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Plasma Dissociated Zircon (PDZ) processing; Influence of the Zr:Si Ratio in the composition, microstructure and thermal re-crystallization

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Abstract

Plasma dissociated zircon (PDZ) has attractive applications in ceramic colouring, as well as the preparation of fine ZrO_2 crystals, coatings and refractory materials. Generally the PDZ is obtained from different natural or synthetic zircon powders, if the cooling rate is high enough a complete dissociation is achieved, with rounded (dendritic) zirconia grains imbibed in a fused silica (non crystalline) matrix. The principal objective of this work is to establish the influence of the incorporation of both products of the zircon dissociation (fused silica and crystalline zirconia) to the initial powders mixture utilized for the processing of PDZ in an indigenous thermal plasma argon furnace. Both structural and microstructural characterization was carried out. A thermal annealing at 1500ºC with different soaking time (1-15 hours) was completed in order to establish the thermal stability to the thermodynamically favoured recombination, showing that after this time a recombination was achieved, and this behaviour was not influenced by the Zr:Si ratio.

The addition of fused silica resulted in an important decrease of the zirconia grains size, while the zirconia addition had the opposite result, showing that within this range (1-10 μm) the final zirconia grains size can be selected and controlled with this processing variable. The present processing route showed an alternative way for obtaining different size of monoclinic zirconia powder.

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1. Introductions

Application of thermal plasma for processing refractory materials has been well known to scientists and engineers for some time. High temperature (10000ºC), good thermal conductivity, and high heat content available in the thermal plasma, make it ideally suitable for processing of refractory materials such as alumina, zircon, etc; Cao et al. 2004, McPherson, R. 1989.

The more important processing variables are voltage, the plasma gas (generally argon or air) and the gas flow. In these methods the heating and cooling rates are really extreme in comparison with traditional processing like pressureless sintering. Furthermore the rates achieved ($\approx 10^6$ ºC/s Cao et al. 2004) are also much higher than other advance processing routes like electrical current activated sintering (ECAS) processes like Spark Plasma Sintering (SPS) (200 °C/s) Grasso et al. 2009, Rendtorff et al. 2011, Rendtorff et al. 2012. Due to this fact the reactions kinetics are usually increased in several orders Cao et al. 2004.

Zircon dissociation mechanism was recently reviewed Kaiser 2008. The presence of impurities decreases the dissociation and usage temperatures, Kaiser 2008. At high temperature the stable zirconia phase is the tetragonal zirconia (t-ZrO_2) one. The resulting tetragonal zirconia during the cooling might transform into monoclinic zirconia which is the stable phase at room temperature. It is well known that this phase transformation is accompanied by a significant volume change which introduces microcracks inside the zirconia particles dispersed into the ceramic matrix Hannink et al. 2000, thus, resulting in a detrimental effect on the mechanical properties.

Zircon based ceramics have been processed by normal uniaxial press, hot pressing, sol–gel methods and slip casting. Besides, methods based on the mixture of amorphous ZrO_2-SiO_2 revealed the incomplete powders crystallization under heat Taraj et al. 1996, or laser treatments Schelz et al. 2008. Zircon materials sintered in the range between 1500 °C and 1650 °C overcome the 99% of the theoretical densities, depending on the processing route. Fully dense zircon based ceramic avoiding zircon dissociation has been recently processed by SPS and high energy ball milling Rendtorff et al. 2011, Rendtorff et al. 2012.

The thermal dissociation is thermodynamically reversible, both oxides recombine to form the silicate Kaiser 2008. But if the cooling rate is fast enough (quenched) the recombination is avoided, the product of the dissociation is known as dissociated zircon (DZ) and if the dissociation was carried out by a thermal plasma processed it is commonly known as plasma dissociated zircon (PDZ) McPherson et al. 1985, McPherson and Shafer 1984, Evans and Williamson 1979, Ananthapadmanabhan et al. 1994. Plasma dissociated zircon (PDZ) has attractive applications in ceramic colouring, as well as the preparation of fine ZrO2 crystals, coatings and refractory materials.

