



Good afternoon ladies and gentlemen. First of all I'd like to thank the organisers of this conference for the opportunity to talk about zircon and zirconia. Last year we asked Carlos Olabe if he would speak at our own conference and inform our members about the investment casting industry in general and its use of zircon in particular. His presentation was entitled The Role of Zircon in a Strategic Industry. In this presentation Carlos raised a number of issues and concerns, some technical, some more commercial in nature.

The theme of this presentation is "an informed value chain." We believe that it is to the advantage of all participants to understand their counter-parties' issue and problems and we hope that this presentation we will give you some insight into our industry and address some of the issues raised by Carlos.

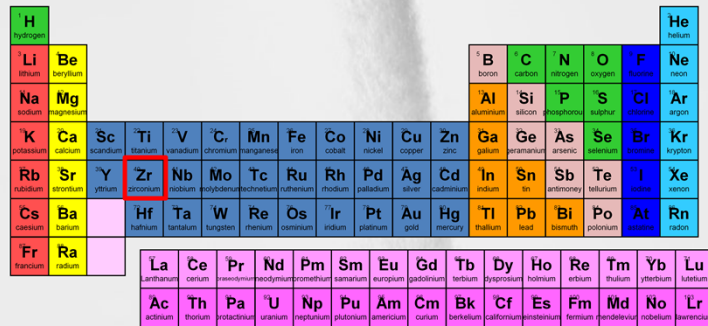
## Disclaimer

**This presentation is intended for information purposes only and is not intended as promotional material in any respect. The contents are not intended as an offer or solicitation for the purposes of sale of any financial instrument, are not intended to provide an investment recommendation and should not be relied upon. The contents are derived from published sources, together with personal research. No responsibility or liability is accepted for any such information or opinions or for any errors, omissions, misstatements, negligence or otherwise for any other communications, written or otherwise.**



Secondly, the usual disclaimer - in essence, don't bet your life savings on the basis of anything that you see or hear during this presentation.

## Presentation overview



The image shows a standard periodic table of elements. The element Zirconium (Zr) is highlighted with a red border. It is located in the 5th period, 4th group, with atomic number 40. The table includes elements from Hydrogen (H) to Oganesson (Og), with the lanthanide and actinide series shown separately at the bottom.

- Quick introduction to ZIA and the zirconium value chain
- Some industry data
- Zircon supply - historical and future
- Properties of zircon and applications in investment casting
- Regulatory issues
- Concluding remarks

The content of my presentation is as per this slide .....

## Genesis and focus of Zircon Industry Association

### Genesis

- ZIA was conceived in 2012 and became a reality on January 1<sup>st</sup> 2013.
- Its genesis was the primary objective of facilitating demand expansion through education, information and promotion.
- At the same time, like all commodities, zircon and its derivatives face a number of threats:
  - from thriving and competition from substitute materials
  - from ever increasing regulation
- The zirconium value chain had no industry body to represent and promote its interests.

### Members

- miners, millers, zircon & chemical producers, distributors, developers, consultants

### Focus

- Market development and support:
  - Existing applications
  - Innovation and new applications
- Regulatory support:
  - NORM
  - Other regulations
- Communications:
  - Getting the right messages to stakeholders



→ As said here, the Zircon Industry Association was conceived during the course of 2012 and was born on January 1<sup>st</sup> 2013. Its genesis was a proactive move, aimed at facilitating demand expansion through education, information and promotion to stakeholders, both present and future.

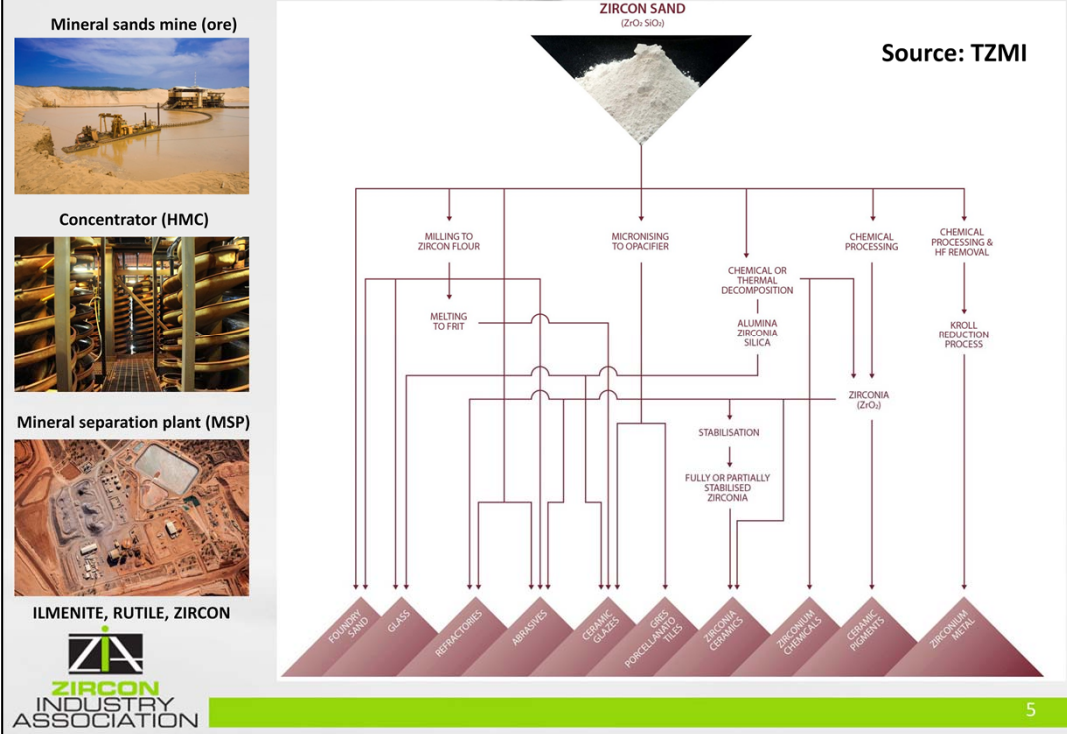
At the same time, this strategy would enable the industry to respond to some of the threats common to many commodities, for example thriving and competition from substitute materials and an increasingly regulated industrial and consumer environment.

