ZIRCON INDUSTRY ASSOCIATION

ZIRCON AND ZIRCONIA: VALUE-ADDING MATERIALS FOR THE GLOBAL INVESTMENT CASTING INDUSTRY

Chris Barrington, Jorge Masbate, Dave Podmeyer

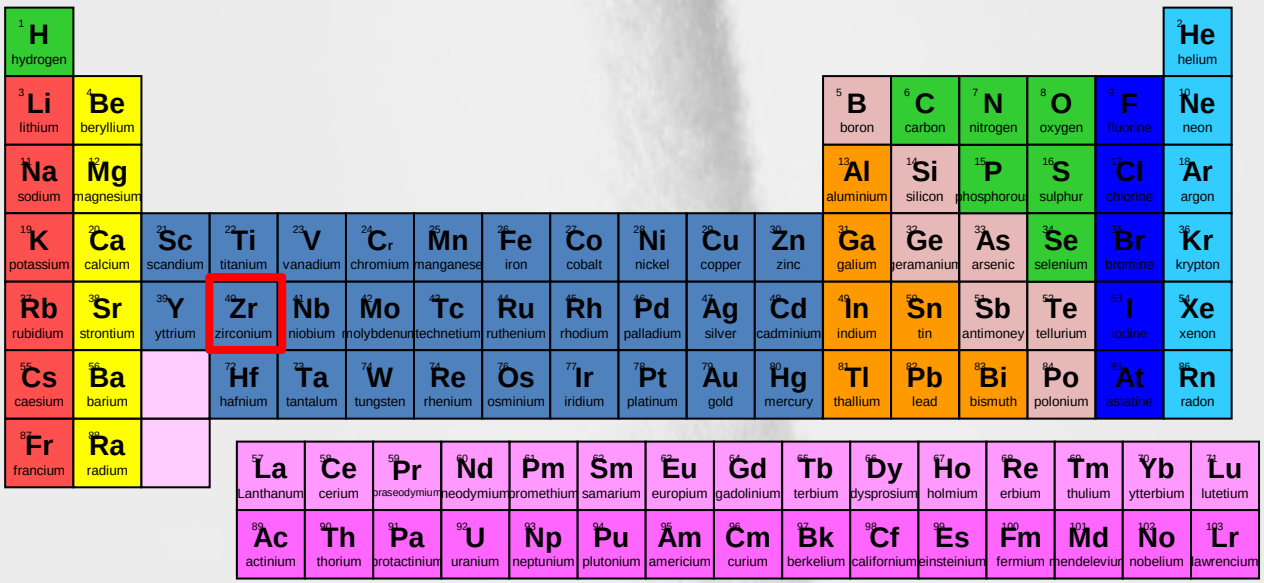
14th World Conference on Investment Casting

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.

ZIRCON INDUSTRY ASSOCIATION

Presentation overview



- 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

ZIRCON INDUSTRY ASSOCIATION

Genesis and focus of Zircon Industry Association

Genesis

- ZIA was conceived in 2012 and became a reality on January 1st 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 thrifting 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

