mechanical damage [4]. Zircon sands used for ceramic manufacturing also need to comply with specific attributes, including [4]:

- A particular whiteness index depending on the ceramic type.
- Iron oxide, titanium dioxide, and aluminium oxide contents below specified levels.
- Thorium and uranium content typically below 500ppm.
- A grain hardness that facilitates milling to micron size.

Ceramic pigments

Whilst zircon can act as an opacifier, zirconia has an important role in the production of ceramic pigments used in ceramic tiles, tableware and sanitary ware, among other products. As explained by Selby [30], zirconia, quartz, sodium fluoride and other mineralisers (fluxing agents) are fired together at around 900°C with small amounts of other compounds containing Fe, V, Pr, Cd, S, and Se to produce the pigments. Some of these elements enter the zircon lattice to partly substitute Zr or Si (and act as colour centres), while others form discrete pigment particles that are enveloped by a transparent colourless zircon layer, with iron producing pink, vanadium 4⁺ producing blue and vanadium 3⁺ producing orange. These pigments are suitable for this application because they possess the high temperature resistance required for glazes and enamels and because they increase the pigment’s resistance to attack by molten glasses [11,30,35]. Producing a black pigment from cellulose in a single step process has been recently described [36].

3.3.2 Advanced ceramics

Advanced Ceramics is a well-known significant commercial application area for zirconia. Traditional ceramics such as clays, bricks and tiles are usually hard, porous and brittle. The term ‘advanced ceramics’ refers to ceramic materials that have been specially designed to improve those characteristics and overcome the issues arising from traditional ceramic’s poor mechanical properties. Zirconia is an example of material that can produce an advanced ceramic: in its pure form, zirconia has limited mechanical applications. However, in its stabilised form (produced by adding calcium, magnesium or yttrium oxides, resulting in partially stabilised zirconia [PSZ] or tetragonal polycrystalline zirconia [TPZ]) or when mixed with other compounds such as alumina (e.g. zirconia toughened alumina), zirconia becomes an ideal ceramic for a wide range of mechanically demanding applications. As explained by Elsner [5], the fine tetragonal crystal phase in PSZ and TZP displays a distinctive characteristic among advanced ceramics; when exposed to high mechanical stresses, the crystallites transform from tetragonal to monoclinic. This process results in a considerable volume expansion of the crystallites, which generates micro fractures in their surrounding matrices. The volume expansion and micro fractures generated from the crystal conversion process work as an opposition force against the propagation of fractures generated in the material during exposure to high tensile stresses, resulting in the stoppage or deceleration of these fractures. This phenomenon gives PSZ and TZP ceramics a high strength when used at temperatures under 600°C. Additionally, the high fracture toughness is associated with ferroelastic domain switching in other zirconia ceramics containing the tetragonal phase,
as suggested by Chevalier and Gremillard [37]. In summary, these materials hold the following important characteristics [5, 38, 39]:

- High temperature stability and melting point.
- High density.
- High bending fracture and tensile strength.
- High fracture toughness.
- High hardness, wear resistance and corrosion resistance.
- Low thermal conductivity.
- Thermal expansion similar to cast iron.
- Young’s modulus similar to steel.
- High chemical stability and purity.
- Oxygen ion conductivity.
- Ionic conductivity above 600°C.

These characteristics have allowed the use of zirconia in a wide number of specialty applications requiring high levels of strength, hardness and toughness, as well as wear and corrosion resistance. In addition, the ionic conductivity of the material above 600°C has led to its use in oxygen sensors and fuel cells. As explained by Chevalier and Gremillard [37], these characteristics are associated with the stabilisation of the zirconia tetragonal and cubic phases through alloying with aliovalent ions. The large concentration of vacancies introduced during this alloying process is responsible for zirconia’s high ionic conductivity and low thermal conductivity. Market uses for zirconia and zirconia compounds’ uses are discussed in the following subsections [38, 39].

**High stress applications**

Due to its good strength, high toughness, fracture, wear and corrosion resistance, zirconia is commonly employed in the manufacturing of high-stress components such as [40]:

- Precision ball valves (balls and seats)
- Pump seals, valves and impellors
- Bushings
- Thread guides
- Bearings
- Thermal insulators
- Tube and rod mill rolls
- Stamping, extrusion and drawing dies

**Abrasives**

Stabilised zirconia is widely used in the manufacture of abrasive materials due to its ultra-hard, tough and dense characteristics. Common zirconia abrasive materials include Yttrium stabilised zirconia (YSZ) and zirconia toughened alumina (ZTA) [26, 41]. Typical zirconia abrasive products contain around 25-40% zirconia [30], and include:

- Grinding wheels
- Sharpening stones
- Abrasive papers
- Other high density grinding media
3.3 Ceramics

Cutting tools

Yttrium stabilised zirconia (YSZ), zirconia toughened alumina (ZTA), and alumina toughened zirconia (ATZ) are also used to produce cutting blades and cutting tool inserts [38, 41]. The key characteristics that make zirconia attractive for this application include [40]:

- Fine grained microstructure allowing for honing very fine and tough cutting edges.
- Low friction and low energy surfaces minimise adhesion to cut materials.
- High hardness and toughness lead to long cutting edge life.
- High hardness allows cutting hard, abrasive and tough materials.
- High hardness and corrosion resistance allows the use of harsh cleaning chemicals or abrasives without damaging the tool.

Zirconia susceptors

Yttrium stabilised zirconia (YSZ) has found an application as a radio frequency heating susceptor element. These devices are zirconia ceramic tubes commonly used in induction heating equipment, manufactured through a plasma spraying process. When exposed to a radio frequency, the atoms in the zirconia (YSZ) susceptor devices start vibrating, generating heat as a result. Its high melting point (>2300°C) and thermal shock resistance makes Yttrium stabilised zirconia an ideal material for this application [42].

Ionic conduction

There are three main applications that take advantage of zirconia’s ionic conduction:

- Oxygen sensors

The stabilisation process of zirconia, which occurs by placing it in a solid solution with 4 to 12 mol% MgO, CaO or Y_2O_3, results in the establishment of oxygen ion vacancies in its crystal lattice, enhancing the mobility of oxygen ions at high temperatures [43]. This condition is exploited during the use of zirconia in oxygen sensors, where stabilised zirconia is employed as a ceramic solid electrolyte tube with platinum electrodes deposited on the inner and outer surfaces, working as a very low voltage battery. The outer and inner layers of the tube are isolated from each other and exposed to different gases (e.g. in car engines, the outer layer is exposed to the exhaust gas stream before the catalytic converter, while the inner layer is exposed to the reference atmosphere). The difference in oxygen ions between the inner and outer layers generates a drop in the electrochemical potential, thus producing a very small voltage at the electrodes. The operation temperature needs to be kept above 350°C for the ionic conduction to take place appropriately [43, 44].

- Ceramic oxygen generators

As explained by Guan [45], a ceramic oxygen generator (COG) is an electrochemical device that employs an oxygen-ion-conducting electrolyte to electrochemically generate oxygen from gases such as air, carbon dioxide or water vapour. Yttrium-stabilised zirconia is the most commonly used electrolyte material due to its great oxygen ion mobility. A typical ceramic oxygen generator arrangement consists of a zirconia electrolyte
crammed between two porous electrodes: input gases are passed through the cathode where they are electrochemically reduced to form oxygen ions by combining with electrons from an external circuit. Oxygen ions combine to produce oxygen molecules at the anode, releasing electrons to the external circuit, while an external power supply provides electron flow in the circuit from the anode to the cathode [45].

- **Solid oxide fuel cell membranes**

Solid oxide fuel cells employ a similar operation mechanism to ceramic oxygen sensors and generators, consisting of two porous electrodes separated by a dense, oxygen conducting electrolyte. As explained by Singhal [46], the high oxygen ion conductivity of yttrium stabilised zirconia (YSZ) over wide ranges of temperature and oxygen pressures has led to its use as an electrolyte in solid oxide fuel cells (SOFCs). These cells employ yttrium stabilised zirconia as an electrolyte through which the oxide ions $O^{2-}$ migrate from the air electrode (cathode) side to the fuel electrode (anode) side, where they react with the fuel (H$_2$, CO, etc) to generate an electrical voltage in a clean and highly efficient way. Yttrium stabilised zirconia is the most effective electrolyte tested.

**Medical implants and biocompatible devices**

In addition to the already mentioned properties, advanced zirconia ceramics have an excellent biocompatibility, which is defined by the ASTM [47] as the inherent ability of a material to remain biologically inert with the host in its intended application. Alumina was traditionally used to manufacture medical prosthesis devices such as hip joints or femoral ball heads until it was observed that the material suffered from critical fracture problems in these applications. Zirconia has displaced alumina in this field due to its higher strength and hardness, wear resistance, stability, resistance to scratching and bicompatibility with the human body [48–51]. In addition, zirconia-based prosthesis compete with metal-polyethylene or metal-metal prosthesis because they can significantly reduce the amount of wear debris generated during their use [48].

### 3.3.3 Electro-ceramics

Zirconia has dielectric and piezoelectric properties that allow its use in the fabrication of special electro-ceramics for use in a wide range of applications in the automotive, aerospace and telecommunication sectors, among many others. The most common zirconia-based electro-ceramic is lead zirconate titanate (PZT), which has good machinability and can be easily formed into tubes, rings, discs, plates and other complex shapes, in sizes from microns to centimetres. Important PZT characteristics include [52]:

- As a dielectric, PZT is capable of storing an electrical charge with low electrical loss, thermal stability and resistance to interference from electromagnetic fields.
- As a piezoelectric, it has the attribute of producing an electrical charge when mechanically compressed or vibrating when an electrical charge is applied [11].
- As a pyroelectric material, it holds the ability to develop a voltage difference across its faces when experiencing a temperature change [53].
- As a ferroelectric material, it can have spontaneous electric polarisation that can
be reversed by the action of an external electric field [53].

As a result of these properties, PZT has been employed in a wide range of products and industries, including [11, 52, 54, 55]:

- Microwave dielectrics.
- Radio frequency power capacitors.
- AC/DC high voltage capacitors.
- General high voltage capacitors.
- Gas furnaces and fire igniters.
- Microphones.
- Phonograph crystals.
- Ultrasonic transducers for agitation in cleaning tanks.
- Underwater sonars, beacons, and current meters.
- Gyroscopes, accelerometers, and level sensing devices for airplanes.
- Medical high intensity focused ultrasound, medical imaging, phacoemulsification tools for cataract surgery, dental descaling tools, tissue ablation, medication delivery, hearing enhancement, and bubble detection.
- Ultrasonic toothbrushes, jewellery cleaners, contact lens cleaners, computer hard drives, touch screen displays, integrated, and ultra-thin speakers.
- Flow and level sensors for industrial applications, ultrasonic welding, intrusion alarms, solder dispensing, and machine vibration monitoring.
- Optical switching of telecom lines, buzzers and alarms.
- Mobile phone cameras.
- Automotive power seat controls, distance and contact sensors.
- Nano positioning stages for scientific use.
- Scanning probe microscopy.
- Drill tool monitoring in oil exploration.

An additional application of zirconia can be found in the manufacturing of ferrules for fibre optic cables. The smooth surface finish achievable with fine zirconia powder leads to high performance connectivity. Zirconia also possesses a thermal expansion coefficient similar to optical fibre, in addition to its good elasticity and impact resistance [4].

3.4 Glass

Zircon has found a minor application in the glass sector, where it is commonly used as an X-ray absorber in cathode ray glass tubes for televisions and formerly in computer monitors [4, 26, 30]. Zircon flour not only can absorb the X-rays emitted by the electron gun in the tube, it can also increase the refractive index and toughness of the glass [26, 30]. Demand for this application has diminished since the arrival of LCD and plasma screens. However, zircon is also used in plasma screens to enable the manufacture of faceplate glass [4]. Zircon content in cathode ray tubes is in the range of 3-5%, while that in LCD and plasma screens ranges between 1-2% [30].