Market support and development are vital for the sustainable growth of any industry and individual companies' activities in this area can be enhanced by an industry approach. In the regulatory space, regulators generally prefer to deal with industry associations rather than individual companies.

→ Our membership spans the zirconium value chain → and as shown by the box on the right side, our activities are now focussed on the three pillars of market development and support, regulatory support and communications.



# Zirconium value chain



Zircon is found in so-called mineral sands, containing mainly the titanium minerals ilmenite and rutile, and zircon. Mineral sands undergo two main stages of beneficiation - first production of a heavy mineral concentrate and secondly separation into the various constituent minerals.

→ I am indebted to TZMI for this chart, depicting the zirconium value chain, from mining through to downstream users - although not down to the ultimate end users - zircon and its derivatives can be found in many aspects of our daily lives.

Zircon can be used directly in sand form, as a milled product down to micron sizes and as feedstock for a wide range of oxides and chemicals for eventual use in a wide variety of end uses.

## Zircon uses and applications

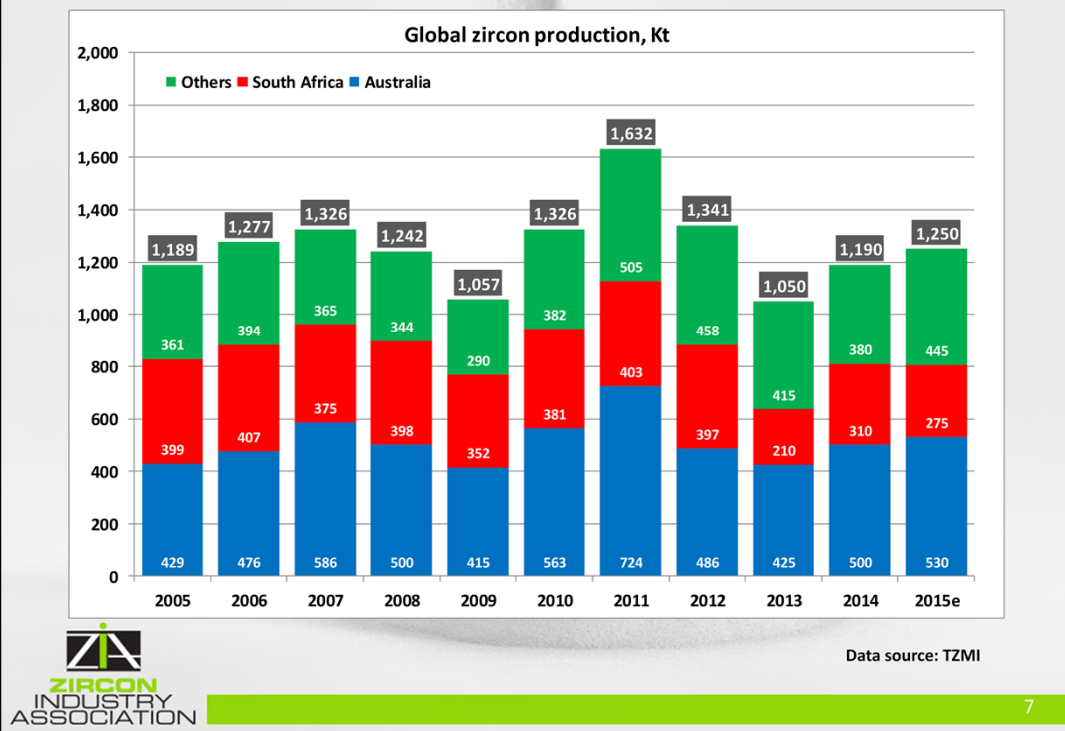
<p><b>Ceramics</b> ~50% of demand</p>  <p>Zircon is opaque, water, chemical and abrasion resistant</p>	<p><b>Refractory and Foundry</b> ~30% of demand</p>  <p>Zircon is heat resistant and non-reactive Uses include steel and glass manufacturing and metal casting</p>	<p><b>Zirconia, Zirconium Chemicals and Metal</b> ~20% of demand</p>  <p>Zircon has many unique properties Uses include fibre optics, medicine, electronics, catalytic converters, nuclear fuel rods, cosmetics</p>
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This chart, borrowed from a member's website, is a broad representation of the global zircon market.