Previous studies, Suzuki et al. 2005, Garvie 1979, Khor 1997, Yugeswaran et al. 2010, have shown that quenching rates and particle size of the zircon feedstock affect the microstructure and phase composition of PDZ. In PDZ the proportion of tetragonal ZrO_2 increases with decreasing initial zircon particle size and increasing cooling rate; Suzuki et al. 2005.

Generally the PDZ is obtained from different natural or synthetic zircon powders, and as mentioned, if the cooling rate is high enough, a complete dissociation is achieved, with rounded (dendritic-sphererulitic) zirconia grains imbibed in a fused silica (non crystalline) matrix.

The principal objective of this work is to establish the influence of the incorporation of both products to the zircon dissociation, fused silica and crystalline zirconia to the initial powders mixture utilized for the processing of PDZ. For this a structural and microstructural characterization was carried out to the different processed materials. Finally, the same characterization was carried out to the same materials submitted to different thermal annealing treatments at 1500ºC (1 to 15 hours) in order to analyze the effect in the thermal stability and re-association.

Finally, as a result of this study, it is expected to show an alternative way of obtaining a zirconia precursor capable of providing powders with different but controlled size.

2. Experimental procedure

The actual processing reactor was extensively described before; Khor 1997, S. Bhattacharjee et al. 2000 The most important feature of the reactor is that, due to electromagnetic pumping action of the plasma jet, heat transfer efficiency to the charge kept in the hearth is very high S. Bhattacharjee et al. 2000. The typical process parameters consisted in: Arc Voltage 40 V; Arc Current 300 A; Argon gas flow 2 l/min; Duration 5 min; 100g Powder Mixture Weight.

Table 1: Rietveld-Le Bail quantification results.

Sample	Zircon	Monoclinic Zirconia m-ZrO_2	Tetragonal Zirconia t-ZrO_2	Non-Crystalline Phase*	Quartz SiO_2
ZN	1.0	70.4	0.5	28.1	-
ZNS	0.6	55.4	1.6	42.4	-
ZNZ	4.6	69.5	0.7	22.0	3.2
*Le Bail Method					

The principal starting powder, Zircon, was introduced as zirconium silicate (Mahlwerke Kreutz, Mikron, Germany), this mineral shows a chemical content of ZrO_2 = 64 – 65.5 wt%, SiO_2 = 33 – 34 wt%, $Fe_2O_3 \leqslant$ 0.10 wt% and $TiO_2 \leqslant$ 0.15 wt% and D_{50} = 1.5 μm. With a specific gravity of 4.6 g/cm3 and melting point of 2200 °C. Silica fume (ElKEM 965, Norway) and electrofused zirconia (Zhengzhou Zhenzhong, China) were employed for changing the Zr:Si ratio of the starting mixtures. The mixtures were named as following: ZN (100% Zircon), ZNZ (15%m-ZrO_2) and ZNS (15% SiO_2). The initial powder mixtures were performed via ethanol dispersion in order to achieve a homogeneous starting powder for the later fusion.

Crystalline phases formed were analyzed by X-ray diffraction (XRD) (Philips 3020 equipment with Cu-Kα radiation in Ni filter at 40 kV–20 mA). The Rietveld quantitative mineralogical analysis using the Rietveld full-pattern fitting method method developed by Rietveld 1969 and Bish and Howard 1988, was used to characterize the present crystalline phases in the materials. In this work we evaluated the amorphous silica, product of zircon dissociation by the described method which has already proved to be suitable for this kind of materials if the glassy content is over 5% Conconi et al. 2011. Le Bail demonstrated that it is possible to include the silica glass in the Rietveld refinement through a structural model with crystalline defects.

Before introducing the non crystalline phase in the refinement of the studied samples, the pure amorphous silica was analyzed for determining the crystalline and profile parameters.