Zircon and zirconia have also been employed for the production of special glasses for optical and ophthalmic applications, where the addition of these materials provides high refractive indices and increases durability and resistance [5]. Examples include
state-of-the-art applications

borosilicate glass fibre formulations with 4% zirconia, AR fibre glass with 16-21% zirconia, and other lead-free crystal glasses with ranges of 0.5-17% zirconia [26].

3.5 Major industrial zirconia and zirconium chemical applications

Zirconium metal can be extracted from zircon and further processed to form numerous zirconium chemical compounds employed in a wide range of intermediate manufacturing processes and end use applications. As explained by Elsner [5], zirconium metal is a highly reactive element that can form stable bonds with oxygen, sulphur, nitrogen and carbon, therefore serving as a base material for the production of zirconium chemicals. Zirconium oxychloride (ZOC) represents the most important zirconium compound due to its use as a base material for the production of zirconia. Other important zirconium chemical compounds include (list created by Elsner [26]):

- Zirconium oxychloride (ZOC)
  - Formula: ZrOCl₂ x 8H₂O
  - Applications: white TiO₂ pigment application, antiperspirants and catalysts. It is also the most popular precursor for manufacturing other zirconium compounds.

- Zirconium sulphate (ZOS)
  - Formula: Zr(SO₄)₂
  - Applications: popular TiO₂ pigment particle surface treatment reagent (enhances weather resistance), substitute for chromium chemicals as a tanning agent in leather production, accelerator in adhesives, gelatin hardener in photography, paper pigment, catalysis promoter.

- Zirconium basic carbonate (ZBC)
  - Formula: ZrOCO₃·xnH₂O
  - Applications: aid in paint drying, as a thixotropic aid, as a deodorant, in photo catalysis and in paper manufacture.

- Ammonium zirconium carbonate (AZC)
  - Formula: (NH₄)₃ZrOH(CO₃)₃·2H₂O
  - Applications: catalysis, paint drying, water-proof surface coatings for paper and packaging, printing inks, adhesion promoter for plastics and metals, bonding agent and accelerator in adhesives, moulding material binder and for waterproof textiles.

- Acetates (ZAC), propionates, and acetylacetonates
  - Applications: electro-ceramics, catalytic hardener for epoxy resins and silicones, paint drying, water repellent for paper and non-wovens, printing ink adhesion promoter for plastics and metals, thixotropic agent in cements, welding fluids and clay stabilisers, chromium substitute in aluminium processing, moulding material binder, gelatin hardener in photography.

- Potassium zirconium hexafluoride (KFZ)
- Formula: K$_2$ZrF$_6$
- Applications: in Fe alloys, refractory, ceramics and glass and electrical materials for the nuclear industry; flame proofing of wool.

- Zirconium phosphate
  - Formula: Zr(HPO$_4$)$_2$
  - Applications: catalysts in the synthesis of methyl-iso-butyl-ketones and in polymerization, hydrogenization, oxidation, hydration and dehydration reactions, in addition to its use as a catalyst in ion exchange for kidney dialysis and water treatment.

- Zirconium hydroxide
  - Formula: Zr(OH)$_4$xnH$_2$O
  - Applications: production of catalysts and ceramics, ion exchange applications, in paints and colorants, in absorbents, in deodorants and as an additive in plastics and glass.

- Zirconium oxynitrate
  - Formula: ZrO(NO$_3$)$_2$
  - Applications: base material for zirconium catalysts, chemicals and ceramics, used as a white pigment and filler, a moulding material binder, and a bonding agent and accelerator in adhesives.

- Zirconium hydride
  - Formula: ZrH$_2$
  - Applications: oxidation promoter in pyrotechnics, gas binder in the manufacture of vacuum tubes, hardener and bronzer for carbides and ceramics, reservoir for high-purity hydrogen, hydrogen source in metal foaming, and in zirconium powder alloys.

- Zirconium fluoride
  - Formula: ZrF$_4$
  - Applications: ceramic paints, optical fibres and special glasses, gemstone processing and metal treatment.

The list above has mentioned numerous applications of zirconium chemical compounds. However, most of these applications represent only a marginal percentage of Zr chemical uses. The most important applications of zirconium chemicals are summarised in Figure 3.1, where it can be seen that gemstone production accounted for almost half of zirconium chemicals market share in 2010, followed by their use in the nuclear industry (21%), TiO$_2$ coatings (13%), deodorants (9%), paper coatings (9%), and paint driers (4%). The following subsections discuss the main categories of Figure 3.1 in further detail, while Section 3.6 focuses on the remaining 2% (labelled as “other” in Figure 3.1), which concentrates a considerable number of smaller applications.
3.5.1 Gemstones

Zirconia can exist in three phases: cubic, tetragonal and monoclinic. Naturally occurring pure zirconia (Baddeleyite) is a monoclinic mineral in which the cubic phase is only stable at high temperatures. In order to stabilise the cubic phase at low temperatures, zirconia is commonly mixed with oxides such as CaO, MgO and Y$_2$O$_3$. For example, typical market grade cubic zirconia contains 87.5% zirconia and 12.5% yttrium oxide (Y$_2$O$_3$) \[56\]. This improves the thermo-mechanical properties of cubic zirconia and stabilizes it at low temperatures, giving it a very high strength, toughness, and thermal-shock resistance \[57\]. This material has become a popular gemstone due to its optically clear single crystals and high refractive index, in addition to its ability to maintain its colour and brilliance unaltered \[58\]. Important properties include:

- High density (1.7 times higher than diamond).
- Hardness: 6.5-8.5 Mohr scale.

Cubic zirconia is classified as a soft to semi-hard gemstone \[58\] and it is available in colourless form or with different colours depending on the dopants applied during production. Red, orange and yellow gems can be obtained with cerium as a dopant, while yellow, amber and brown can be obtained with copper, iron, nickel, praseodymium and titanium oxides. Pink, violet, blue and green can also be produced \[59\].

3.5.2 Nuclear industry

Zirconium alloys are widely used as structural components in the nuclear industry such as pressure tubes, fuel channels, guide tubes, grid spacers, for fuel cladding, for fuel containers, or even as the core structural materials of water-cooled nuclear reactors \[60, 61\]. Common alloys include \[61\]:

- Zircaloy-1 (Zr with 2.5% tin).
- Zircaloy-2 (98.25% Zr with additional Sn, Fe, Ni, Cr and Hf).
- Zircaloy-4 (98.23% Zr, plus Sn, Fe, Cr and Hf).
- Zr-Nb alloys.
- Zr-Sn alloys.

These alloys present good mechanical and thermal properties, excellent corrosion and irradiation creep resistance, and a low neutron-absorption, which is critical to increase the efficiency of a nuclear reactor given that the lower the neutron absorption, the greater the efficiency \[4, 60, 61\]. These properties are constantly being improved due to the natural drive for higher efficiencies in the nuclear industry, which leads to either a better control of the alloys microstructures or the development of new alloys, as explained by Dupin et al \[60\]. These materials have to be able to withstand common operational conditions that include high temperatures and reactive conditions such as irradiation, oxidation and hydrogen pick-up \[61\].

Zirconium metal employed in zirconium alloys is obtained from zircon by a carbochlorination process at 2000°C, following the removal of hafnium and its subsequent reduction with metallic magnesium \[30\].
3.5 Major industrial zirconia and zirconium chemical applications

3.5.3 TiO$_2$ coatings

Titanium dioxide, also known as titania, is widely used as a pigment in the global paints industry due to its optical properties, non-toxicity and chemical inertness [62]. However, titanium dioxide has a high photo-catalytic activity under ultraviolet irradiation which leads to the decomposition of paint films. Zirconium coatings are used on TiO$_2$ particles to improve their photo-stability and shield the photo-catalytic effect [62].

Titanium dioxide has also been successfully employed as a photocatalyst that can oxidise and decompose harmful organic contaminants such as bacteria, viruses, volatile organic compounds (VOCs) and algae spores, among others [63], based on its strong oxidising properties. This material has been commercialised as a spray that can be applied as a coating on a wide range of materials, particularly on walls and other interior surfaces in buildings and houses. Photocatalysts such as titania need to absorb light to be able to oxidise organic compounds. One limitation of TiO$_2$ is the fact that, due to its large band gap of 3.2 eV, it can only be activated by UV light [64]. Considering that UV light covers only 5% of the solar light spectrum [64], it would be desirable if photocatalysis could also be triggered by the more abundant visible light. Zirconium has been used as a dopant to increase the photocatalytic activity of TiO$_2$ by increasing the efficiency of the process and allowing the absorption of visible light [65]. As explained by Kim et al [64], the addition of zirconium leads to enhanced phase stability, smaller particles, and increased surface area, which results in increased photocatalytic activity. In this way, zirconium doped TiO$_2$ coatings have become more effective at triggering the oxidation reactions necessary to improve air quality in closed building spaces.

3.5.4 Cosmetics

According to the European Commission Scientific Committee on cosmetics and non-food products and the US Food and Drug Administration [66, 67], zirconium and zirconium compounds should not be used in cosmetic products with the exception of zirconium lakes, salts and pigments of colouring agents and the following Aluminium Zirconium complexes:

- Aluminum zirconium octachlorohydrate up to 20 percent.
- Aluminum zirconium octachlorohydrex gly up to 20 percent.
- Aluminum zirconium pentachlorohydrate up to 20 percent.
- Aluminum zirconium pentachlorohydrex gly up to 20 percent.
- Aluminum zirconium tetrachlorohydrate up to 20 percent.
- Aluminum zirconium tetrachlorohydrex gly up to 20 percent.
- Aluminum zirconium trichlorohydrate up to 20 percent.
- Aluminum zirconium trichlorohydrex gly up to 20 percent.

Aluminium Zirconium complexes are commonly used in antiperspirants, where they help to dissolve sweat and stop its flow to the surface of the skin. They are mostly contained in sticks, gels and other solid products. Toxicity testing has not shown any significant concerns.
3.5.5 Paper and printing

Zirconium chemicals are widely used in the paper industry as coatings that add strength and water resistance to paper. Common zirconium compounds used in paper manufacturing include [11]:

- Ammonium zirconium carbonate
- Potassium zirconium carbonate
- Zirconium acetate
- Zirconium stearate

Ammonium zirconium carbonate (AZC) is the most frequently used compound for paper applications. When applied on paper, zirconium ions in this compound link the starch and synthetic size (coating) to the fibres (crosslinking), as well as the CaCO$_3$ within the paper [68]. This results in the immobilisation of the surface coating near the surface and a more tightly bound surface. Zirconium ions have a strong affinity to oxygen and other reactive groups, which allows them to initiate crosslinking reactions while the solution cures. Ammonium zirconium carbonate is a valued coating crosslinker due to its high cure speed, lack of formaldehyde, and the ability to cure carboxylated coating binders such as latex and protein [68]. The ability of zirconium compounds to replace formaldehyde, which the paper industry wishes to remove, is well exploited in the paper industry.

3.5.6 Paints and inks

Zirconium chemicals are employed as additives in paints and inks to promote adhesion to the substrate and to increase their resistance to heat, scrubbing, water and solvents [69]. Zirconium compounds have also been used as driers in solvent-based paint [70], as well as thixotropes in water-based paints. Commonly used compounds include:

- Zirconium carboxylates.
- Zirconium propionate.
- Ammonium zirconium carbonate.
- Zirconium acetate.