As you can see ceramics accounts for the single largest market share with about 50% of the market, probably somewhat less than 50%. In this chart refractory and foundry [which includes investment casting] is shown as about 30%. A recent industry report from Roskill Information Services estimated that the share of foundries and investment casters in 2013 was 8%, then accounting for about 190,000 tonnes. I don't have any more detailed information than that, but clearly, your industry is important to us.

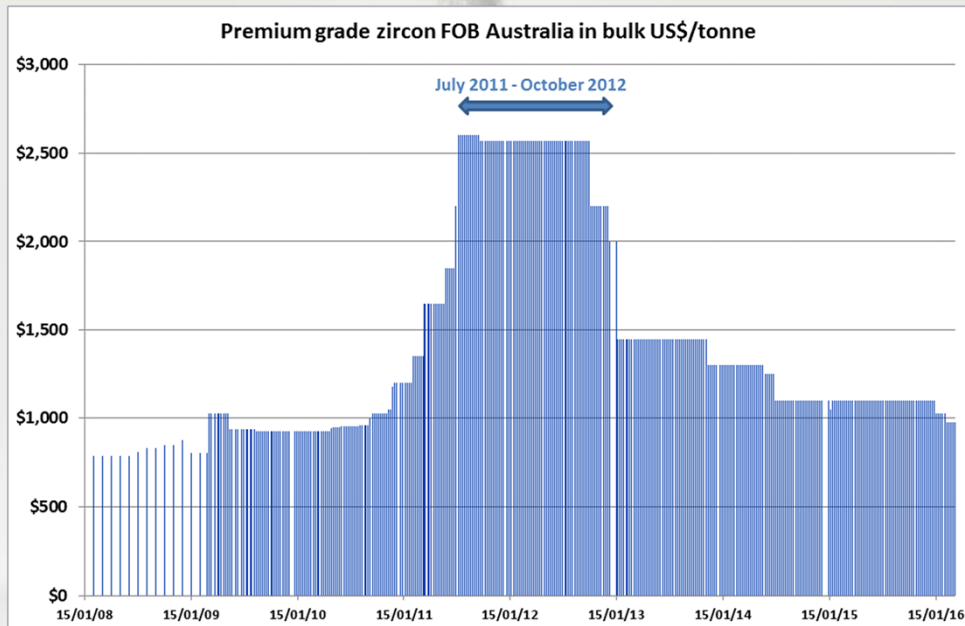
## Zircon supply



As can be seen from this chart, the main sources of zircon are Australia and South Africa. Others include Mozambique, Senegal, India, Vietnam, China and Indonesia. The peak production level was in 2011 with more than 1.6 million tonnes. Production fell dramatically over the next couple of years, to just over one million tonnes in 2013, but has started growing again over the last couple of years.

It can be implied from this chart is that there is considerable latent capacity out there - the delta between the high of 2011 and the low of 2013 was about 580,000 tonnes. However, it should be said that the top slice of the production in 2011 was induced by the strength of demand which allowed prices to rise very rapidly - some of this incremental production is not economic at today's less stratospheric price levels. It is also arguable that the rapid increase in prices incentivised some buyers to go long in anticipation of further price rises - considering some of the price forecasts being made by analysts at the time, such a strategy was not unreasonable.

## Zircon price history



Data source: Industrial Minerals

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One of the issues mentioned by Carlos in his presentation to us was that of price volatility. This chart is based on historical price data from Industrial Minerals magazine. It shows the FOB price of premium grade zircon going back to 2008. My history in the zircon industry goes back to 1990 and I know well that prices have often reacted to short term events affecting supply and demand, as happens with almost any commodity. However, it was the development during 2011 and 2012 that remains in many peoples minds. This prolonged price spike was caused by a combination of factors, first and foremost the phenomenal and rapid growth of demand from China, but also by some supply side problems. Another important factor was a shift in the industry contract and pricing model from longer term to shorter term arrangements and the development of a significant spot market.

I think that this chart proves that we have returned to a more stable and less volatile price regime.

## Zircon supply-demand forecast - TZMI



One of ZIA's key messages is that there is adequacy of supply potential for the foreseeable future. I could have chosen from several representations of the future supply-demand balance - this one is from TZMI, recognised consultants in our industry [and incidentally a ZIA member]. TZMI's analysis is not significantly different to those of other analysts.

The forecast shows over-supply of zircon out to 2019, market balance in 2020 and the need for new supply thereafter. Part of the over-supply in the next few years relates to excess inventory along the supply chain, both as work-in-progress and finished product. As you would expect, as this inventory is turned into cash, major production assets are being operated in accordance with demand from the market. A positive impact of this is that the zircon industry is well placed to respond to any unexpected increase in demand.

## New zircon production capacity

- **Base Resources: Kwale mineral sands project in Kenya**
  - capacity 30,000 tpy zircon over first seven years, dropping to 19,000 tpy for following 6 years [22,416 t produced in 2015]
- **TiZir Ltd: Grande Côte project in Senegal**
  - mining started in March 2014, ± 50,000 tpy zircon capacity [45,200 t produced in 2015]
- **Kenmare Resources: Moma Phase 2 expansion project**
  - zircon capacity increase from 50,000 t to 75,000 tpy [51,800 t produced in 2015]
- **Southern Ionics: Georgia operations, USA**
  - mineral separation plant started up in 2015 - current capacity about 15,000 tpy - readily scalable to 25,000 tpy - zircon calcining capability
- **MZI Resources: Keysbrook, Western Australia**
  - Started-up Q4 2015, eventual capacity 29,000 tpy 56% zircon concentrate



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There have been several new entrants to the market over the last couple of years, as well as some capacity expansions, as shown here. In the interests of time I will leave you to study them at your leisure.