ZIRCON INDUSTRY ASSOCIATION

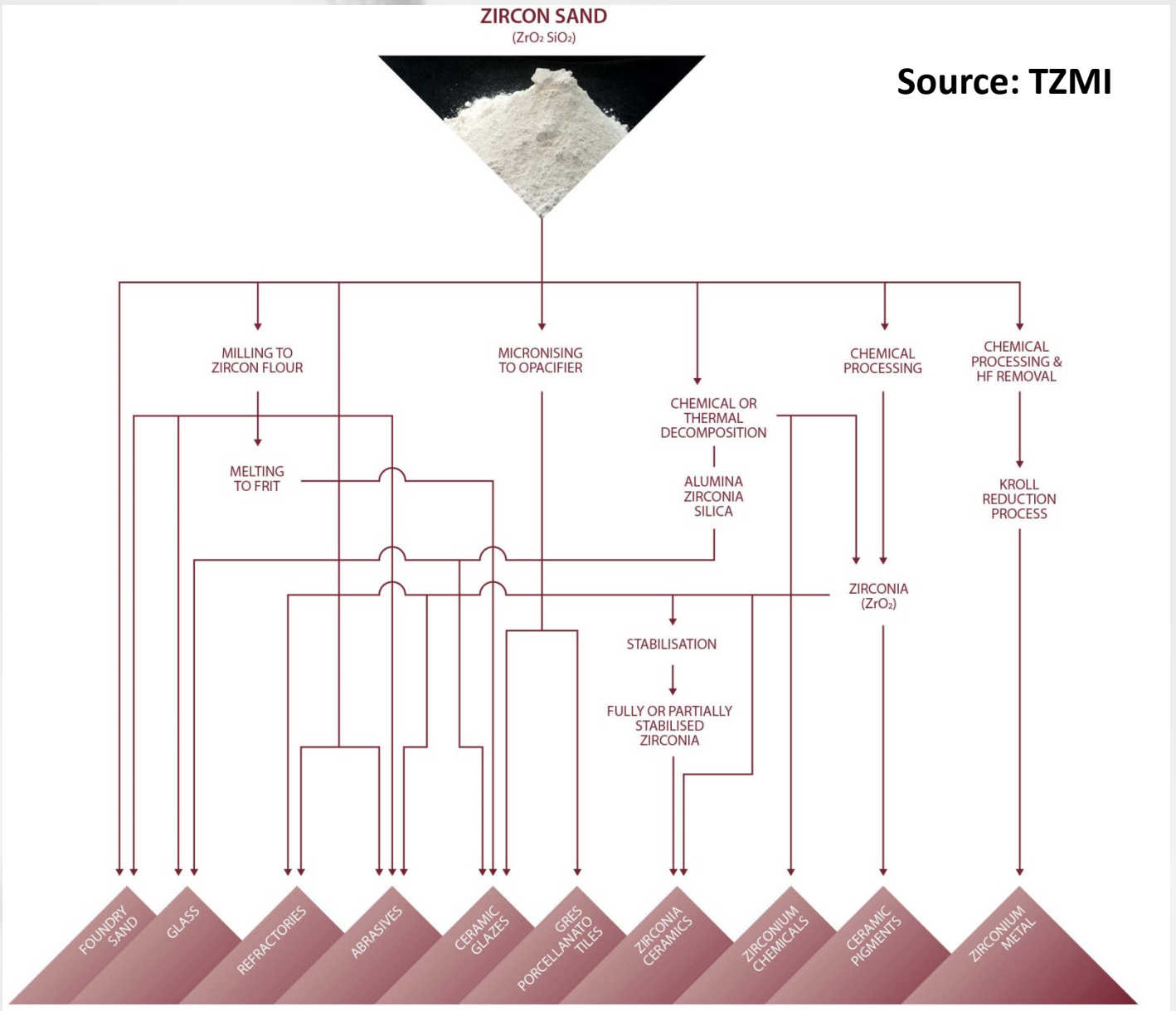
Zirconium value chain

Mineral sands mine (ore)

Concentrator (HMC)

Mineral separation plant (MSP)