As a paint drier, zirconium has been employed as a substitute for lead, which has been banned across most of the world due to its toxicity [71]. In inkjet coatings, zirconium compounds are used to improve the water-fastness of the coating and print quality. These compounds reduce ink spread and excessive migration into the coated layer [72]. In addition, these types of zirconium chemicals promote a better adhesion of the ink to plastic and metal substrates [11]. As an adhesion promoter in inks, zirconium propionate has substituted titanium acetylacetonate to improve adhesion to difficult substrates [69]. In this application, zircon is capable of forming covalent bonds with oxygenated species on the surface of the substrate as well as with the ink resin, working as a solid link between ink and substrate [69]. Zirconium also acts as a nitrocellulose cross-linking agent in nitrocellulose based inks. This cross linking increases the molecular weight of the ink, which results in a higher heat dissipation ability and resistance to scrubbing [69]. Recently, an ink shas been developed for electronic component [73].
3.6 Minor chemical applications

3.6.1 Ammunition and explosives

Zirconium powder is highly flammable and can be easily ignited. This property has led to its use in the following applications [5]:

- Ignition charges.
- Ignition mechanism for automotive airbag inflators.
- Pyrotechnics and squibs.
- Military applications such as incendiary charges.

3.6.2 Gas purification

Getters are materials that can be placed inside a vacuum system to remove small traces of gas from the system through chemical combination or adsorption. Zirconium is a highly effective absorbent because its surface bonds with almost any gas species, including O₂, H₂O, N₂, CO₂ and methane [75]. Zirconium getters are typically operated at temperatures around 350-450°C. At this temperature range the adsorption efficiency is increased because impurities diffuse into the bulk, leaving a bigger surface area available for adsorption [76]. Typical applications include vacuum systems for semiconductor
manufacturing and other ultra-high purity environments.
In this chapter, three emerging technologies which are making their way to market are described. They are presented in order of growing potential for the growth in use of Zr. They are all currently available on the market, albeit not necessarily at scale. They were chosen based on the explosive growth of citations concerning them, the aforementioned market availability and their relation to media trends.

### 4.1 3D printing consumables and photo-polymerisable ceramics

![Graph showing growth in number of citations for Zirconium 3D printing](image.png)

**Figure 4.1:** Growth in the number of citation on Zr applications in 3D printing technology topic over time. This graph has been generated by querying Google scholar for papers published each year corresponding to the search string ‘zirconium 3d printing’.
Emerging R&D – highlights

3D printing offers the promise of net-shape manufacturing with very little material loss during fabrication, as well as creating otherwise impossible geometries. Zirconium oxide suspensions are highly suitable for what is becoming one of the most promising 3D printing technology, dubbed inkjet. A ceramic suspension – typically zirconium and other oxide powders in water – is deposited as droplets, the water evaporated, and the powder sintered to solidify the part [77].

Emerging developments

Additive manufacturing methods have recently been shown to produce ceramics with mechanical properties comparable to those produced using other methods such as machining [78]. The applications make use of the freedom offered to shape the products. Dental prostheses can be printed to match exactly the required shapes. Zirconium-based ceramics are already widely used for that purpose due to their excellent biocompatibility. 3D printing is a relatively slow manufacturing process. It is therefore more suitable for low-volume manufacturing. 3D printing is thus very well suited to the production of moulds for investment casting. In particular, CaO-CaZrO$_3$ ceramic moulds produced using inkjet 3D printing have been demonstrated [79]. More established is the use of powder-bed technologies such as laser sintering or selective ion beam melting. All these technologies depend on the manufacture of suitable ceramic powders.

3D printing can generate geometrically complex shapes useful in solid oxide fuel cells which benefit from high effective surfaces in their electrodes [80]. Both yttria-stabilised Zirconium oxide electrolytes and cathode interlayers have been demonstrated as possibly manufactured in this way [81].

Market potential

The growing demand for energy storage as intermittent power sources become more prominent in the energy mix will likely fuel the growth in this sector. The market for such fuel cells is currently approximately 60 000 units sold worldwide every year although it is growing [82]. These units go from portable personal ones to cells providing megawatts of power. The amount of Zirconium potentially used in such application depends on the type of cell, but the cathode represents approximately 1% of the mass of a fuel cell (see e.g. [83]). Thus assuming an average mass of 500 kg for fuel cell, which is typical for an automotive application, only approximately 300t of Zirconium might be used for this application. The other applications would not grow significantly the market for Zr, as they are in effect an alternative over existing manufacturing technologies for mature applications.

4.2 Solar cells

Context

The drive to increase the share of renewable energy in electric production has led to an explosion in the market for solar cells. The enormous growth in that market has in turn fueled the development of better or more versatile cells. A promising solar cell technology is the dye sensitised cell. There are two technologies which have been
4.2 Solar cells

Figure 4.2: Growth in the number of citation on Zr applications in solar cell technology topic over time. This graph has been generated by querying Google scholar for papers published each year corresponding to the search string “zirconium solar cell”.

developed based on the same physical basis. One uses a liquid electrolyte, and can be used in architecture as coloured glass windows which double as solar panels, and Perovskite (any material with the same type of crystal structure as calcium titanium oxide (CaTiO$_3$)) solid-state cells which can be deposited as thin films on flexible surfaces, allowing for many other applications. Both these technologies currently typically use titanium dioxide as the semiconductor. For it to be efficient, it needs to be doped with Zirconium. Research indicates that 1% doping provides optimal band properties in terms of power conversion, but values ranging up to 5% are commonly reported [84].

Figure 4.3: Dye-sensitised solar cells. A uses liquid electrolytes, B and C are Perovskite type cells, with C the latest proposed printable solar cell using only ZrO$_2$ as semiconductor.

Emerging developments

Perovskite solar cells are the most promising due to the flexibility they offer notably for wearable applications, but in general as a surface treatment transforming any cladding
into a solar panel. Printable perovskite solar cells use mesoporous TiO$_2$ and ZrO$_2$ layers which are infiltrated by the Perovskite and the die. This layered arrangement is advantageous for large scale production and has been shown to be both efficient and stable [85]. More recent development suggest using only Zr could be not only cheaper but more efficient [86].

**Market potential**
Currently, the market is dominated by production of Si-based solar modules, and thin films represent only about 11% of the market. Solar cells producing approximately 50 GW of electricity are installed every year. Assuming 11% as a typical load factor, an efficiency of 20%, and an input from the sun of 1 kW, this represents 2.27 billion m$^2$. If the share of thin films stays the same, and the technology moves to using ZrO$_2$ films exclusively, this amounts to 25,000 t of ZrO$_2$. This number is expected to double by 2050, following the projections for solar power growth from the International Energy Agency.

### 4.3 Shape memory alloys

![Figure 4.4: Growth in the number of citation on Zr applications on shape memory alloys over time. This graph has been generated by querying Google scholar for papers published each year corresponding to the search string ‘zirconium shape memory’](image)

**Context**
Ceramics containing zirconia undergo an martensitic transformation when their temperature is raised. This transformation changes the volume of the material, making it possible to macroscopically reconfigure its shape.

Shape memory alloys (SMA) are used most commonly in fastening mechanisms: the
cooled piece is put into place, and snaps to its final shape at ambient temperature, locking into place. This is used in aerospace applications, but also in medical settings: shape memory allows the placing and deployment of stents using minimally invasive procedures [87]. For this later purpose Ti-Zr alloyed with Nb or Mo and Sn alloys are the most common [88]. The amount of material involved in this market is small however, only a couple tonnes. In general, research is focussed on substituting Ti with Zr in existing alloys and understanding the role of Zr [89]. This work is driven by economic considerations, but the new alloys are also lighter, which is useful in certain applications. Although actuators seem like a natural use for shape memory alloys, in reality the temperature control required, in particular the cooling phase, makes them relatively impractical, and few industrial application have emerged.

Emerging developments

Recently, superelastic zirconia has been shown to be capable of very high actuation stresses in micro-applications, making it an excellent material for such [90]. As an indication of this trend reviewed here [91], shape memory alloy automotive parts have entered service (this was used as a marketing highlight in the Corvette Stingray from 2014)

Market potential

Traditionally, SMAs are more commonly used in the aerospace industry, albeit for the purpose of fastening. The potential Zr market for aerospace actuators is perhaps only 1-2,000 tonnes, assuming 1% of the aircraft mass is actuators, and deliveries of about 1,600 airliners yearly. By contrast, there is a growing number of actuators in cars. Assuming that a fraction of them would use SMA rather than electrical motors, potentially as much as 100g of zirconium per car could be required. As the yearly production of cars approaches 60 million, and this number is expected to rise as the world develops, the potential demand for zirconium in this instance is as high as 6 Mt. This is an upper bound which is unlikely to be reached, but underscores the large potential of this market.

Figure 4.5: Some of the automotive actuators which could use SMA technology.
This section initially presents the results of a thorough literature survey designed to
discover the current research and development trends in the world of zirconium and
zirconium compounds. This survey focused not only on identifying new material science
developments, but also paid special attention to new application trends for zirconium
and zirconium based materials. In the third revision, it consisted of the review of
abstracts retrieved from Google Scholar search engine after looking for the keywords
‘zircon’ (45,000 results, classified 2,880), ‘zirconia’ (62,900 results, 5,200 classified),
and ‘zirconium’ (72,600 results, 3,300 classified), restricting the search to the last seven
years (from 2008 to 2015). The search included both scholarly articles and patents. Only
the material deemed relevant to each category was considered and cited in the sections
below, accounting for a total number of 532 references. This analysis is based on R&D
publications and therefore the market applicability is not yet known.

The section was updated with the top publications from 2015–2018, classified according
to the previous scheme. The 250 most relevant publications as returned by scopus were
looked at for each year, corresponding approximately to the top 10% of all academic
publications on the topic of Zirconium during that period. A number of new subsections
have been added, reflecting the emergence of new possible applications. In total 172
new references were added in the fourth revision of the handbook.

The next subsections explore the relevant literature for several application areas. These
are listed in Tables 5.1 and 5.2, that also identifies the new application areas and those
that are already served by zirconium chemicals.

Metal-organic frameworks are a very active area of research [92], with Zr-based MOFs
attracting the most interest. Most Zr-MOFs feature Zr$_6$O$_8$ clusters as nodes, coordinated
to carboxylate-terminated organic linkers. They offer the possibility of flexibly generat-
ing a wide range of organic catalysts [93]. They have a wide range of properties, and are
in particular photosensitive [94]. Their efficient synthesis is becoming better understood,
increasing their attractiveness [95, 96]. They now appear in all areas of research, and
understanding their production as well as their stability in a range of environments and
temperatures is continuously being refined [97]. The latest developments look at the production of MOFs whose porosity changes with the environment [98] and in producing a greater range of microstructures [99].

5.1 Advanced coatings and functional materials

5.1.1 Paper

Glyoxal has been traditionally used for paper coating crosslinking and colouring. However, zirconium compounds such as ammonium zirconium carbonate (AZC) and Potassium zirconium carbonate (PZC) have been proposed and successfully used for the same function [100]. Zirconium chelates have also been used as insolubilisers for coating binders for paper and starch, as well as for substitution of AZC [101, 102]. The colouration, viscosity and surface properties that these zirconium compounds confer to the paper coatings are advantageous for its manufacturing and other applications such as high speed inkjet printing [103].

5.1.2 Plastics

Zirconia particles have been proposed as constituents of elastomers in the fabrication of gloves; their properties allow not only a durable interaction but also alter the strength and flexibility properties of the material [104]. Anti-bacterial properties have also been introduced into gloves and other apparel by zirconium phosphate [105]. The use of advanced zirconium compounds coatings is not limited to the formulation of plastics or elastomers, they are also key elements for their fabrication: zirconium oxide and zirconium alloys are used in latex forming moulds for improving durability in their
5.1 Advanced coatings and functional materials

### Table 5.1: Newly served application areas by zirconium chemicals.

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fabrication [106]. Another property conferred to elastomers and hybrid materials by zirconium is thermal stability. For example, zirconium propoxide has been used to improve silicone hybrids such as PDMS and other siloxanes [107]. Polyurethane is used in several applications, from shoe soles to packaging, and zirconia nanoparticles have been used to incorporate chemical inertness, thermal stability, high refractive index and high hardness [108].