## Projects of the major producers

- **Iluka Resources:**
  - Cataby, in WA - 8.5 year mine life (DFS completed)
  - Balranald in NSW - 8 year mine life [DFS final stages]
  - JA satellite deposits in SA (PFS stage)
  - Puttalam, Sri Lanka [PFS planned to commence in 2016]
- **Richards Bay Minerals (Rio Tinto Iron & Titanium):**
  - Zulti South mine, KwaZulu-Natal, South Africa (25 year mine life, investment decision in 2016)
- **Tronox Sands**
  - Fairbreeze mine, KwaZulu-Natal, South Africa (replacing Hillendale mine, under construction, 2016 start-up, 55,000 tpy zircon, 13/15 year mine life, extendible)



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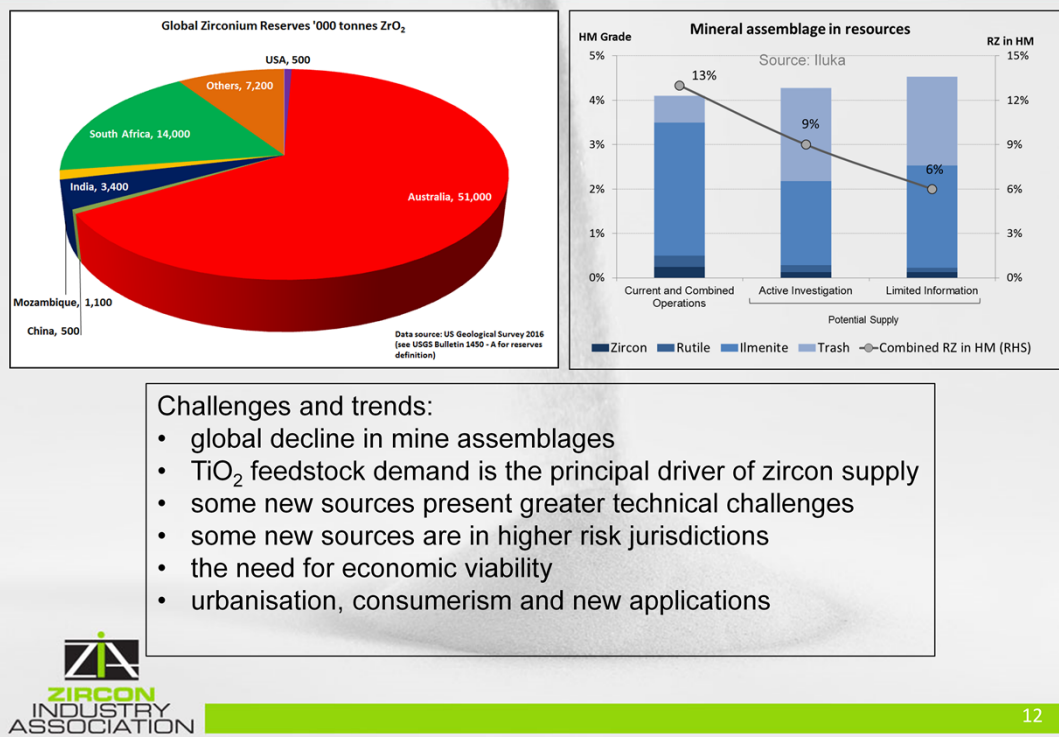
One should not forget that the existing mineral sands mines are at varying stages of maturity and that production from some of them can be expected to decline in the years ahead, meaning that new, replacement capacity will be needed to support existing and incremental demand.

The three major zircon producers, Iluka Resources, Richards Bay Minerals and Tronox Sands all have projects at various stages of development. These are listed on this slide and represent sustaining as well as potentially expansionary capital investment.

There are many other projects out there with the potential to add to the zircon supply.



## Long term supply – issues and drivers



In conclusion on the supply side, it seems reasonable to say that existing and planned capacity is adequate for the foreseeable future, whatever that is, let's say 5-10 years. Beyond that there is plenty of potential supply, waiting to be developed. The US Geological Survey estimates global zirconium reserves at 78 million tonnes expressed as ZrO<sub>2</sub>, of which 51 million tonnes is in Australia, 14 million tonnes in South Africa, but excluding Indonesia, as shown by this chart. However, I would be being economical with the truth if I did not admit to some longer term challenges.

→ First of all it is a fact that the grade of known deposits is declining, as shown by the chart on the right. The combined content of rutile and zircon in currently worked resources is 13%, but this falls to 9% in new resources under active investigation and to 6% in other known resources. However, in considering current operations, note that Iluka's Eucla Basin resources of 389 millions tonnes contain almost 19 million tonnes of heavy mineral, grading 29% zircon alone or 32% zircon plus rutile. This compares with Iluka's average of 10% zircon or 16% zircon plus rutile.