ILMENITE, RUTILE, ZIRCON



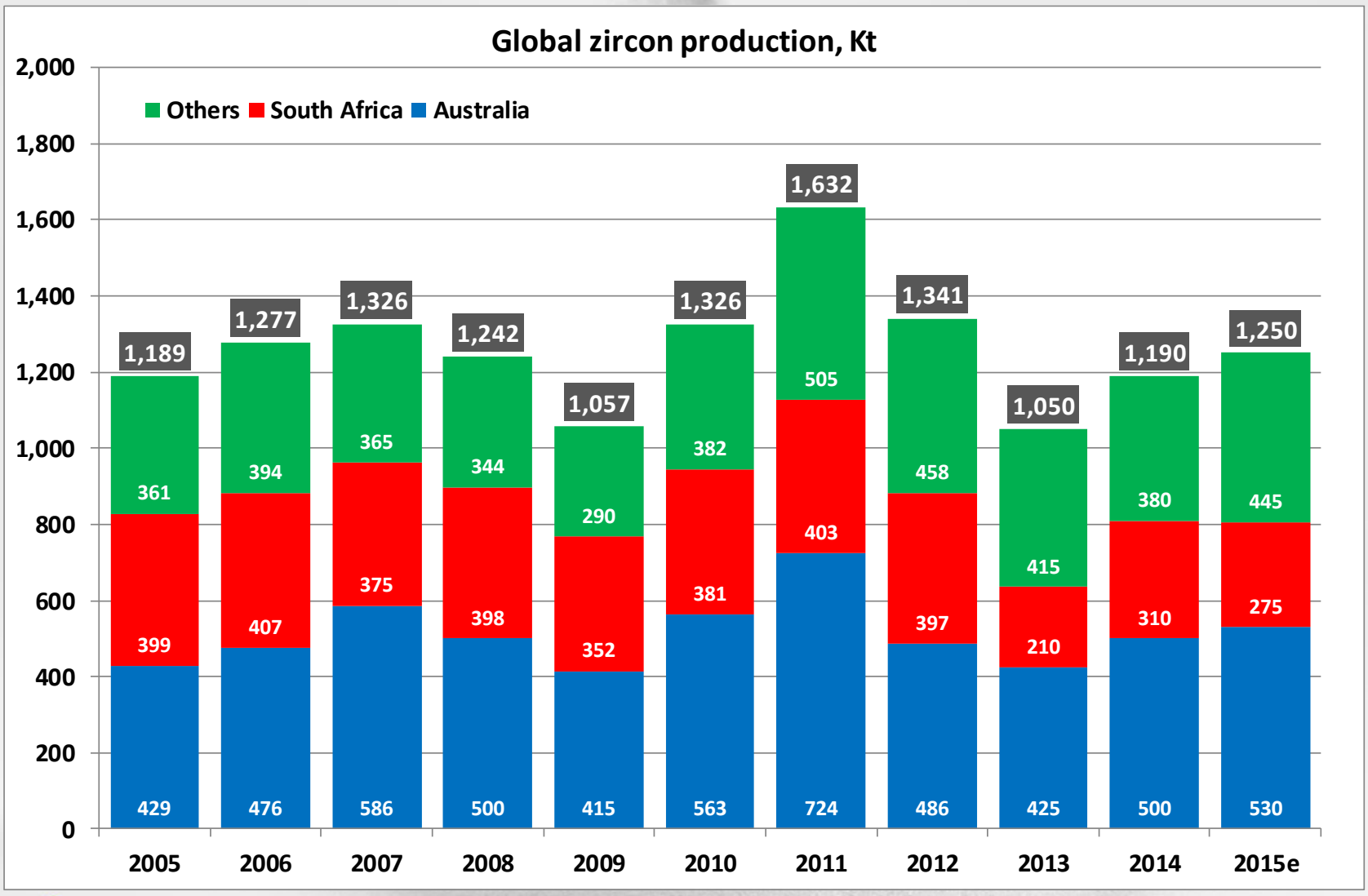
Source: TZMI

ZIRCON INDUSTRY ASSOCIATION

Zircon uses and applications

ZIRCON INDUSTRY ASSOCIATION

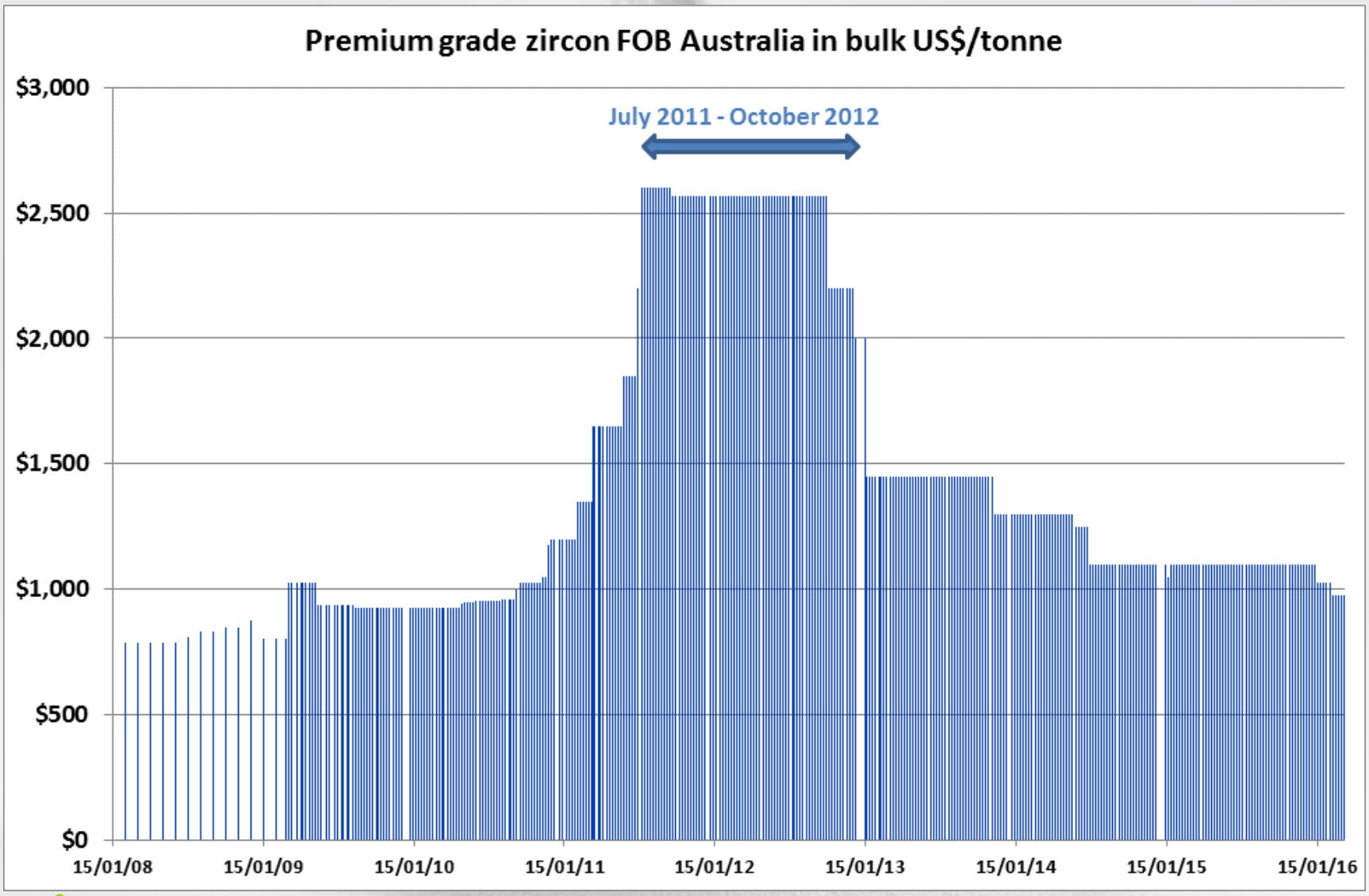
Zircon supply



Data source: TZMI

ZIRCON INDUSTRY ASSOCIATION

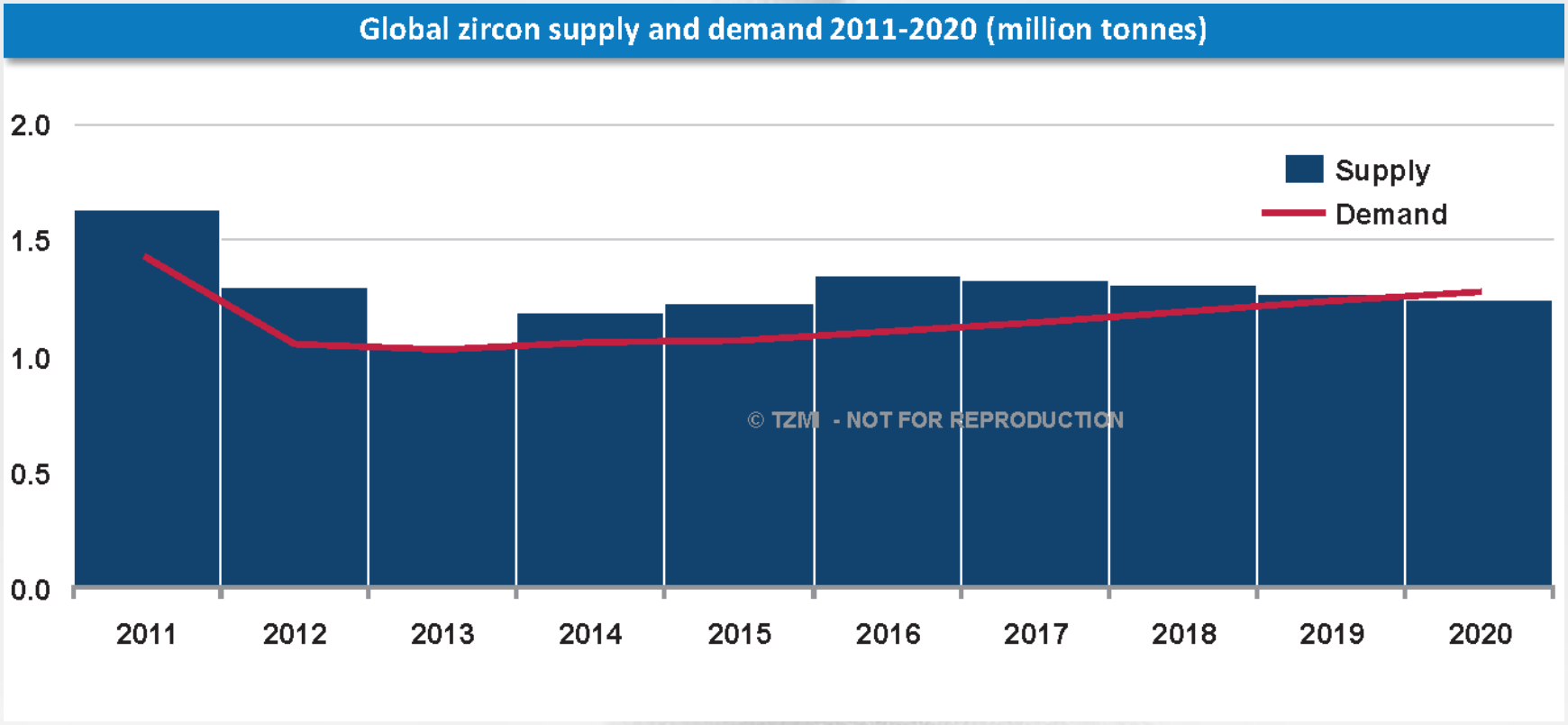
Zircon price history



Data source: Industrial Minerals

ZIRCON INDUSTRY ASSOCIATION

Zircon supply-demand forecast - TZMI



TZMI permission to use granted

ZIRCON INDUSTRY ASSOCIATION

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
- Mineral Commodities Tormin Project, South Africa
  - started 2014, produced 42,00 t zircon/rutile concentrates in 2014/15

