Microstructural and analytical analysis of plasma dissociated zircon

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Abstract. The investigation of the microstructure and distribution of impurities was carried out on plasma dissociated zircon (PDZ). The morphology of the PDZ and crystalline nature of the zirconia was determined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) while energy dispersive X-ray spectrometry (EDS) provided compositional information. The SEM and TEM results indicate that the morphology and crystalline nature of the zirconia varies as a result of the existence of a thermal gradient. The EDS results show that the majority of the impurities segregates to the silica phase of the PDZ.

1. Introduction
Zirconium is a major component in many alloys due to its thermal stability and resistance to corrosion [1]. These alloys, known as zircaloy, are used in the nuclear power industry for structural parts in the core; such as pressure tubes, channels, guide tubes or fuel cladding [2] due to its low thermal neutron cross section [3]. The mineral zircon (ZrSiO₄) is the primary source of zirconium metal. Zircon is mined as one of several products from heavy-mineral sand deposits associated with ancient shorelines [4].

The chemical inertness of zircon makes the separation of the zirconium and silicon components by chemical techniques difficult. The application of thermal plasma technology has shown to be an effective technique for the separation of the zirconia and silica phases [5]. In this process the zircon can be made chemically more tractable by dissociation in a plasma flame above the melting point (1687°C) into zirconia (ZrO₂) and silica (SiO₂). This product is known as plasma dissociated zircon (PDZ). The structure of PDZ material can be described as finely dispersed zirconia crystals (m.p. 2700°C) embedded in a glassy silica matrix (m.p. 1650°C). The amorphous silica can be dissolved by acids or bases to obtain pure zirconia.

The zirconia in PDZ exists in three crystalline structures: monoclinic which is stable below 1180°C, tetragonal which is stable in the range of 1180-2370°C and cubic which is stable above 2370°C [6]. Characterization of the size and distribution of zirconia within the silica produces important information regarding the efficiency of the dissociation process. Microanalysis of the zirconia phase is thus important since the presence of impurities is detrimental to the physical properties of zircaloy.

The present work investigates the phase morphology of zirconia crystals as well as the redistribution of impurities within the PDZ material.
2. Materials and methods

South African zircon mined at the Namakwa Sands project was used in this study. The PDZ material as-supplied by the South African Nuclear Energy Corporation (NECSA) was produced using a non-transfer arc plasma system. The as-received samples were resin embedded and polished to produce cross sections which were analysed in a scanning electron microscope (SEM) using the backscattered electron (BSE) imaging mode. Analysis of the impurity distribution within each phase was determined by energy dispersive X-ray spectrometry (EDS).

Material for analysis in the transmission electron microscope (TEM) was prepared from a suspension of finely powdered PDZ material in ethanol and placed in an ultrasonic water bath to ensure a uniform dispersion of particles. The fine powder was then collected on a carbon coated copper grid.

3. Results and discussion

3.1. Microstructural analysis

An SEM BSE micrograph showing the two distinct zones (A and B) within a partially formed PDZ grain is shown in figure 1. Zone A consists of undissociated zircon, while zone B contains two distinct phases namely zirconia (bright) and silica (dark). Figure 2 shows a PDZ particle consisting entirely of zirconia spherulites in a silica matrix. Spherulites are non-crystallographic branching arms that extend in all directions [7].

![Figure 1. BSE Micrograph of partially PDZ material.](image)

![Figure 2. BSE Micrograph of PDZ material, showing the spherulite growth morphology.](image)

The observed morphologies has been previously described, [7, 8], and will be discussed. According to the phase diagram of the ZrO$_2$-SiO$_2$ system based on the work of Butterman and Foster [9], the zirconia which has dissociated out of the zircon will be stable in the tetragonal or cubic crystal structure. The quenching of these particles forces its crystalline structure to change to the monoclinic structure resulting in a volume increase. The zirconia grows in a spherulitic fashion, thus they are called spherulites. Spherulites forms from large zirconia crystals due to the low surface heat transfer rate of these drops, as a result the temperature remains sufficiently high for crystal growth to take place.

The zirconia crystals that dissociated out of the zircon possessing a small surface area retain the tetragonal and cubic crystal structure. Due to the high heat transfer rate that these small zirconia particles possess, the formation of the spherulites is prevented. These particles crystallises into oval and spherical shaped zirconia particles as shown in figure 3.

The ZrO$_2$-SiO$_2$ phase diagram from McPherson and Shafer [7] shows that molten zircon could enter the miscibility gap if cooled rapidly to inhibit the formation of zirconia crystals. In this gap the
Zircon separates into a zirconia rich and silica rich liquid. This is known as spinodal decomposition as shown in figure 4. The zirconia rich liquid would rapidly crystallise during cooling producing a dispersion of very fine spherical particles of tetragonal and cubic zirconia in glass. The silica rich liquid would form a glassy matrix which also undergoes further separation to produce zirconia rich droplets in the glass.

![Figure 3. BSE Micrograph of PDZ material, showing spherical zirconia crystals.](image)

![Figure 4. BSE Micrograph of PDZ material, showing spinodal decomposition.](image)

The microstructure of the PDZ as analysed in the TEM revealed amorphous (light) and nanocrystalline (dark) regions as shown in figure 5. Measurements of the d-spacings of the fast Fourier transform (FFT) in figure 6 show the zirconia to have the monoclinic and tetragonal crystal structures. Reflections A and B corresponds to that of monoclinic zirconia with Miller indices 100 and ̅110 respectively. Reflections C and D corresponds to that of tetragonal zirconia with Miller indices 101 and 211 respectively. The cubic crystalline structure could not unambiguously be identified as X-ray diffraction (XRD) analysis found the ratio of the of monoclinic to tetragonal to cubic zirconia present in PDZ to be 100:10:1 [9].

![Figure 5. TEM micrograph of PDZ material](image)

![Figure 6. FFT of the zirconia phase.](image)

3.2. Quantitative analysis

The results of the impurity analysis of the PDZ as determined by SEM-EDS are summarized in the table.
Table. Impurity analysis of PDZ (weight percentage)

|               | Al  | Fe  | Ti  | Ca  | Hf  |
|---------------|-----|-----|-----|-----|-----|
| Undissociated zircon | 2.0 | 0.5 | 0.3 | 0.2 | 0.1 |
| PDZ zirconia phase   | 0.2 | -   | 0.1 | -   | 0.4 |
| PDZ silica phase     | 1.3 | 0.7 | -   | 0.3 | -   |

The analysis revealed that majority of the impurities present in zircon segregates to the silica phase during dissociation. However the hafnium and titanium segregated to the zirconia phase. The hafnium concentration is higher than the standard specification for nuclear grade zirconium metal (100ppm) [10], but is lowered to the required amount by sublimation and reduction reactions with magnesium.

4. Conclusion

The nucleation of the zirconia crystals from zircon arises from the solidification that occurs during the cooling process of the dissociated zircon. There exists a range of possible thermal histories and the morphologies of the zirconia observed depend upon the cooling rate. Large zirconia crystals grow in a spherulitic manner and have the monoclinic crystal structure. Some smaller crystals formed via a rapid cooling process appear to retain the tetragonal or cubic crystal structures rather than relaxing to the monoclinic structure, and this may be because such nanocrystals are stabilised by small surface area or constraints from surrounding materials. Spinodal decomposition occurs at lower temperatures which results in the formation of a zirconia and silica rich liquid.

Impurity distribution analysis of the PDZ showed that majority of the impurities present in zircon segregates to the silica phase during the dissociation process.

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