→ Secondly, it is also a fact that in very few cases is zircon the major constituent in mineral sands - the most important being ilmenite, the main feedstock for the titanium dioxide pigment industry, either directly or via further processed materials such as TiO<sub>2</sub> slag and synthetic rutile. Thus, the pigment industry - and beyond it the paint and plastics industries - is the main driver of the mineral sands business. Few operations can survive on zircon alone. It is beyond the scope of this presentation to talk about the TiO<sub>2</sub> industry, however I will note that demand for TiO<sub>2</sub> pigments correlates rather well with general GDP growth. The trends of urbanisation and consumerism in China - and eventually in other developing economies - bode well in this respect.

→ Other challenges are technological and jurisdictional and, of course, the need for

economic viability.

## Use of zircon in investment casting

	HIGH VALUE PARTS	COMMERCIAL PARTS
SLURRY COMPOSITION EXAMPLES	<b>Primary (1<sup>st</sup> coat)</b> 100 litre Silica sol binder + additives for wetting and deflocculation 550 kg Zircon	<b>Primary (1<sup>st</sup> coat)</b> 100 litre Silica sol binder + additives for wetting and deflocculation 550 kg Zircon
	<b>Secondary (back-up coats)</b> 100 litre Silica sol binder + additives for wetting and deflocculation 450 kg Zircon <i>Patents zircon/alumina flour mixes</i>	<b>Secondary (back-up coats)</b> 100 litre Silica sol binder + additives for wetting and deflocculation 170 kg alumino-silicate
SHELL MOULD MATERIALS	<b>Slurry flours:</b> Zircon, Alumina, Mullite <b>Flour sizes:</b> 200 – 350 mesh (nominal 0.075 – 0.045mm)	<b>Slurry flours:</b> Zircon, Alumina, alumino-silicate, silica <b>Flour sizes:</b> 200 – 350 mesh (nominal 0.075 – 0.045mm)
	<b>Stucco grits:</b> Alumina, Mullite, Zirconia (specialist use) <b>Stucco sizes:</b> 16 – 60 mesh (nominal 1.00 – 0.25 mm)	<b>Stucco grits:</b> Alumino-silicate, silica <b>Stucco sizes:</b> 16 – 60 mesh (nominal 1.00 – 0.25 mm)

Let's now talk a bit about the use and benefits of zircon in investment casting. I make no apologies for referring to Carlos's presentation to our members from which this table is taken. I do not intend to lecture you on what you already know very well and will therefore not dwell on this table, but I did want to include it for the sake of completeness.

## Benefits of zircon for investment casting

- Zircon exhibits several properties making it an ideal material for the manufacture of casting moulds, among which are:
  - low expansion (zircon stucco based)
  - high refractoriness
  - reduced wettability by molten metals (inertness)
  - high thermal conductivity, and high heat capacity
  - ability to combine with other shell refractories
- Low expansion gives improved stability of the moulds at high temperatures
- Reduced wettability and refractoriness result in improved surface finish and reduced mould penetration
- High thermal conductivity and high heat capacity result in improved control of metal solidification
- Without forming low melting compounds or very hard compounds.



Neither do I want to dwell on this slide for the same reason - this is what Carlos told us! I'm also under strict instructions not to make a sales pitch and nor will I - these points are well known.

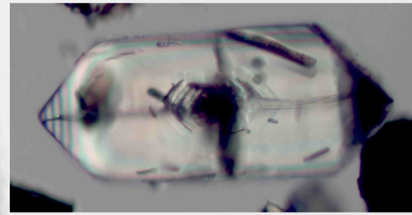
## Zircon - Mineral Impurities & Calcining

**Inclusions:** Other mineral species included in the zircon crystal. These can be the source of contaminants like iron, phosphorus and alkaline earth metals

**Coatings:** Zircon grains are often covered with post-depositional coatings of organics or iron.

**Metamict:** Zircon's own radioactivity damages the grain and crystal structure from the inside.

**Calcining:** High temperature heat treatment helps reverse metamictization, dehydrates, increases density, hardness and refractive index



The photograph shows a zircon crystal that has undergone metamictization of its core structure with a resultant expansion that cracked the later growth zircon surrounding the core. This zircon is from Lake Poway Park in Southern California.

Source:  
<http://www.microlabgallery.com/MetamictFile.aspx>  
9/18/15

### Impact on Investment Casting:

Slurry pot properties are greatly improved with low impurity, calcined zircons, often lasting many months with proper surveillance



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Zircon is used in investment casting applications in both the calcined and uncalcined states. Zircons differ from deposit to deposit and from mine to mine - mineralogy, chemical impurities and physical properties are an intrinsic part of the material and cannot always be readily or economically modified beyond what Mother Nature and the normal beneficiation processes have already done. Acid washing of Fe staining is a good example of further beneficiation beyond the basic concentration and mineral separation steps.

The common perception that calcining is performed to remove residual organics is true, but the benefits to the zircon mineral quality can go far beyond that, as explained in this slide. However, not all zircons respond to calcining in the same manner, dependent upon their mineralogical, chemical and physical properties. There is no "one size fits all" solution for the industry and there are various considerations, not the least of which is the metal or alloy and type of part being cast. As I understand it, in the USA and Western Europe, the predominant usage is of calcined material, although not exclusively so. In Asia, use of uncalcined material is more common than in the US and Europe.