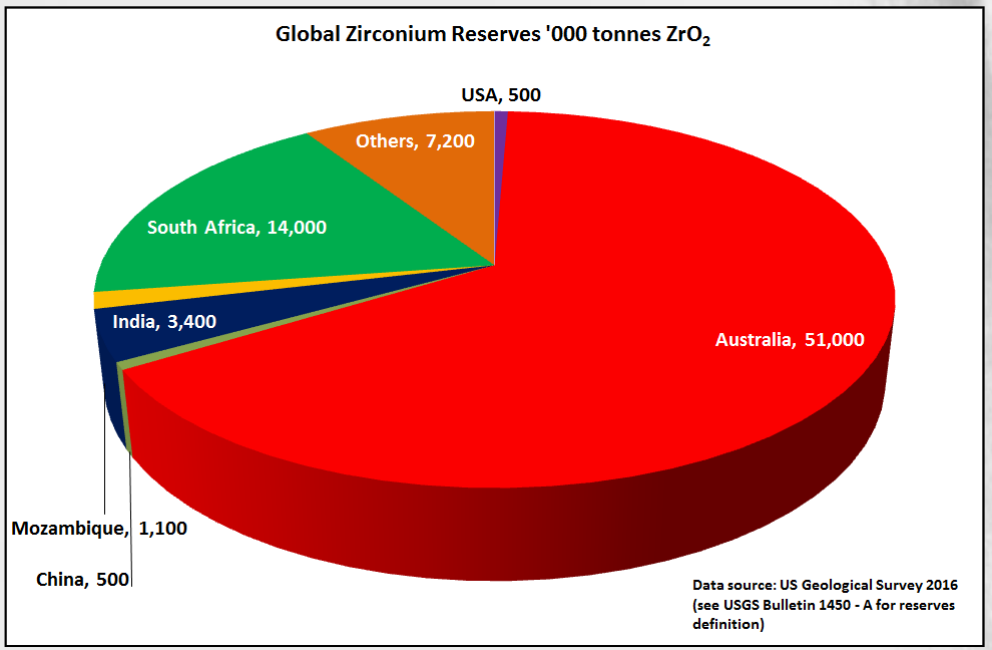
Projects of the major producers

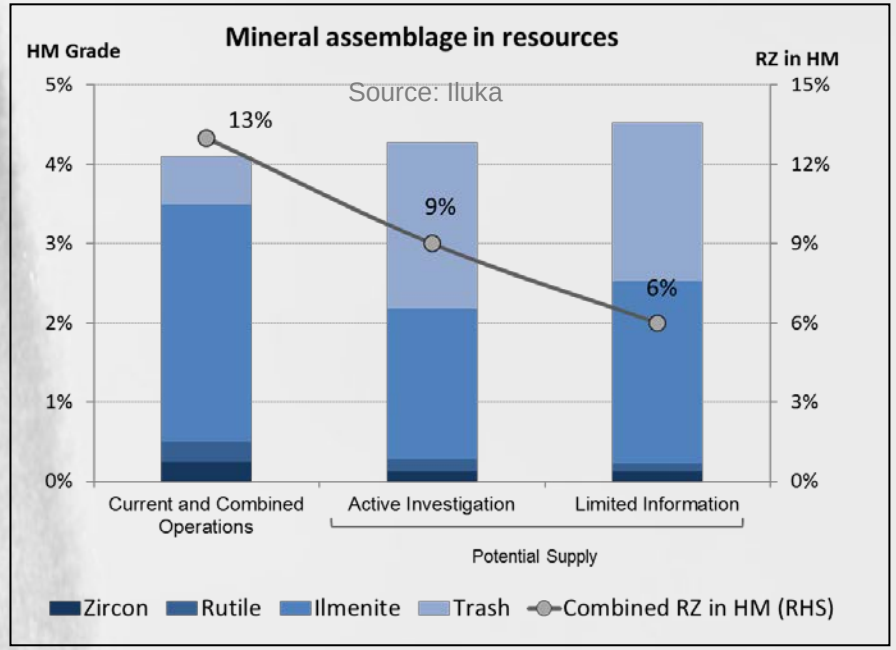
- **Iluka Resources:**
  - Cataby, in WA - 8.5 year mine life (DFS completed)
  - Balranald in NSW - 8 year mine life [DFS final stages]
  - JA satellite deposits in SA (PFS stage)
  - Puttalam, Sri Lanka [PFS planned to commence in 2016]
- **Richards Bay Minerals (Rio Tinto Iron & Titanium):**
  - Zulti 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, just commissioned, 55,000 tpy zircon, 13/15 year mine life, extendible)

Other mineral sands projects

- Mineral Commodities Ltd.
  - Xolobeni, South Africa
- Image Resources Ltd.
  - Various deposits in Perth Basin, WA, Australia
- Diatreme Resources
  - Cyclone Project, WA, Australia
- Strandline Resources
  - Coburn project, WA, Australia
- Astron Corp.
  - Donald project, Murray Basin, Australia + Niafarang project, Senegal
- Sheffield Resources
  - Thunderbird project, WA, Australia
- Savannah Resources
  - Jangamo project, Mozambique (JV with Rio Tinto)

Long term supply – issues and drivers





Challenges and trends:

- global decline in mine assemblages
- TiO_2 feedstock demand is the principal driver of zircon supply
- some new sources present greater technical challenges
- some new sources are in higher risk jurisdictions
- the need for economic viability
- urbanisation, consumerism and new applications

ZIRCON INDUSTRY ASSOCIATION

Use of zircon in investment casting

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

Source: EICF presentation to ZIA conference September 2015

ZIRCON INDUSTRY ASSOCIATION

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.

Types of zircon

- 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.
- There is no “one size fits all” solution for the investment casting industry and there are various considerations, not the least of which is the metal or alloy and type of part being cast.
- 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.