#### 5.1.3 Wood

Radiation curable coatings in the wood flooring industry have been modified by the use of alumina and zirconia acrylate composites [109]. Although the particles did not show any improvement in the polymerizability of the coatings, their use led to improved weathering performance and better fire protection for wooden claddings due to their refractory properties [109–111]. Zirconium and other nanoparticles have also been proposed to improve the strength and waterproofing of wooden materials [112, 113].
### Table 5.2: Already served application areas by zirconium chemicals.

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### 5.1.4 Fabrics and textiles

Zirconium dioxide nanoparticles have been used to confer functional properties to linen, cotton and other fabrics. Among these properties are UV protection and antibacterial protection [114, 115]. Similarly, these materials have been used for the treatment of wounds [115, 116]. Zirconium oxychloride and zirconium phosphates have been used in wool and polyester fabrics to improve the limiting oxygen limit, thus improving flame retardancy [117, 118]. Salts of zirconium have long been used in waterproof textiles and, with the rise of nanotechnology, nanostructures with improved water repellency properties have emerged for their use in fabrics and textiles [119, 120]. Following these developments, it was found that α-zirconium phosphate compounds increased the thermal stability and flame retardancy of various polymers [121, 122].

### 5.1.5 Glass

Zirconium’s nature has allowed its wide use in coating and functionalisation of glass. Bending stress and toughness improvements have been reported as a result of addition of zirconia nanoparticles to glass mixtures before sintering [123]. Thermal and chemical resistant glasses have also been fabricated with the presence of zircon and zirconia.
particles in the glass mixtures [124]. Other uses include super-hydrophobic zirconium compounds in anti-icing coatings on glass surfaces [120], zirconium oxide particles as dopants for porosity in photon active glass [125], and Y-PSZ to alter the crystallisation behaviour of certain glass [126].

5.1.6 Concrete

Zirconium compounds have been used to confer additional properties to concrete mixtures. For example, fibre reinforced concrete requires the fibres to be stiffer than the concrete matrix and resistant to the alkaline concrete paste [127]. Glass fibres containing zircon (16%) are alkali resistant and have been used in reinforced concrete because of their high tensile strength (2-4 GPa) and elastic modulus (70-80 GPa) [127–129]. High performance concrete has indirectly benefited from the zircon industry: by-products such as micro-silica and fumed-silica from the zirconium industry are used for novel high-performance concrete applications [130, 131]. Zirconium compounds have been used in the past as colourants for cement and concrete mixtures [132], and new improvements on zircon pigments colouration are under development to improve colour or reduce toxicity [133, 134]. For cold climate applications, asphalt joints can be replaced with Zr tungstate, making roads more durable [135].

5.1.7 Gems

Current developments in the modification of gemstones are directed to alter the colour or optical properties of zircon or zirconium compounds [136, 137]; for example, treating the gemstones under gaseous atmospheres at certain temperatures could result in colour improvement or changes in its crystal structure [138, 139].

5.1.8 Ceramic surfaces

Zirconium compounds can be used as an integral part of ceramic materials, as shown in 3.3, but also as coatings, for example zircon is widely used as a glaze opacifier [140] or means of functionalising surfaces. These can be applied to ceramics used in a range of applications, from dental to piezoelectric (See Section 3.3 and 5.2) [141, 142], and also to influence their optical properties [143].

5.1.9 Smart coatings with enhanced properties

Zirconium compounds are used in multi-purpose coatings looking to improve the heat resistance, abrasion resistance, thermal barrier or stability, or durability of many materials. Zirconium nitride, for example, has been used as a heat-treatable material to produce scratch resistance surfaces of zirconium oxide [144]. Rare earth zirconates such as Gd$_2$Zr$_2$O$_7$ in pyrochlore phase are also under evaluation for thermal barrier coatings [145]. Other uses of zirconium compounds include thermal barrier applications for manufacturing specialty chemicals, steel, aluminium, or other alloys [146–148]. Zirconia-based films have also been used for corrosion protection in mild [149] and stainless steel [150]. In addition, zirconia can be used to emulate the microstructure of ceramic finishings on materials such as magnesium [151]. The type of microstructures
Emerging R&D

produced by zirconia may also confer superior mechanical and thermal properties, as well as porosity, that in combination improve the overall finishing of the coated material [152, 153]. Chemical properties can also be enhanced by the presence of zirconium compounds in coatings. For example: abrasion resistance can be conferred to diverse materials by coating them with an alloy of zirconium silicate and nickel [154]; the mechanical properties of oxide dispersion strengthened ferritic steels containing aluminium can be enhanced by adding zirconium [155]; the corrosion resistance of an aerospace aluminium alloy was also shown to be improved with a zirconium-cerium conversion coating [156, 157]; similarly, improved refractory properties in other casting materials can be enhanced by zircon coatings which can also affect the thickness of the casting skin of metals [158–160].

5.1.10 Coating technologies

Novel coatings are accompanied by innovative coating technologies that suit particular applications. For example, turbine blades may be coated by suspension plasma spraying with yttria stabilised zirconia (YXT), resembling EB-PVD layers [161–163]. This technique has been used to modify the microstructure of the blades in order to improve their thermal stability, as well as improving their reliability and manufacturing reproducibility [161]. It has also been used for the incorporation of nickel dopants directly on ceramic composites [164]. Air plasma sprayed zirconium diboride coatings can be used to increase emissivity of surfaces of hypersonic vehicles [165]. Other industrial applications include the use of plasma sprayed magnesia stabilised zirconia for thermal barrier coatings [166]. Additional techniques used for ceramic glazing, corrosion resistance, and fabrication of ceramic coatings are sol-gel processes, photocatalytic curing processes, and electrolytic oxidation of zirconia [167–170], some enabling new colours with enhanced properties [171, 172]. Mullite-based coatings from alumina and zircon powder have been achieved by plasma spraying and laser remelting, where the laser remelting reduces porosity and increases the coatings’ hardness [173]. In addition, stainless steel has been coated with thin films of zirconium oxynitride to enhance its corrosion resistance [174]. A process to coat steel plate was described in [175]. Coating technologies are of particular importance for the purpose of accident-resistance in nuclear reactors [176–178].

5.2 Advanced ceramics

The addition of zirconium compounds and nanoparticles to ceramics can lead to novel properties for specific applications. Similarly, the addition of chemical compounds to traditional zirconium ceramics has also proven useful to alter and enhance their physical and chemical properties [179–181]. There are several examples of these enhancements in literature, as described in the sections below.

5.2.1 Ceramics with tunable properties

Zirconium dielectric and piezoelectric properties have been incorporated into ceramics, transforming them into responsive materials. Barium zirconium titanate ceramics have
been used as tunable dielectric ceramics whose dielectric constant changes as a function of temperature [182, 183]. Other composite ceramics such as lead zinc niobate–lead zirconium titanate are also known to change dielectric and piezoelectric properties [184].

5.2.2 Ultra-High temperature, high-wear and extreme applications

Ceramic composites and alloys containing zirconium have recently been proposed for aerospace, automobile, and military applications which require material performance at extreme temperature. It has been shown that SiC ceramic composites with ZrB$_2$, ZrC and other zirconium compounds offer useful characteristics for high temperature applications such as improved thermal shock resistance [185–188]. Zirconium carbide, in particular, is commonly used for high-temperature applications and coatings for nuclear particle fuels, and has been modified with additives to improve its sinterability and cavitation resistance even further [189]. In general, there is active research in protective coatings for Zr-based alloys [190], as well as fabrication using alloys such as MoTiZr [191]. The infiltration of melts with ZrC composites has found applicability in rocket nozzles for aerospace vehicles [192, 193]. Similarly, the use of nicalon-reinforced zirconium phosphate composites has been proposed for defensive missiles to survive high speed aerodynamic heating or spatial applications [194, 195]. Further developments show that fibre reinforced ceramic composites such as carbon fibre reinforced ZrB$_2$–SiC or ZrC could demonstrate further improvements for ultra-high temperature applications and result in a remarkable improvement of the mechanical properties of the composites [185, 186, 196, 197]. The latter can also be used as a protective coating [198]. It is also suggested that the use of higher purity materials, in the case of zirconium diboride-silicon carbide-boron carbide ceramics, could lead to significant improvements in ultra-high temperature strength [199]. The production process to obtain fully dense ceramics is also being optimised [200], as well as the preparation of the required powders [201], and other production routes which maximise properties [202]. Ceramics from pure ZrC have been produced by plasma spark sintering [203]. Al, Si and other alloys used in automobile components (e.g. brakes), aircraft, marine vessels, and other industrial machines, are exposed to high temperatures and wear, thus their reinforcement with zircon particles has been extensively studied in recent scientific literature [204–212]. Recent work suggests as much as 12% reinforcement is optimal [213]. Radiation-hardened electrical components can be produced using PVA-PEG-PVP-ZrO$_2$ nanocomposites [214].

5.2.3 Dental implants

Advanced ceramics have also been intensively developed for dental applications, not only due to their strength and resistance to temperature, microfracture and fatigue, but also due to their biocompatibility [215–221]. Zirconium compounds are used mainly as structural ceramic materials for dental implants and ceramic crowns. Additionally, they have also been used in the veneering of dental parts [222–227]. These applications and current R&D are further discussed in §5.5.2.
5.2.4 Composite and alloy fabrication technologies

As the demand for novel alloys and ceramic composites grows, the techniques for developing such materials improve. Research and development regarding the fabrication of zirconium alloys and composites includes microwave sintering and sol-gel techniques. These techniques have demonstrated capacity for producing composite materials, including metal matrix composites, and reports in literature show success in improving their properties [228–232]. An example is the use of tetragonal zirconia to reinforce glass-ceramics composites, which result in a significant improvement of their mechanical properties [233]. Phase composition and crystal structure of zircon-type composite ceramics have also been studied, revealing possible applications in microwave devices and low temperature co-fired ceramic technology [234].

5.3 Casting and moulding

The use of zircon, zirconia and zirconium compounds in casting and moulding represents an application in continuous development and optimisation (see Section 3.1) where research is carried out to fulfil particular process requirements. Some of these requirements include hydraulic cement casting, high manganese steel casting, inclusions removal, casting skin control in iron melts, and crucible and porosity control when casting TiAl alloy turbine blades [159, 160, 235–239]. A study has explored the effect of processing technique and TiO$_2$ addition on alumina-zircon refractory materials, showing that fired bricks processed by the gelcasting technique have improved properties compared to those that underwent a semi-dry pressing process. These bricks also had similar properties to those currently used in lining the basin of electric glass melting furnaces, which are fusion-cast [240]. Other examples include, zirconium hydride used in liquid phase metal foam processing techniques [241] and the addition of zirconium to a magnesium-zinc-calcium alloy has shown to delay texture weakening during rolling [242]. Other materials have also been used in combination with zircon to improve its melting or solubility properties [243].

5.3.1 Enhanced modulus refractories

One focus of research in casting applications is the modification of rheological properties of castable refractories. Casting moulds encounter several challenges to accommodate castable materials and casting technologies: sometimes they need to behave as elastic materials but also preserve certain microstructure. The use of zircon sands and other zirconites has been shown to improve these characteristics [244, 245]. In addition, their use as fillers has found success in anti-corrosion applications [246].

5.3.2 Injection moulding ceramics

The alteration of rheological properties in inorganic materials by the addition of zirconium compounds has found applications in certain industrial processes. The manufacture of plastic materials commonly employs injection moulding to mass-produce consumer goods. This process can also be applied to ceramics as long as the rheological properties
of the ceramic adapt to the injection systems for fast moulding techniques. Thus, the addition of zircon or zirconia to ceramics pastes is fundamental for their use in injection moulding [247–250]. Recent development focus on environmentally-friendly production routes [251].

5.3.3 3D printing consumables and photo-polymerisble ceramics

A novel application derived from the appearance of mouldable ceramics and cements is their use for 3D printing. Zirconium compounds can be used in combination with ceramics, hybrid plastic-ceramics, or metal alloys for 3D printing applications [252,253]. The incorporation of organic compounds and polymers in ceramic and cement mixtures has led to innovation in polymerisable and photo-polymerisable ceramic materials which use zirconium compounds as additives [254, 255]. Zirconium compounds are also preferential materials used by selective laser sintering technologies [256].