## Calcined Zircon Supply

### Current Suppliers of Calcined Zircon

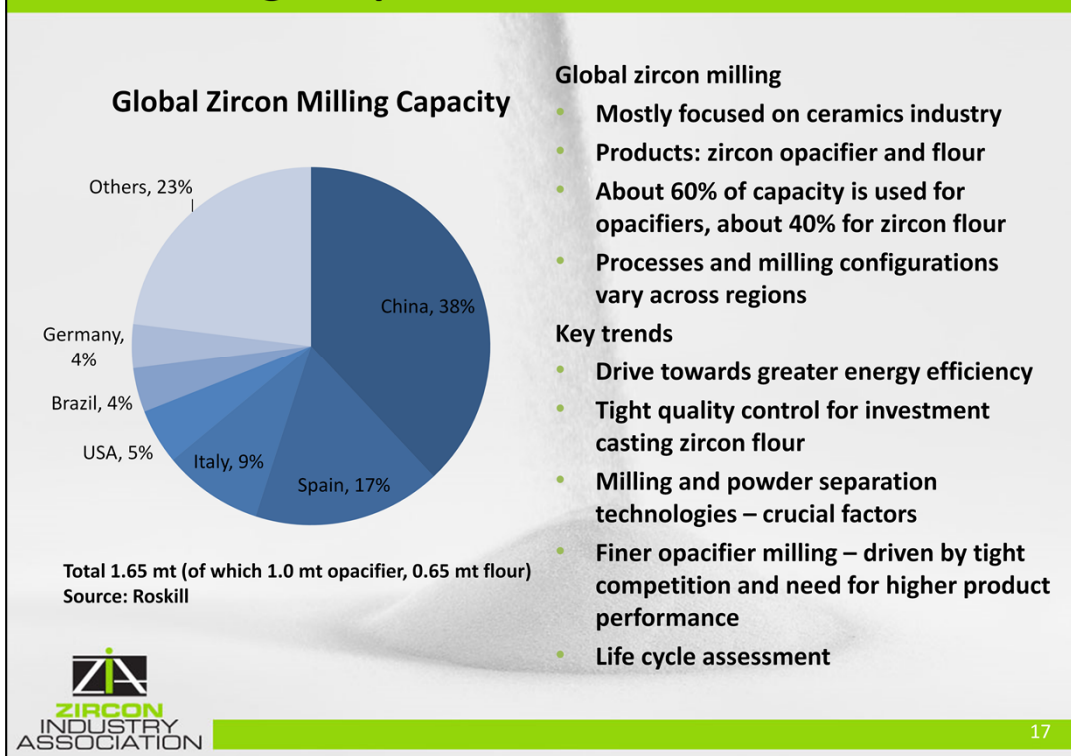
- **Chemours (ex DuPont)**
  - announced mine extensions for 20+ years
- **Richards Bay Minerals - Prime Calcined**
  - marketed by Rio Tinto
- **Southern Ionics Minerals**
  - new South Eastern USA mine with 25 year life
- **Zircosil, Spain (formerly Endeka Ceramics)**
  - Post mine calcining capabilities
- **Other Smaller 3<sup>rd</sup> Party Calciners , e.g. CMMP France, Rasa Japan**
- **Zircon calcination capacity  $\pm$  100,000 tpy**



Relatively few mine operators choose to calcine their zircon at source, cost-benefit analysis often being a factor. Some companies further down the supply chain choose to calcine zircon closer to their markets in order to meet their customer requirements.

For the benefit of those interested in calcined zircon, here is a list of companies known to have calcining capability → - total capacity, excluding any in China, is about 100,000 tonnes - of course a significant part of this is directed to markets outside the investment casting industry, notably ceramics.

## Zircon milling – capabilities and trends



A large part of the demand for zircon from the investment casting industry is in the form of flour, so I thought that I would include some information about milling capacity here. As can be seen from the chart on the left, zircon milling capacity is of the order of 1.65 million tonnes, of which 60% is geared to production of opacifiers for the ceramics sector.

I will not go into milling technologies or processes here, but of course they vary from one company to the next, for example wet milling versus dry milling.

Milling of zircon is a competitive business and millers are driving efficiencies in their processes as well as technological improvements. In the ceramic opacifier sector, particle size is trending finer to improve performance and of course for investment casting tight quality control and consistency are essential.

We live in an age of responsible sourcing and sustainable production - life cycle assessment is very much the flavour of the day and ZIA is taking steps to bring zircon up to date in this respect.



## Zirconia in investment casting of titanium alloys

High reactivity of titanium alloys (reaction with standard ceramic moulds/binders based on  $\text{Al}_2\text{O}_3\text{-SiO}_2$ ) lead to Alpha Case formation (resulting in surface deterioration and weakening of mechanical properties).

Stable oxides (such as fused  $\text{Y}_2\text{O}_3$ , Ca-stab  $\text{ZrO}_2$ ,  $\text{Al}_2\text{O}_3$ ) may be used to build up mould for investment casting. These moulds do not give significant surface reactions with titanium alloys.