ZIRCON INDUSTRY ASSOCIATION

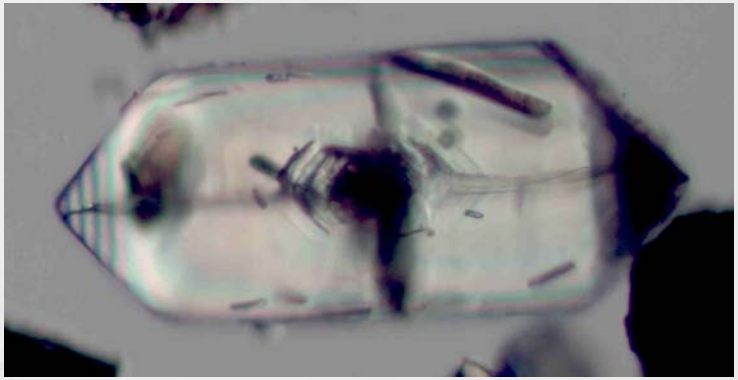
Zircon - Mineral Impurities & Calcining

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

`

ZIRCON INDUSTRY ASSOCIATION

Calcined Zircon Supply

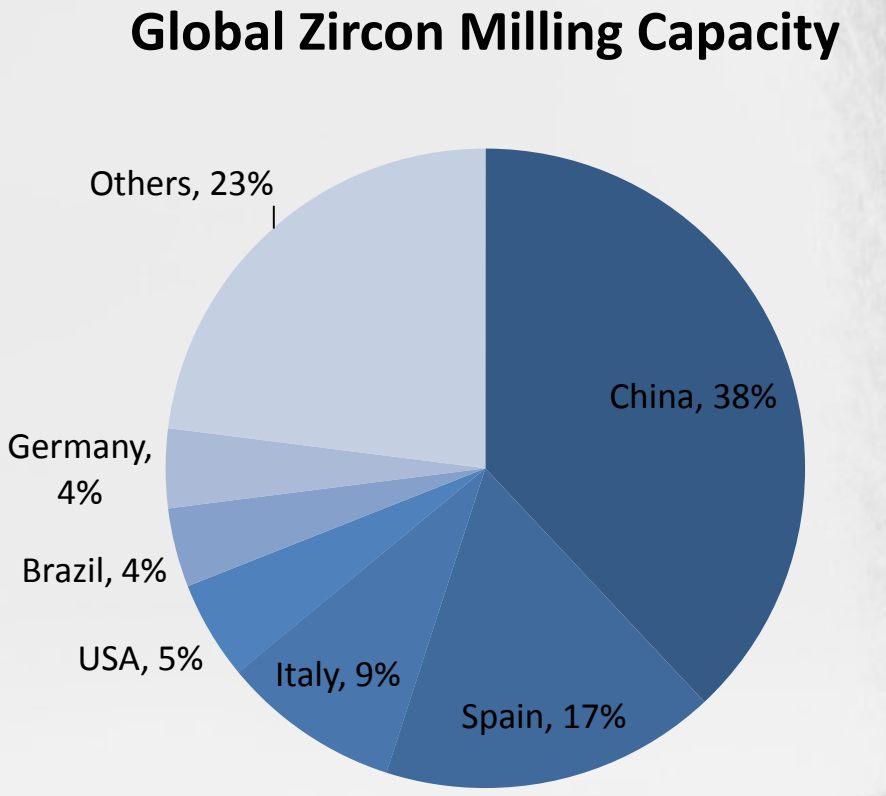
Current Suppliers of Calcined Zircon

- **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 3rd Party Calciners , e.g. CMMP France, Rasa Japan**
- **Various millers, traders and distributors**

Total capacity ± 100,000 tpy (not all for investment casting)

ZIRCON INDUSTRY ASSOCIATION

Zircon milling – capabilities and trends



Total 1.65 mt (of which 1.0 mt opacifier, 0.65 mt flour)
Source: Roskill

Global zircon milling

- Mostly focused on ceramics industry
- Products: zircon opacifier and flour
- About 60% of capacity is used for opacifiers, about 40% for zircon flour
- Processes and milling configurations vary across regions

Key trends

- Drive towards greater energy efficiency
- Tight quality control for investment casting zircon flour
- Milling and powder separation technologies – crucial factors
- Finer opacifier milling – driven by tight competition and need for higher product performance
- Life cycle assessment

ZIRCON INDUSTRY ASSOCIATION

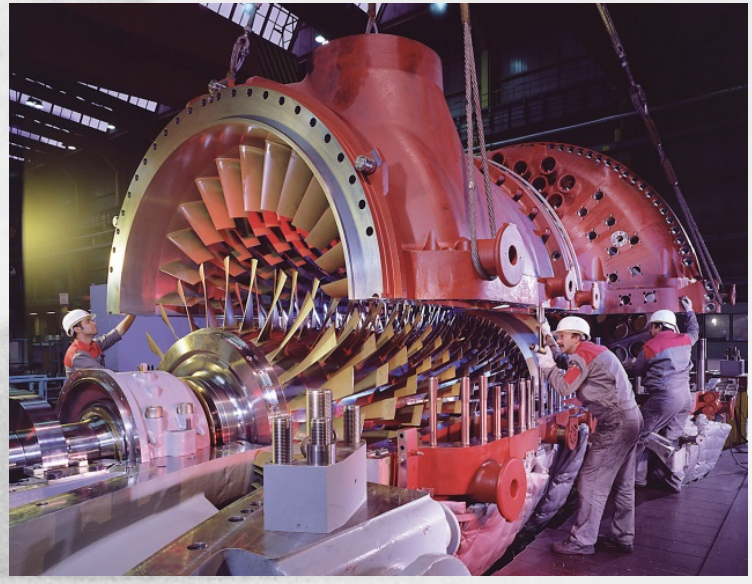
Zirconia in investment casting of titanium alloys

High reactivity of titanium alloys (reaction with standard ceramic moulds/binders based on Al_2O_3-SiO_2) lead to Alpha Case formation (resulting in surface deterioration and weakening of mechanical properties).