5.4 Grinding media and grinding technologies

The durability and hardness of zirconium compounds are often exploited for grinding in current state of the art applications, while novel compositions and technologies are constantly being developed. Sintering zircon based particles with other compounds allows control over the hardness and wear rate of grinding media [257, 258]. Precision grinding is also possible by carefully controlling the grinding temperature of nano-zirconia ceramics [259].

5.5 Biomedical applications

5.5.1 Implants

The properties of zirconia have found use in the biomedical sciences mainly for the production of durable implantable materials. On the one hand, having high strength and fracture toughness allows zirconia to be used as a structural substitute for bones, hips or dental parts; on the other hand, its ionic conductivity and low thermal conductivity allow its acceptance in living tissue. A drawback of its use when exposed to water vapour for long periods of time (decades) is that it experiences low-temperature degradation and aging. However, this can be overcome by alloying the material, particularly with alumina [37, 260–262]. Thus, research about its use in orthopaedics and arthroplasty (i.e. surgical modification of joints) is carried out continuously. However, it is still not clear to what extent zirconium implants can be an alternative to titanium implants [263], although recent studies suggest that zirconia particles are less bioactive than titanium particles [264]. In addition, the conventional and early loading of titanium-zirconium alloy implants have also been explored, demonstrating that these implants have a comparable biomechanical outcome to conventional titanium implants [265]. Zirconia (and other zirconium compounds) have been used for the reconstruction of hips, hip joints, femoral heads, and knees, amongst other body implants [37, 260, 261, 266]. Novel zirconium alloys and composites are currently proposed in the scientific literature.
as biocompatible materials for implants due to their combination of corrosion resistance, bearing resistance, and mechanical properties [267–269]. One example is the use of zirconia and polydimethylsiloxane hybrid coatings to promote tissue-implant integration [270]. Alloys of magnesium, zirconium and strontium have also been investigated for use as biodegradable orthopedic implants [271]. Whilst yttria-stabilized zirconia foil could have applications in the fabrication of ultrathin implantable devices [272]. MOFs can be used to generate singlet oxygen, which is toxic to cells; this has potential as targeted cancer therapy [273].

5.5.2 Dental parts

Dental parts have a strong aesthetic connotation but must also be biocompatible and provide resistance and durability to the mouth environment. The properties of zirconium compounds allow its use in dental implants that show less biofilm formation [274, 275], and in dental veneering [222, 276]. Veneering is a cosmetic treatment in which a thin layer of material is deposited on the surface of teeth. This material has to undergo thermal cycles during its application and must possess high shear bond strength to stay in place, as well as to match the colour and brightness of the teeth. The strength and durability of zirconia for veneering has been extensively studied in recent scientific literature [223–225, 227, 277]. The colour of the veneering is important for aesthetic purposes and the addition of particles for colouration has also been studied as a factor influencing the shear strength and durability [226]. Similarly, the application of adhesives and surface treatments are an important factor influencing the shear strength [278–280]. Zirconia ceramics are used not only for covering the surface of teeth, but also to fix partial dentures or for dental reconstructions [222, 281–283]. Titanium/zirconium alloys have been used as implants in the molar region of the mandible, and after 1 year of function these show similar results to pure titanium implants [284]. The advances in moulding techniques for zirconia ceramics presented in Section 5.3 having also proven applicability in dentistry with computer aided design and manufacturing of fixed dentures [218, 285, 286], the first cohort studies of pure ceramic implants have concluded successfully [287].

5.5.3 Biocompatibility

It is important to evaluate the permanence of dental fixtures and other implanted ceramics in the body, thus extensive clinical research is continuously conducted to evaluate their impact in human subjects. New zirconium based materials are tested with in vivo or in vitro animal studies to show their positive compatibility and some suggesting that the biocompatibility of zirconia is greater than titanium [264, 288–294]. The acceptance or rejection of the material by the living tissue or cells is an important research question, as well as the effects of the material on the molecular mechanisms of the cells. Factors that may influence this are not only biochemical, they can also include the physical structures and surfaces [295]. There are several studies investigating how organisms respond to zirconium based materials, what structures are built in response to them, and how the findings can be used to benefit future applications. For example, it was observed that in adult pigs, collagen fibres in connective tissue oriented around zirconia
implants, providing some adhesion to the tissue [296]. Zirconium has also been used with protamine sulfate to trace haematopoietic progenitor cells (HPCs) when intrabone injected in order to maximise marrow retention of HPCs [297]. It is also important to evaluate the impact of the biological environment on the implants and composites. It was recently shown, for example, that saliva affects the bonding of zirconia implants [298]. Efforts were then directed towards finding reliable zirconia bonding agents for implants, and novel silane-based zirconia primers have been proposed and investigated for this purpose [299, 300]. Mechanical solutions are also proposed so that zirconia abutments, crowns and posts can be safely fixed [301, 302].

**Osseointegration**

The largest biomedical application of zirconium compounds, particularly zirconia alloys and composites, is their use as bone replacements. Current research efforts are aimed at understanding the material properties that best suit this application. The chemical composition of the implants plays a key role in the acceptance, but also in the durability and strength as discussed before. The aim is to achieve successful osseointegration, which has already been proved for zirconia implants [303, 304]. Several material combinations have been suggested for improving this, for example, graded hydroxyapatite-zirconia (HA-ZrO$_2$) or zirconium modified calcium-silicate ceramics (Ca$_3$ZrSi$_2$O$_9$ (Baghdadite)) [305–310]. Structural and surface modifications have also been studied as important factors in the acceptance of implants by osteoblasts [311]. Zirconia toughened alumina is widely used as an orthopaedic graft material and it has been shown that altering its structure to a porous one permits its bioactivation and better acceptance [312, 313]. Oxidised zirconium shows promise for use as the bearing surface for femoral heads in total hip arthroplasty, with initial studies showing lower wear compared to cobalt-chrome, although long term analysis is still required [314]. In addition, magnesia-stabilised zirconia is being studied for use as a femoral component in knee arthroplasty [315]. When evaluating osseointegration in vivo, direct observations are useful, however biochemical and genetic activity could be better indicators of cell proliferation and give insights into which interactions the cells prefer [316, 317]. In addition, zirconium ions seem to induce proliferation and differentiation of primary human osteoblasts during in vitro culture [318]. An ultimate osseointegration would be one that not only mimics the material properties and surface structures of bones and other tissues, but also incorporates molecules that biochemically enhance the acceptance of the implant materials. A study showed that it is possible to go down to the level of mimicking interaction with neurotransmitters and protein interactions on zirconia ceramics to enhance osseointegration [319]. Further experimentation shown that sol–gel-derived Si/Zr O$_2$ coatings could promote the osteogenic differentiation of mesenchymal cells, opening applications in tissue engineering. Similarly, Zr-based coatings were found as efficient as a material already employed in clinical practice to promote the growth of osteoblasts [320].

Replacing cartilage, which is a non-regenerative tissue is an important medical application. A Zirconium-based hydrogel has been proposed for that purpose [321].
Biodegradation

Understanding the biodegradation pathways of zirconium based materials is important for the design and proposal of new composites and coatings [322]. For example, ZrN/Zr has high corrosion resistance and has been used to coat magnesium alloys used in biomedical implants, improving its corrosion resistance [323]. Sometimes it is desirable that natural biodegradation occurs, and hybrids of biomaterials and zirconia nanoparticles have been used for this purpose [324].

5.5.4 Bioconjugation

Zirconium compounds possess electrochemical properties that allow interaction with biomolecules at the nanoscale. These interactions permit communication with the biomolecules at the electronic level allowing electron transfer and their incorporation into electrochemical devices. Haemoglobin and myoglobin have been directly conjugated with zirconium derived compounds for electrochemical studies [325, 326]. These conjugations can be taken further to analyse the interactions of the conjugated molecules with other ones; thus, the use of zirconium compounds can be seen as a bridge for reading molecule interactions, which is the basis for biosensing (explored in detail in Section 5.9.4).

5.5.5 Drug delivery and pharmaceutical formulations

The element zirconium has been proposed as an inhibitor of human smooth muscle cell proliferation for treating various diseases [327]. Other compounds, such as silver-carried zirconium phosphate (AgZrP), have been tested as powerful antibacterials able to annihilate E. coli and kill up to 99.9% of S. aureus at low doses [328]. Sodium zirconium cyclosilicate has been tested for use as a selective cation exchanger to reduce serum potassium levels in people with hyperkalemia [329–331], as well being shown as a urgent treatment option for severe hyperkalemia [332]. Most zirconium compounds are safe to use in the human body due to their biocompatibility, and can be easily excreted without negative effects. Thus, zirconium compounds can be used as delivery systems [333], such as zirconia/polyethylene glycol [334, 335] and monodisperse zirconium metal-organic frameworks [336]. An example of this use is the nanoencapsulation of insulin in zirconium phosphate cages (ZrP, which has shown no cytotoxicity) and their use as delivery systems [337]. In addition, molybdocene dichloride has been intercalated into zirconium phosphate to develop a potential anti-cancer drug [338] with zirconium phosphate nanoplatelets also suggested for drug delivery for cancer therapy [339]. Targetted delivery may be possible using photosensitive MOFs encapsulation [340].

5.5.6 Bioimaging

Imaging through the use of zirconium compounds is an important research area that is finding broad applicability in the biomedical sciences. Zirconium-89 radiation has been used as an indirect labelling system for biomolecules, particularly using chelates for its attachment to antibodies [341–344]. This emerging technique is called Immuno-PET (Positron Emission Tomography) and takes advantage of zirconium-89 as a positron
emitter. A specific example is where chelator-free zirconium-89 has been used to label mesoporous silica nanoparticles to enable PET image-guided delivery of this drug for use in nano-oncology [345]. Further development have looked at the promising safety of the new methods [346]. Fluorescence has also been used for imaging: it has been found that doped zirconia nanoparticles with lanthanides are fluorescent and can be functionalized for imaging biomolecules [347]. Some doping elements, such as Eu, Tb or Gd, have also shown magnetic properties that can be used in combination with fluorescence for dual imaging applications [348]. Research had suggested the use of this technique for characterising tumours and monitoring the therapy outcome in cancer patients [349], this technique has now been applied in breast cancer treatment [350].

5.6 Catalysis

Zirconium based catalysts have been used in a large number of chemical reactions due to the versatility and abundance of this element. It has been used as a catalyst for pollution control, automotive applications, chemical refining, and hydrocarbon reforming, among other areas. Organic reactions catalysed by zirconium include hydrogenation, oxidation, amination, isomerisation, and pyrolysis, among others. A famous reaction is the zirconium-catalysed asymmetric carboalumination developed by Nobel laureate Ei-ichi Negishi [351]. Because of its versatility to form chemical compounds, it can be used as a strong base or strong acid, as well as in different physical forms such as slurry, tablets, extrudate, or foams, augmenting the number of possible catalytic reactions. The particle size, surface area, porosity and crystallinity of certain zirconium compounds can also be modified to fulfil particular catalytic applications. Furthermore, zirconium compounds are also used as support media for other catalysts. One emerging catalyst is the use of mesoporous zirconium phosphonates to catalyse a cycloaddition reaction between aziridines and CO$_2$ as a method to fix CO$_2$, for use in carbon capture and storage [352–354]. This section summarises current R&D for zirconium catalysts.