### Applications

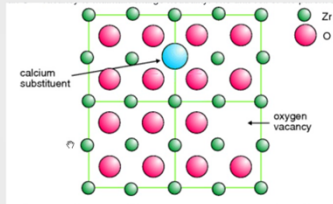
Aviation, Aerospace, shipbuilding,  
industrial areas, golf clubs



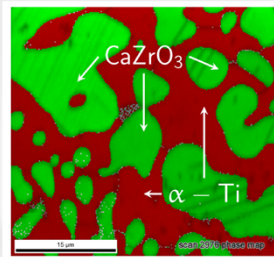
Different metals require different materials in investment casting moulds. When casting titanium alloys one of the main difficulties is the high chemical reactivity of titanium alloys with the refractory oxides. The ceramic oxides may be reduced and the oxygen then dissolves in the molten titanium alloy resulting in the formation of so-called Alpha-Case, i.e. an oxygen-enriched layer on the titanium surface.

Certain fused oxides, in particular lime stabilised zirconia, yttria and alumina are commonly used when casting titanium alloys – by production of those oxides in electric arc furnaces the resultant products exhibit high material density (i.e. no porosity) and low BET surface area with relatively „clean“ surfaces which equate to high stability in investment casting slurries.

## Zirconia in investment casting of titanium alloys



Richard J.D. Tilley: Understanding Solids: The Science of Materials, John Wiley & Sons, 2013



### Primary face coat & stucco:

- Lime stabilised zirconia (ideally cubic crystal structure with low thermal expansion and no sudden change in volume at phase transition temperature)

### Binder:

- often based on zirconium chemicals, such as zirconium acetate and ammonium zirconium carbonate

### Crucibles for vacuum induction melting of Ti-6Al-4V:

- Stoichiometric calcium zirconate ( $\text{CaZrO}_3$ ) shows no dissolution with melt in contrast to calcia stabilised zirconia

### EBSD phase distribution at boundary to Ti-6Al-4V (Schafföner et al, J. Eur. Ceram. Soc. 35 (2015), 259)

Beyond zircon, various different zirconium products used in investment casting. For the prime coat a fine-milled lime stabilised zirconia flour, typically below 75 or 45  $\mu\text{m}$  is used for the direct contact of molten titanium alloys with the casting mould.

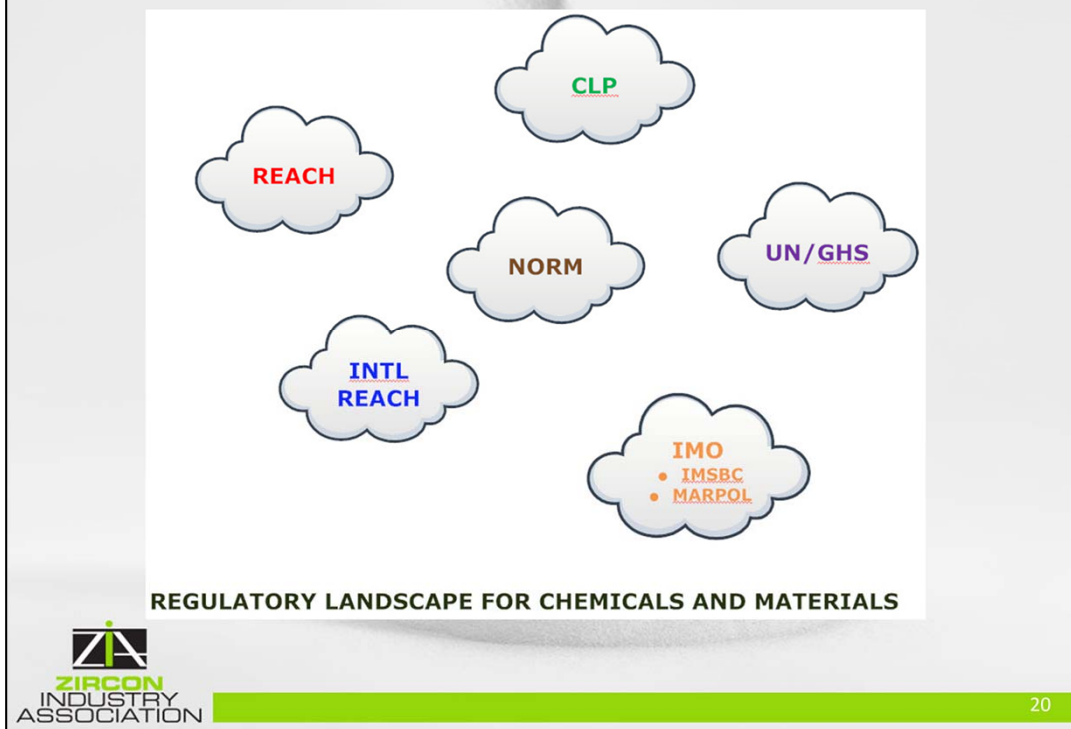
„Pure“ zirconia made from carbothermal reduction of zircon sand exhibits a monoclinic crystal structure at room temperature and undergoes transition to tetragonal and cubic phases at higher temperature. The transition to tetragonal phase is accompanied by a large volume change. The cubic (and/or) tetragonal phase can be stabilised at room temperature when a certain number of zirconium ions is replaced by other metal ions, for example Ca or Y or Mg, in the crystal structure. The change in volume when heating to high temperature (or cooling down!) is less pronounced, if visible at all.