Stable oxides (such as fused Y_2O_3, Ca-stab ZrO_2, Al_2O_3) may be used to build up mould for investment casting. These moulds do not give significant surface reactions with titanium alloys.

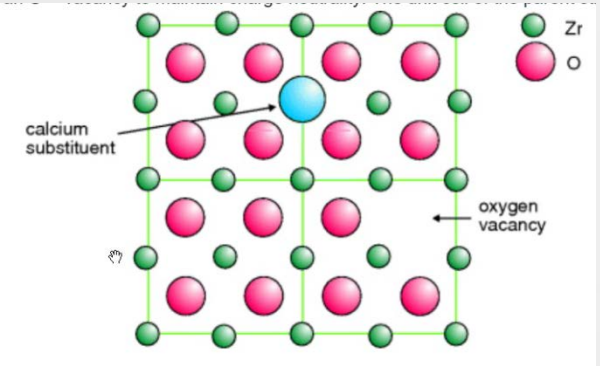
Applications

Aviation, Aerospace, shipbuilding, industrial areas, golf clubs

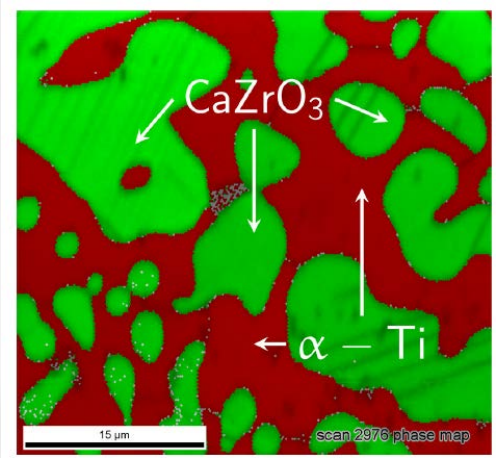


ZIRCON INDUSTRY ASSOCIATION

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**

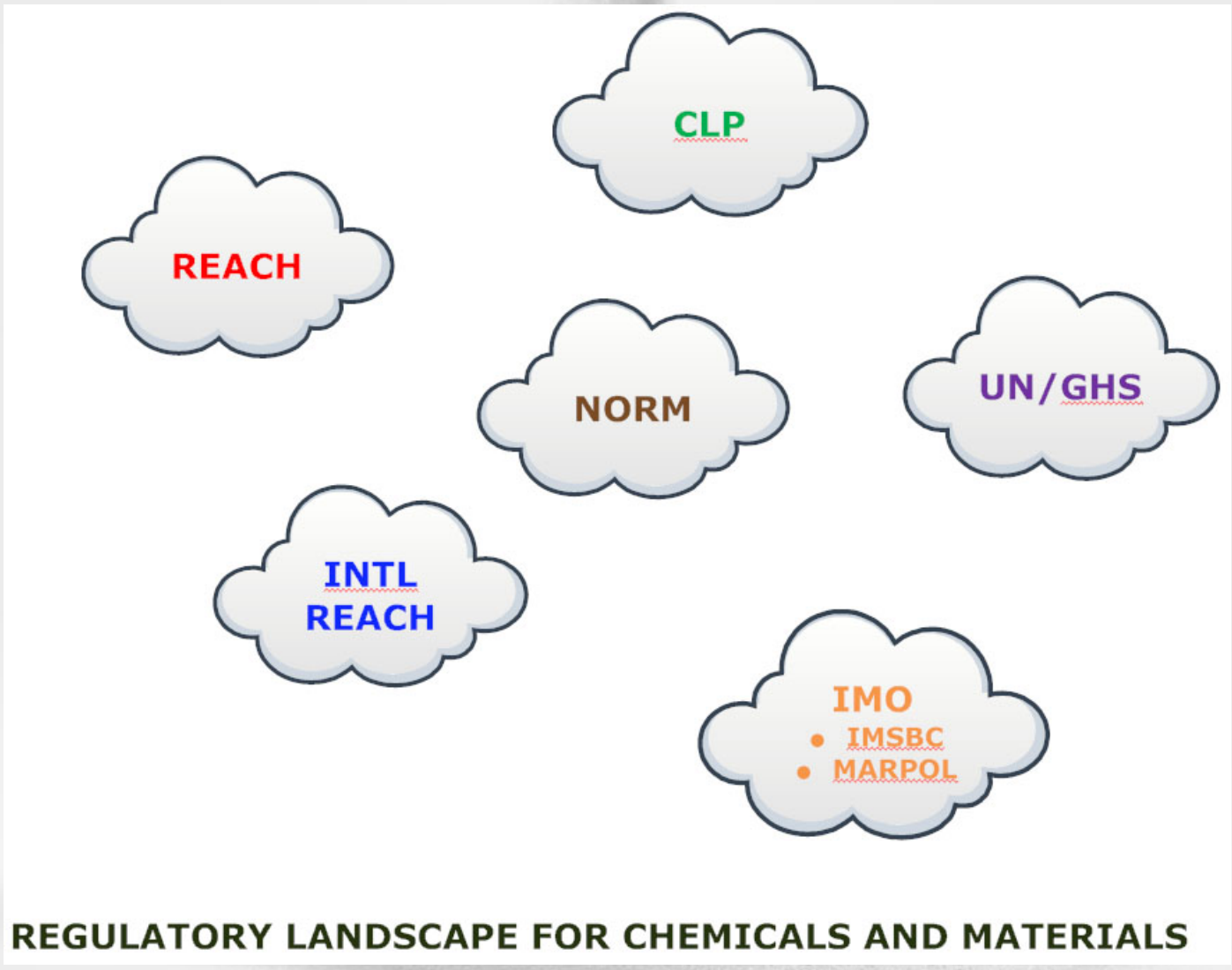
Crucibles for vacuum induction melting of Ti-6Al-4V:

- **Stoichiometric calcium zirconate ($CaZrO_3$) 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)

ZIRCON INDUSTRY ASSOCIATION

Regulatory support



REGULATORY LANDSCAPE FOR CHEMICALS AND MATERIALS

ZIRCON INDUSTRY ASSOCIATION

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)

- Transition between transport and exemption regulations is a grey area
- National regulators may apply the regulations differently to each other
- Prior to cross-border movements, regulators in destination country should be contacted and provided with activity data prior to dispatch
- Carriers should also be informed about the nature of the material and relevant regulations
- MSDS to include relevant information and be included in shipping documents

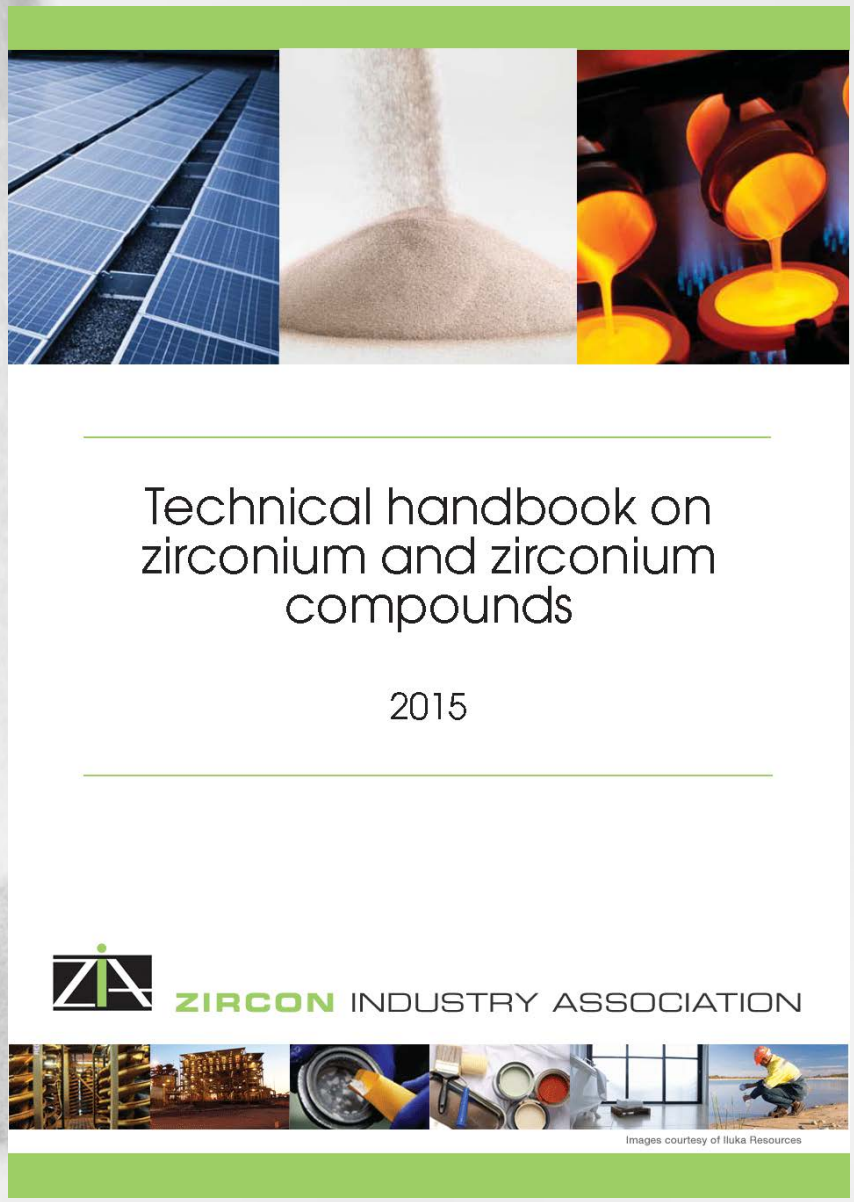
ZIA intends to produce guidance to facilitate cross border movement of zircon and zirconia.

ZIRCON INDUSTRY ASSOCIATION

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



ZIRCON INDUSTRY ASSOCIATION

The end

Thank you for your attention!

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

ZIRCON INDUSTRY ASSOCIATION