5.6.1 Inorganic catalysis

Redox reactions

Oxygen mobility in zirconium oxide particle surfaces allows for good redox properties with thermal stability. Ceria-Zirconia oxides have been used to emulate the redox properties of similar particles in solution [355]. Activated zirconium carbide may also be used for oxygen reduction [356]. Zirconium-porphyrin frameworks also show properties as precursors for oxygen reduction reaction catalysts [357]. Recently, these have been produced as thin thilms MOFs [358]. A highly selective synthesis reaction of hydrogen peroxide from H$_2$ and O$_2$ can be catalysed by zirconia doped catalysts [359]. Photoactive srilankite-type zirconium titanate hollow spheres look to be promising candidates for photocatalytic reduction due to higher redox potential [360]. Meerwein–Ponndorf–Verley organic-inorganic reduction is efficiently catalysed using a Zr–phytic acid hybrid [361]. Zirconium is emerging as a substitution for the much more expensive ruthenium chelates in photoredox catalysis [362].
Emerging R&D

Crystal growth control

Crystal growth can be accelerated or slowed by zirconium based compounds. For example, the presence of zirconium silicate has been found to produce accelerated abnormal grain growth in rutile TiO$_2$ [363]. On the other hand, the glass former CuZr induced slower crystal growth rates [364]. Not only the growth rate can be influenced, a zirconium acetate complex has been shown to have ice shaping properties similar to those of antifreeze proteins [365].

5.6.2 Gas catalysis

Hydrogen production

The ability of zirconium compounds to catalyse redox reactions has found applications in gas catalysis, particularly for the production of hydrogen gas for fuel cell applications (see Section 5.7). One popular reaction that can be catalysed by zirconia is the ‘water gas shift reaction’ in which water and CO are combined to produce H$_2$ and CO$_2$. Zirconia is usually doped with gold and it is known that its crystal phase affects the performance of the reaction [366, 367]. CeO$_2$–ZrO$_2$ ceramic foam is also used to perform this reaction [368]. Other methods for hydrogen production are based on water splitting systems catalysed by ZrO$_2$ in a similar fashion, making use of the semiconducting properties of zirconia when doped with other materials such as TaNO, WO$_3$ [369], or when coating SiC structures for thermochemical production [370, 371]. Hydrogen can also be obtained from other compounds by steam reforming or hydrolysis. For example, CeO$_2$–ZrO$_2$ coated metallic foam and NiAl$_2$O$_3$–ZrO$_2$ catalysts are used for reforming liquefied natural gas obtaining H$_2$ gas [372–375]. Ethanol has been used in a similar process based on nickel Ce/Zr catalysts [376, 377] and silica and zirconia supported catalysts [378]. Hydrolysis of hydrogen rich compounds such as sodium tetrahydroborate is achieved by sulphate-zirconia based catalysts [379–381]. In addition, the magnetocaloric parameters of zircon-type DyCrO$_4$ and HOCrO$_4$ suggest they could be used as magnetic refrigerant materials for the liquefaction of hydrogen [382].

Gas oxidation and reduction

Partial oxidation of gas molecules is important for industrial applications related to the production and storage of gases. Carbon monoxide, methane, nitrous oxide, methanol and hydrogen are amongst the most popular gases for this processes [383–387]. The configuration of the catalysts used for this purpose are nickel and yttria-stabilized zirconia, PtCe-Zr mixed oxides, molybdenum zirconium, and CuCe-Zr [383–390]. The oxidation of incomplete catalysed hydrocarbons, also known as soot oxidation, is also catalysed by this type of zirconia based catalysts [391, 392]. Similarly, reduction reactions can be catalysed by zirconia supported catalysts for the production of methanol or the reduction of gases such as NO [393–395].

Gas purification

Since various gas species can be transformed or absorbed by zirconium oxide based catalysts, these compounds can be applied for the production of pure inert gases such as xenon and others (e.g. in car exhausts) [76, 396]. Ceria-zirconia mixed oxides has
also been used to reduce soot emissions of a diesel engine [397]. A composition of zirconium, cerium and niobium are used as a catalyst to treat gases containing nitrogen oxides, which are emitted from motor vehicles [398]. A three-dimensional zirconium modified TUD-1 mesoporous material has been synthesized and successfully used as a catalyst for the hydrodesulfurization of FCC diesel [399].

5.6.3 Organic catalysis

Esterification, transesterification, acetylation and ketonisation

It has been found that sulphated-zirconia, tungsten-zirconia, and other modified zirconia, namely zirconium-based metal organic frameworks, can be used for homogeneous esterification and transesterification of natural oils, lipids, triglycerides, soybean oils, oleic acids, and waste oils [400–406]. Ketonisation of biomass derived species and carboxylic acids can also be achieved by similar solid state zirconia catalysed reactions [407,408]. Acetylation of glycerol and selective oxidation of cyclohexane are some other examples of the broad range of organic reactions that can be catalysed by zirconia and zirconium compounds [409–411]. Zirconium(IV) Phosphonate-Phosphates can be used to select ions in solution, enhancing specificity of reaction involving hydrocarbons [412].

Enantioselective and Regioselective reactions

The advantage of using zirconium catalysts for organic chemistry is due to their enantioselectivity and regioselectivity. This allows modification of chemical compounds on specific sites and regions. Reactions that have been possible include the enantioselective alkene hydroamination, and the synthesis of amino alcohols and alkyl indoles by regioselective ring-opening of epoxides, amongst others [413–417].

Synthesis of specialty compounds

There are many reactions that can be catalysed by zirconium compounds, most of which are catalysed in the solid state: from acetic acid reforming to warfare agent degradation, all can be catalysed by a zirconium derived catalyst or zirconia supported catalysts [418–421]. Some examples taken from current scientific literature include: synthesis of dimethyl carbonate [408], hydroxylation of phenol over molybdoovanadophosphoric acid modified zirconia [422], total oxidation of toluene by nanostructured mesoporous zirconia [423], four-component synthesis of pyranopyridine derivatives [424], tetrahydroxyridines [425], solvent free aza-Michael addition with sulphated zirconia [426], bis and tris (indolyl) methanes with tungstophosphoric acid on zirconia [427], hydroxy derivatives of 4-methyl coumarin [428], glycerol dehydration to acrolein by sulphated zirconia [429], aerobic oxidation of aldehydes to alcohols by polyoxometalate-zirconia (POM/ZrO$_2$) nanocomposite [430], SBA-15 catalytic activities in sulphated zirconia [431], hydrogenation of haloaromatic nitro compounds by hydrous zirconia supported iridium nanoparticles [432], Lewis acidic three-dimensional mesoporous zirconium catalyst [433], and synthesis of dimethyl carbonate from urea and methanol over ZnO–CeO$_2$ [434], hydrolysis of nerve-agent simulants with a zirconium based metal-organic framework [435], amide formation using a zirconium chloride catalyst [436, 437], a low waste Heck reaction of methyl acrylate and styrene with
palladium nanoparticles on layered potassium $\alpha$-zirconium phosphate [438, 439], AgCl-based composite photocatalyst obtained from nanosized silver exchanged $\alpha$-zirconium phosphate as a precipitating agent [440], synthesis of xanthene derivatives promoted by zirconium dodecylphosphonate [441], conversion of glucose, fructose and sucrose into 5-hydroxymethyl-2-furfural with mesoporous zirconium phosphate catalyst is a hot research topic [442–445], hydrodeoxygenation of guaiacol over ceria-zirconia catalysts [446] and synthesis of 2,3-dihydroquinazolin-4(1H)-ones, which has a wide range of biological activities, with sulphated zirconia [447]. Polypropylene oxide can be produced from CO$_2$ using zirconium complexes [448]. Thioanisole can be selected for by NPF-201, a Zr-MOF [449].

**Fuels and Biofuels**

One significant application in which zirconium catalysts play an important role is organic catalysis for fuels and biofuels. Continuous research has been devoted to the use of zirconium compounds in improving the performance of the cracking of naphtha [450]. Synthesis of biodiesel has been achieved by zirconia supported tungstates [451], KOH [452], acid modified zirconia [453], and sulfated zirconia [454] while synthesis of high-octane gasoline from carbohydrates has been achieved by Pt/zirconium phosphate [455, 456]. Zirconia supported metallic catalysts have also been used for the reforming of gasoline, diesel, butane, propane, and ethanol, and are under continuous research [457–461]. Synthesis of ammonia from air has been shown [462]. Size-selective oxidation of alkanes may also be catalysed by heteropolytungstic acids incorporated in mesoporous zirconia [463]. Zirconia catalysts have also been used for desulphurisation of liquid fuels [464]. Cleaning biogas and upgrading to natural gas is an important industrial process for the full utilisation of these environmentally friendly fuels. This process can also be catalysed by zirconium compounds such as zirconium terephthalate, zirconia-titania or zirconia-alumina catalyst supports [465–468]. Sustainable production of biofuels is the topic of ongoing research [469]. Not only the transformation but also the combustion of natural gas is possible by using zirconia supported catalysts [470]. Zirconium phosphate was shown to be a very effective catalyst for the production of $\gamma$-valerolactone, a key solvent for the dissolution of biomass [471].

**Biocatalysis**

The flexible chemistry of zirconium compounds as catalysts has led to their application in biochemistry. They have been used to mimic biological catalysts such as metalloporphyrins [472], or to achieve biochemical transformations in fewer steps, which can be achieved for example during the dehydration of fructose to 5-hydroxymethylfurfural by sulphated zirconia solid acid [473]. Zirconium based catalysts have also found a niche application as immobilisation matrices for lipases to mediate enantioselective catalysis [474–476]. Zirconium silicate can also be used in the deproteinization of human plasma [477].
5.7 Fuel cells and batteries

The use of zirconium for hydrogen production has been discussed in Section 5.6.2. Hydrogen is a clean fuel that can be easily obtained from one of the most abundant molecules in the planet: water. In addition, hydrogen can also be obtained from hydrogen rich molecules such as uranium-zirconium hydride or borohydrides [379, 380, 478]). Early research also suggests that zirconium acetylacetonate can be used as the electron extracting layers in regular and inverted small molecule organic photovoltaic cells [479]. Zirconium alloys are also used in water-cooled nuclear reactors for nuclear fuel cladding and structural components [480], but can be embrittled by hydride precipitation [481], modelling and electron microscopy is being undertaken to develop strategies to mitigate this aqueous oxidation in zirconium alloys and thus extend their lifetime [480]. This section further explores current research and development trends in the fabrication and optimisation of fuel cells using zirconium.

5.7.1 Proton Exchange Membranes

Traditional fuel cells are produced using proton exchange membranes made of polyanions. Nafion is a derivate of tetrafluoroethylene with sulfonic acid in its porous matrix that allows protons to be transported from one side to the other by exchange with water, freeing electrons in the process. Nafion-zirconia, nafion-sulphated zirconia and nafion-zirconium phosphate composites have been formed by different methods to improve the proton exchange performance in fuel cells [482–489]. Other cation exchange membranes such as MS-4K resins have also been improved by modification with hydrous zirconia [490]. It has been found that these ion transport improvements, gas diffusivity, and proton conductivity properties in zirconia crystals can be used on their own in the solid state and not necessarily in a wet membrane (Section 5.7.3).

5.7.2 Hydrogen storage

Hydrogen as a means of energy storage has been touted as one of the technological solutions to global warming. Although this claim is likely oversold, much work has been devoted to the development of safe liquefied hydrogen storage, usually using metallic foams, which release the gas slowly in the case of a leak. These are difficult to manufacture and shape. In this work by Lv and Huot, a TiFe foam is made more suitable for practical large scale deployment by the addition of 4% of ZrMn$_2$ [491].

5.7.3 Ion transport and conductivity in zirconia

For a solid oxide such as zirconia to be used in hydrogen fuel cell applications, it is required that hydrogen and oxygen diffuse through it [492–494]. Not only is gas diffusion important, but also the cation conductivity that generates the electric potential, while yttria-stabilised zirconia must be able to conduct protons as well [495, 496]. Zirconium hydrogen phosphate, incorporated into the catalyst layer, has also been used to improve the performance and durability of high temperature polymer electrolyte membrane fuel cells [497]. These phenomena have been found to work even better in combination with other solid oxides for high temperature applications, as developed in
emerging Solid Oxide Fuel Cells (SOFC) in the next section.