Lime stabilised zirconia may also be used in the stucco fraction (which is typically in the range of 125-250  $\mu\text{m}$ ) and can only be produced with a fusion process (to ensure that the particles are blocky-dense in nature).

In the slurry binder system, zirconium chemicals, for example zirconium acetate and carbonate, are used. These chemicals bind well onto the dense zirconia particles, giving good green strength.

New developments in investment casting of titanium alloys also evaluate the use of fused calcium zirconate which exhibits the perovskite structure and even lower reactivity towards the molten titanium alloy. Calcium zirconate only be used not only in the primary coat and stucco, but also as a refractory material in the crucibles holding the molten titanium alloy.

## Regulatory support



Now a few words about our regulatory support activities. As the graphic suggests, it's a bit of a minefield out there and our goal is to try and stay ahead of the game and forewarn our members of upcoming regulatory developments and the potential impacts on their businesses.


For zircon, probably the most significant regulatory regime is that for naturally occurring radioactive materials - or NORM. We are now at the end of a NORM regulatory cycle with the new EU regulations due to come into force in 2018, but as we all know regulation is a moving target and we have to keep up with developments. ZIA is active in this area.


Chemical industry regulations such as REACH and its lookalikes in Asia and elsewhere have to be tracked - fortunately as a naturally occurring material zircon is exempt from REACH, but zirconia is not. Some European regulators dream that one day ALL materials will be subject to REACH regulation, so we need to be vigilant.

Maritime regulations can also affect zircon, so it's important to follow developments at the International Maritime Organisation.

As suppliers of zircon and zirconia to your industry, our job is to ensure that we are compliant with the various regulatory regimes.

## Cross-border movement of zircon and zirconia

shipping & transport	storage	post delivery
IAEA TRANSPORT REGULATIONS (zircon & zirconia exempt)	grey area	IAEA EXEMPTION REGULATIONS (zircon & zirconia not exempt)
<ul style="list-style-type: none"> <li>Transition between transport and exemption regulations is a grey area</li> <li>National regulators may apply the regulations differently to each other</li> <li>Prior to cross-border movements, regulators in destination country should be contacted and provided with activity data prior to dispatch</li> <li>Carriers should also be informed about the nature of the material and relevant regulations</li> <li>MSDS to include relevant information and be included in shipping documents</li> </ul> <div style="display: flex; align-items: center; justify-content: space-between; margin-top: 20px;"> <div style="text-align: center;">  <p><b>ZIRCON</b> INDUSTRY ASSOCIATION</p> </div> <div style="background-color: #92d050; padding: 10px; border: 1px solid #333;"> <p>ZIA intends to produce guidance to facilitate cross border movement of zircon and zirconia.</p> </div> </div>		



On the subject of NORM, movement of NORM materials is governed by the Transport regulations, but on arrival at destination the regulatory regime switches to the Exemption regulations.

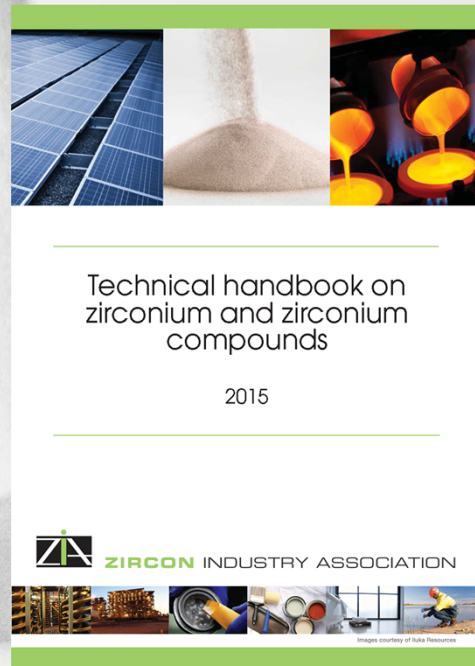
However, there are grey areas at the transition point, for example when the material is in storage. Under the transport regulations, zircon is in effect exempt, but this is not the case for the exemption regulations where the threshold is  $1 \text{ Bq.g}^{-1}$ . There are differences in application of these regulations from one jurisdiction to another and sometimes even within a single jurisdiction.

ZIA does intend to produce guidance to facilitate cross border movements.

## Technical handbook

1. Introduction
2. Material properties
3. State of the art applications
4. Emerging R & D
5. References

Available via the contact form at  
[www.zircon-association.org](http://www.zircon-association.org)



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I'd like to conclude with a quick plug for ZIA's Technical Handbook on Zirconium and Zirconium Compounds, the second edition of which was published in October last year. The handbook has four main chapters as shown as well as a list of references and is available free of charge to anyone who wants it, by application through the contact form on our website.

## The end



**Thank you for your attention!**

Chris Barrington, Executive Director  
cbarrington@zircon-association.org  
www.zircon-association.org



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Finally, I'd like to conclude with two remarks:

We look forward to maintaining contact with the investment casting industry through EICF and perhaps others and sustaining that informed value chain that I mentioned at the beginning. To the extent that it can, the zircon industry wants to be responsive to technical innovation and be solutions driven.

Finally I'd like to thank my co-authors, Dave Podmeyer and Jorge Masbate, for their assistance in putting this presentation together. Thank you for your attention.