5.7.4 Solid Oxide Fuel Cells

There are different types of solid oxides that have been modified with zirconia or doped zirconia for their use in fuel cells. Examples of these include various composites of lanthanides, gallium, magnesium, strontium, cobalt, iron, scandium, bismuth, gadolinium, and manganese oxides, usually modified with yttria stabilized zirconia, which is also a solid oxide [498–506]. Nickel-zirconia anodes have also been investigated for solid oxide fuel cells, as well as ceria and zirconium thin films, highlighting the importance of the film structure for their performance [507–513]. Micro-tubular solid fuel cells have also been proposed which use porous zirconia [514]. Oxide ion conductivity is a well researched phenomenon that has been transferred to other areas such as gas sensors or the preparation of BASE (sodium 'beta'-alumina+zirconia solid electrolyte) for Na-S-batteries [515].

5.7.5 Batteries

The thermal stability and ionic conductivity of ZrO$_2$ make it an excellent candidate for separators in Li-ion batteries, enhancing safety [516]. Further, there is ongoing work on developing solid-state batteries using ZrO$_2$ as the cathode.

5.8 Adsorption and immobilisation

Not all reactions with zirconium compounds are reversible and not all of them see the transformation of the reactants: some of these reactions are partially reversible or completely irreversible and may incorporate zirconium permanently, or vice versa. Adsorption and immobilisation of different chemicals onto zirconium compounds is then possible [517] and some applications are described in this section.

5.8.1 Water, food and biological applications

Early work shows a zirconium (IV)-based metal-organic framework membranes as showing significant promise for use in water desalination [518]. There is a particular interaction between zirconium compounds and proteins that has been exploited by the food industry and other biological applications: zirconium dioxide in metallic cages has been used to stabilise proteins of white wines [519]. Similarly, addition of transition metals and zirconium has been found to prevent unwanted aromas [520]. This original selectivity for certain molecules has also been used for chromatographic determination of xanthines and for the extraction and characterisation of melamine residues in milk [521,522]. Adsorption of proteins has also been taken to the microscopic level to absorb viruses from water with colloidal zirconia microfilters [523]. Selective elimination of selenate and selenite has been shown [524]. Zirconia is also suggested as a potential phase for the separation of biological samples [525].
5.8 Adsorption and immobilisation

5.8.2 Remediation applications

Another adsorption application for zirconium compounds is the adsorption of contaminants and toxic compounds. It has been shown that iron-zirconium oxides and hydrous zirconium oxide effectively remove arsenic from water [526, 527], and that a zirconium-based magnetic sorbent for arsenates is possible [528] as well as for mercury [529]. Amongst other applications, hydrous zirconium oxide has been shown to adsorb Cr(VI) from aqueous solutions [530, 531], as has mesoporous iron-zirconium bimetal oxide [532]. Titanium dioxide doped with zirconium element also shows promise for use as a heterogeneous photocatalyst to treat water pollution [533]. Zirconium alginate can be used for fluoride removal [534]. Desulphuration by adsorption has also been possible using copper supported zirconia as adsorbent [535]. Ammonia, which is a common water component, and a contaminant if in excess, can be adsorbed by aluminium-zirconium polycations [536]. Similarly, vanadium can be removed from aqueous solution chitosan-zirconium (IV) composites [537]. Phosphate can be removed using ZrO$_2$ in quaternary-ammonium Chinese reed or treated bentonite [538, 539]. Removing lead (II) from an aqueous solution onto gel spheres of zirconium hydroxide was shown [540], similarly copper (II) and cadmium (II) by adsorption on nano zirconium silicate [541]. Methylene blue has been removed from waste water by polyaniline zirconium (IV) silicophosphate nanocomposite [542, 543], and by photoactive zirconia-titania [544] and Ce and Er doped ZrO$_2$ [545], both showing its potential for environmental purification applications. RhodamineB could be removed from water by a graphene-Zr photocatalyst [546]. Research has also shown that a hydrous zirconium oxide-based nanocomposite can be used to remove trace phosphate from water, particularly at acidic pH [547, 548]. Stable detoxifying of nerve agents using a Zr-based MOF has been demonstrated [549–551]. Similarly, arsenic removal was shown [552]. Emerging pollution remediation can also benefit from the photocatalysis possibilities offered by Zr-doped TiO$_2$ [553]. The same properties have been exploited to degrade methyl orange [554].

5.8.3 Radioactive applications

Zirconium compounds are known for their radioactive shielding and adsorptive properties, and research is constantly carried out to optimise these processes [555, 556]. Neutron adsorption for shielding materials has been done with zirconium borohydride and zirconium hydride [557]. Immobilising nuclear waste is also paramount and zirconium phosphates have been proposed as host structures for this purpose [558]. Zircon ceramics have also shown potential to immobilise trivalent and tetravalent actinides, contained in high-level nuclear waste [559]. Further examples include the removal of uranium (VI) with humic acid immobilised zirconium pillared clays, and the removal of radioactive actinides by doping zirconia crystals [560, 561]. Evidence at nanoscale also suggests that even radiation damaged and highly porous zircon may still be suitable to store in nuclear waste (minor actinides) [562].
5.8.4 Gas storage and adsorption

The adsorption of gas molecules has been identified as a great advantage for gas storage applications in fuels and transport. It has been shown that oxygen can be stored in ceria-zirconia materials with alumina decorating the grain boundaries of ceria-zirconia particles and acting as diffusion barrier [384, 563]. Similarly, it has also been shown that hydrogen can be incorporated into crystalline zircon [492], which can be used for adsorption applications in membranes, as discussed in Section 5.6.2. Metal-organic frameworks containing zirconium are a growing class of materials of potential utility for hydrogen and methane storage in vehicles [564–566]. CO₂ capture is also a growing research area due to the potentially negative consequences of an increased abundance of this gas in the atmosphere: lithium zirconate has been proposed and researched as an effective CO₂ sorbent [567, 568], mesoporous alumina-zirconia-organo-silica composites also show promise for CO₂ capture at ambient and elevated temperature [569], in particular when organised as high effective surface nanosheets [570].

5.8.5 Sorption for catalysis

Sorption of gas molecules can be advantageous for catalytic processes that require the presence of certain gas molecules, which can be fixed onto solid state catalysts for use in the reactions. Examples of these are: the CO adsorption over zirconium oxide cluster ions [571]; water adsorption into monoclinic zirconia [572]; NO, NO₂ and other NOx molecules adsorption over ceria-zirconia mixed oxides [573–576]. Acidic modulators have been incorporated into zirconium-based metal-organic frameworks to improve their structural integrity and thus use in gas sorption [577]. Research also shows the potential of zirconium-based MIL-140 frameworks for CO₂ adsorption, which could have application in carbon capture technology [578].

5.8.6 Sorption of zirconium

In some cases, zirconium can be the adsorbed material rather than the sorbent. This could be done to achieve its recovery or for doping novel materials. In a recent study, Candida tropicalis was used to recover and remove zirconium from its aqueous solution [579]. Graphene has extraordinary conductive properties and so does zirconium; studies of its diffusion on graphene show that it is in fact possible to combine them both for possible applications [580].

5.9 Sensing

When the adsorption is highly reversible, it can be used for detection of the adsorbed molecule. These adsorption mechanisms can be coupled with detection methods for sensing. However, there are other sensing mechanisms that involve zirconium and do not necessarily include adsorption. This section reports sensing applications in current R&D in which zirconium compounds are used.
5.9 Sensing

5.9.1 High temperature and pressure

Zircon sand has been studied with various analytic techniques under several conditions, particularly high temperatures and pressures. Raman spectroscopy has been used to detect changes of pressure in high temperature silicate melt systems [581]. Zirconium based electrodes perform adequately when used to measure chemicals or pH under high temperature and in high pressure environments [582,583].

5.9.2 Gas sensing

The electrochemistry of zirconia is affected when interactions with oxidising gases are present, or when there is an electronic interaction with them. Thus, the electrochemical detection of gases by zirconia is widely investigated and has built substantial knowledge in the R&D literature [584]. Some of these investigations aim at detecting gases in automotive exhausts [585], while stabilized zirconia and NiO electrodes have been employed for the detection of NO\textsubscript{2} [586], and mesoporous ceria-zirconia for the detection of oxygen [587]. Oxygen sensors for steelmaking processes are fabricated using a MgO-partially stabilised zirconia (MgO-PSZ) electrolyte tube [588]. The use of gas-sensors with combined yttria-stabilised zirconia has also been suggested for detection of carbon monoxide, hydrocarbons, nitrogen oxides, hydrogen, volatile organic compounds, and ammonia [589–592]. UiO-66, a MOFs, can be deposited using only Zr foil as a source, creating a sensor for dilute volatile organic compounds [593].

5.9.3 Relative humidity sensing

Sensing relative humidity reliably is difficult. A (PVA-PEG-PVP) blend as a matrix and zirconium oxide nanoparticles as an additive was shown to vary its electrical resistivity as a function of RH. This may lead to improved RH sensors [594].

5.9.4 Biosensing

Detection of biomolecules has also been possible with the use of zirconium compounds. Ascorbic acid, uric acid, and dopamine have been detected with a phosphorylated zirconia-silica composite electrode and adsorbed methylene blue [595]. Zirconia nanocomposites may also be used for vitamin B\textsubscript{2}, B\textsubscript{6}, and C effective detection [596], with titania-zirconia nanocomposites utilised for urea detection [597]. Vitamin C detection and phosphate content in blood serum has also been possible by nanostructured zirconia platforms [598,599]. Furthermore, silanized nanostructured zirconia within a biosensing platform holds promise for the detection of oral cancer [600]. The use of glucose oxidase/chitosan/α-zirconium phosphate ternary biocomposites have also been suggested for biological sample estimation of glucose [601]. Zirconium sensing platforms can be coupled with biomolecules such as enzymes for detection of specific biochemical transformations [602]. Such is the case of ethanol oxidation by immobilisation of enzymes and cofactors onto zirconium phosphate sensors [603]. Recent developments indicate Zr-MOFs can be used in cancer clinical diagnosis [604].
5.9.5 Food and drink applications

ZrO$_2$-based sorbents can be used in a quick and inexpensive analytical method to determine the types and amounts of pesticides that may be present in milk [605]. Hydrogen peroxide can be detected using zirconium molybdate nanostructures [606].

DNA

The specificity of nanostructured zirconium based sensors can be extrapolated to a level in which it is possible to detect complex structures or several types of molecules at the same time. For instance, it has been possible to detect DNA hybridisation [607, 608], or even DNA strings or genes corresponding to particular pathogens such as Mycobacterium tuberculosis and E. coli [608–610]. Subsequent research demonstrated the fabricability of biosensors with good performance with excellent selectivity and high stability [611].

Proteins

The detection of DNA is based on the phosphorus and phosphorylation sites, and this can be taken even further to detect the interaction of genes and proteins or entire proteomes. Microarrays for probing DNA-protein interactions have been fabricated based on zirconium phosphonate [612], and zirconium phosphonate modified magnetic nanoparticles have also been used for phosphoproteome analysis [613]. Similarly, mapping of phosphorylation sites on protein complexes has been possible on acidified zirconium oxide [614].

5.10 Nanomaterials, nanorods, nanostructures and nanofabrication

There is an increasing number of research groups investigating the properties and advantages of nanomaterials and nanostructures for different applications. Zirconium compounds are not the exception and are commonly used for constructing these nanostructures with novel properties.

5.10.1 Nanotubes and ordered arrays

Order at the nanoscale presents different material properties than disordered material in the bulk. Ordered arrays can be formed by uniformly growing the material or by degrading the mould ordering the material. For example, ordered arrays of lead zirconium titanate have been grown on monolayers of latex nanospheres with the aim of exploiting its ferroelectric properties [615]. Similarly, crystalline mesoporous walls have been grown on PMMA nanosphere templates [616]. Chiral zirconia nanotubes have been prepared with a potential of being applied in the fields of asymmetric catalysis and chirality sensors [617]. Examples of directly grown zirconia tubes or arrays are the anodisation of zirconium foils for \textit{in situ} fabrication [618, 619]. The behaviour of zircon-type LaVO$_4$ nanorods has also been studied, identifying an irreversible transition zircon to monazite phase under pressure treatment [620]. In addition, zirconium oxide based electrocatalysts with multi-walled carbon nanotubes have been examined for use
5.10 Nanomaterials, nanorods, nanostructures and nanofabrication

as non-platinum cathodes for polymer electrolyte fuel cells [621].

5.10.2 Foils and thin films

Thin film structures are also common nanoconstructs that allow materials to be used in various dimensions with different properties, along the film plane and across it. The mechanism synthesis and characterisation of the formation of zirconium oxide thin films has been investigated either by laser deposition or chemical deposition of the zirconium oxide molecules [509,622,623]. Ultra-thin films are expected to have enhanced catalytic properties [624]. It has recently been suggested a spray-coating process to manufacture films with a mechanically robust coating that shows excellent gas barrier properties [625]. These films can be then patterned with nanolithography to build circuits or other useful structures [626]. Two dimensional nanomaterials such as \( \alpha \)-zirconium phosphate nanoplatelets have revealed to be effective as lubricant additives [627]. In addition, lead sulfide nanoparticles embedded in a thin-film matrix of zirconium oxide have been shown to have potential use in nanodosimetry of ionizing radiation [628].

5.10.3 Surface modification

Mesoporous walls and surfaces can be fabricated to tune the surface properties of the bulk material and control its wettability (i.e. hydrophilicity and hydrophobicity). Engineered nanostructures of zirconia have been constructed to control these properties, finding use in suitable applications such as load-bearing [629]. Hollow mesoporous zirconia nanospheres offer a promise for active corrosion protection coatings of metals and alloys with self healing ability [630]. Surface modification of layered zirconium phosphates can be used to tailor nanoparticles for varied specific applications [631].

5.10.4 Nanofibres

Ultra-thin fibres mixed with bulk materials have been found to strengthen the host materials and therefore several research efforts have been directed towards the fabrication and growth of these fibres. Particular attention has been paid to composite fibres such as alumina-zirconium [632], zirconium carbide (produced by electrospinning) [633], zirconium nitride (produced by nitridation of electrospun fibres) [634], and zirconia-carbon plasma sintered composites [635]. Semiconducting nanobelts of zirconium oxide have also been fabricated by thermal decomposition [636], the crystalline polymorph of CaO-doped zirconia nanofibres can be fully controlled, for tunable properties [637].

5.10.5 Self assemblies, organic templates, and hybrid materials

Nanofabrication techniques may have limitations for building complex structures of certain zirconium compounds. Thus, researchers have approached biomimetic synthesis or the use of organic templates or assemblies for producing such structures. The complexity can go as far as the organism level: yeast, for example, has been used as a biotemplate for producing mesoporous zirconium phosphate [638]. Self-assembled triblock copolymers, hybrid polymers, metal-organic cages, or metal-organic frameworks have also been used to produce such structures with a higher level of control and
5.10.6 Nanofluids

The heat resistance properties of zirconium compounds have been exploited for decades in solid materials (see Section 3). Since nanoparticles can be included in liquid solutions as colloids, the use and exploitation of the thermal resistance and strength of zirconium particles has been considered for fluidic applications. Nanofluids of zirconia in water have been tested for laminar heat transfer and viscous pressure loss in turbulent fluids, as well as for their effect on surface wettability and critical heat flux [644–647]. Solvent-free zirconia nanofluids have been developed as part of hybrid coatings that have the potential to improve the efficiency of solar energy related devices [648].

5.10.7 Nanoparticles, nanopowders, nanocrystals and composites

Nanoparticles and nanopowders have proved to be useful for certain industrial applications and easy to incorporate in bulk materials due to their mass fabrication. Research and development efforts have been directed towards the synthesis and crystallisation of these particles and powders, particularly for zirconia. These methods include sol-gel processes, hydrothermal methods, hot-air pyrolysis, or microwave sintering [649–654]. Nanoparticles can be functionalized or doped during the synthesis to enhance certain properties: for example, Al₂O₃ can be dispersed with zirconia for mass production of hybrid particles; silane groups for multiple functionalisation can be also added to the particles [655]; and hematite can be doped with zirconia for sensing enhancing [656]. Complex functionalisation of polymerisation can also be achieved during the mass production of these particles: zirconium carbide preceramic polymers, light curable ceramics and films, synthesis of particles on nanotubes for enhancing fracture toughness, or PET-zirconium nanocomposite as fire retardants, are all examples of these applications [657–661]. The use of yttria-stabilised zirconium dioxide nanoparticles has been explored for the cleanup step in post-harvest pesticide residue analysis [662] and the effect of hyperbranched polyester and zirconium slag nanoparticles on the toughness of epoxy resin has been investigated, showing excellent impact and flexural strength [663, 664]. Surface treatment with zirconia nanoparticles have also been shown to improve the tensile and bonding properties of flax fibres [665]. Furthermore, cerium-zirconium binary oxide nanoparticles have been shown to be effective for phosphate adsorption [666]. Whereas the encapsulation of platinum nanoparticles in a zirconia nanocage significantly increases platinum stability and activity, enhancing its use as a catalyst in polymer electrolyte fuel cells [667]. Alternatively, graphene-based foams can be reinforced with nanocrystalline zirconia, improving their oil adsorption capacity [668]. Carbon nanotubes and carbon fibre hybrids with zirconia nanoparticles are of particular interest due to their microstructural properties and strength [669–671]. The uses of these hybrids extend to different application categories, as discussed in other sections here, but the key research regarding their synthesis as mass producible particle suspensions is going to have an impact in the future use of zirconium derivatives.
5.11 Optical materials

5.11.1 Waveguides, fibres and optical substrates

The dielectric properties of zirconium compounds have found applications based on the direct use of the dielectric constants to guide light waves. Magneto-optical waveguides made of cobalt ferrite nanoparticles embedded in a silica-zirconia matrix have been successfully fabricated using the advantages of zirconia composite materials [672]. Similarly, erbium-activated silica-zirconia planar waveguides and other gratings have been successfully used to manipulate the path of light at different frequencies and bandwidths [673–675]. Another advantage of using hybrid zirconium materials is the possibility of using them as optical substrates for cost effective photopatternable organic-inorganic hybrids [676].

5.11.2 Nanostructured colour and dyeing

When the dielectric constant of a material changes in an ordered fashion at the nanoscale, the apparent colour of the structure changes. This characteristic has been used to produce tunable zirconia opals [677], which are photonic crystals with ordered nanostructures. A similar effect is observed in liquid crystals, and zirconia nanoparticles have been used to enhance their electro-optical performance and potential application in liquid crystal devices (LCDs) [678,679]. New developments focus on the scratch resistance of such thin films, and important step in making them practical [680]. Sometimes the colour of the materials is not coming from a photonic structure, but from the absorption of light by the material itself. Zircon has a natural colouration which can be altered by ‘plasma dissociation’ in the known Plasma Dissociated zircon (PDZ) material [681]. The ratio of other elements in this process, and the physical conditions of the process itself, may affect the crystallisation and, therefore, the final colouration [682–684]. These processes and mixtures of elements with zirconium compounds can be controlled in such a way that soluble pigments for particular applications can be produced, such as turquoise $\text{V}^{-}\text{ZrSiO}_4$ [685,686]. A new development claims to significantly improve Zircon-based heteromorphic encapsulation pigment efficiency [687].

5.11.3 Luminescence and emission

Another optical characteristic of zirconium compounds is the emission of radiation in form of light when excited by other forms of energy. Examples of these achievements are: green emitting phosphors based on zirconium oxide phosphate [688], luminescent and photochemical ruthenium complex/zirconium phosphate hybrid assemblies [689], luminescent Pr$^{3+}$ doped yttria-stabilised zirconia nanopowders [690], luminescent lanthanide polyoxometalates based on zirconia matrices to titania [691], vapoluminiscence and vapochromic platinum (II) complexes on layered zirconium phosphate [692], luminescence in Eu-doped nanopowders [693,694], and even zirconia spheres with tunable luminescence [695]. It has also been suggested that Dy$^{3+}$ doped calcium zirconium phosphate $\text{CaZr}_4(\text{PO}_4)_6$:Dy$^{3+}$ could be a promising candidate for use in warm-white LEDs [696], similarly blue-white light was produced from $\text{K}_2\text{ZrSi}_2\text{O}_7$ :Eu $^{2+}$ [697].
5.12 Electronics and solid state devices

5.12.1 Memory devices

Zirconium nitride, zirconium oxide and other doped oxides have found applications in the fabrication of memory cells and memory devices. For example, dielectric structures containing zirconium oxide stacks have been used to fabricate flash memories [698], and particular electronic effects can be observed in this type of materials by embedding gold [699] and other elements [700]. Similarly, embedding ruthenium oxide nanocrystals in zirconium and hafnium oxide capacitors has proved efficient for the fabrication of electronic memories [701]. Resistive-switching memory cells can also be fabricated using zirconium nitride [702].

5.12.2 Electrical gates and transistors

Dielectric zirconium compounds are playing an important role in the design of electrical gate stacks, particularly zirconium oxides and germanium oxide doped zirconium oxides [703]. The future of graphene electronics seems promising, and thus the use of zirconium compounds. For example, zirconium oxide nanowires have been used as high dielectric constant electric gates and have found applications for certain configurations using graphene nanoribbons [704]. In addition, zirconium diboride shows promise for the use in high temperature thin film electronics [705], zirconium oxide is suggested for use in a semiconductor structure [706] and dysprosium-doped zirconium oxide thin films are being assessed for use as dielectric in metal-insulator-metal electronic devices [707].

5.12.3 Superionic conductivity

The production of superionic conductors has represented a step towards the miniaturisation of electronics to a level called ‘deep-sub voltage nanoelectronics’ [708]. Low-temperature superionic conductivity has been shown in strained yttria-stabilised zirconia [709], thus zirconium compounds may play an important role in the future of electronics.

5.13 Research trends

This section provides further insight into the potential impact of emerging research and development areas by looking at the average number of citations per paper for all references included in each research topic presented in Section 4 (Figure 5.2, Figure 5.3).

A few important comments need to be made about this analysis:

- The number of citations can vary substantially with time and more recent papers will obviously have fewer citations. Additionally, the publication type may affect the number of citations (e.g. a book will get more citations than a patent because of the generality of its topics). References in Section 4 of this report include papers, patents and books from the last 7 years only.
5.13 Research trends

- The number of citations per paper was extracted from a scholar search engine and reflects all data available until 10 August 2015. However, the choice of references included in this report was inevitably selective, based on the criteria explained in the introduction of Section 4.
- The classification of each paper based on the maturity level of their application and their relation to higher level research trends was performed according to the authors’ criteria and does not necessarily represent the absolute research trends about zirconium and its derivatives in the future. The data shown here applies only to the references used in this study.

5.13.1 Number of citations per research topic

The average number of citations per paper for all references included in each research topic presented in Section 4 are given in Figure 5.2
Figure 5.2: Geometric mean number of citation of citations per research topic in the last 4 years — All categories (X-axis: geometric mean number of citations per paper for all references in each category).
5.13 Research trends

Figure 5.3: Geometric mean number of citation of citations per research topic in the last 4 years — Main categories (X-axis: geometric mean number of citations per paper for all references in each category).


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REFERENCES


REFERENCES


REFERENCES


REFERENCES


REFERENCES


REFERENCES


REFERENCES


REFERENCES


[511] Y. Guo, Y. Lin, R. Ran, and Z. Shao, “Zirconium doping effect on the performance of proton-conducting BaZr$_{0.8}$Ce$_{0.2}$Y$_{0.8}$O$_3$ for fuel cell applications”, Journal of power sources, vol. 193, no. 2, pp. 400–407, 2009.


REFERENCES


REFERENCES


REFERENCES


REFERENCES


REFERENCES


REFERENCES


REFERENCES


REFERENCES