In order to establish the thermal stability of the processed materials, samples were submitted to different annealing thermal treatments of 1500ºC for different soaking times (1-15 hours) in an electric furnace at air atmosphere. After this treatment an XRD-Rietveld-Le Bail analysis was carried out as well.

3. Results and discussions.

Figure 1A shows the XRD patterns of the three materials processed. Table 1, shows the results for the Rietveld – Le Bail phase quantification. In the three cases the principal crystalline phase is the monoclinic zirconia (B), showing that the dissociation was effectively achieved and that the re-association did not occurred during the natural cooling of the reactor. The values thus obtained are comparable with other PDZ. At operating temperature ($\geqslant$ 5000ºC), the material is completely fused. Below 2700ºC and 2300ºC the cubic and tetragonal zirconia are respectively stable, Hannink et al. 2000, but at room temperature ($\geqslant$ 1100ºC) the monoclinic phase is the stable one. In the three materials processed only this last one appeared accompanied with small amounts of t-ZrO_2. The tetragonal zirconia is only stable at room temperature if it is chemically stabilized by the presence of dopant cation like Calcium, Yttrium, etc. or if the particle size is smaller than a critical size which also depends on the matrix in which it is imbibed Chraska et al. 2000.

The other product of zircon dissociation, the silica, was in the three cases principally amorphous. Non crystalline SiO_2 was detected by the XRD as mentioned. This amorphous phase presumably composed of pure silicon oxide was quantified by the Le Bail Method. The results correspond to the dissociation stoichiometry. The addition of silica to the initial formula (ZNS) conducted to a proportional increase in the amorphous phase. (While after the introduction of zirconia (ZNZ) no important increment in on the amorphous phase was observed.) In fact as some ($\approx$5%) of the zircon recombined silica was observed. On top of this, a small amount of crystalline quartz was detected by XRD also in detriment of the amorphous phase.
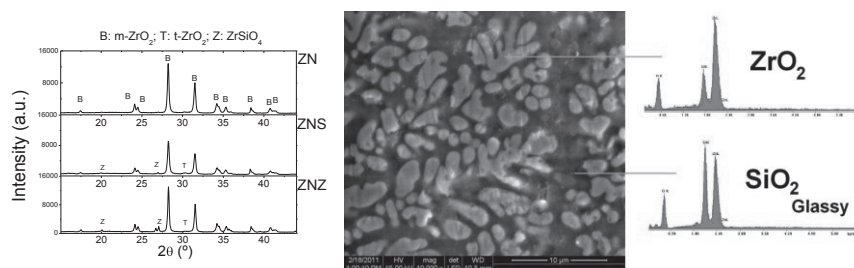

Figure 1 (A) XRD patterns of the PDZ studied materials after the plasma treatment. (B) SEM image of the Zn Material (x10000) together with the EDX spectrums; both: dispersed zirconia grains and glassy silica matrix

Figure 1B shows the SEM image of the Zn material, together with the EDX spectrums of the distinguished phases where the the typical final microstructure of these materials can be seen. A continuous silica matrix (dark gray) can be seen presenting arrangements of homogeneously distributed zirconia grains (light gray) showing the typical growth pattern called spherulytic, which is consequence of the diffusion limited aggregation, in a non equilibrium condition. This type of growth is expected for the zirconia crystallization in the ZrO_2-SiO_2 magma during rapid cooling.

Figures 2, show the SEM images of the three processed materials (x 10000). The three materials showed the described configuration but the diameter of the zirconia grains were strongly influenced by the composition of the starting solution (the only processing variable). Specifically, the pure zircon (ZN) presented a characteristic diameter size between 2 and 4 μm. It was around 5-8 for the ZNZ material, and finally the resulting diameter was ten times lower in the case of material made from the mixture of zircon and silica (diameter ZNS :0,2-0,4μm). This fact shows that interpolating this variable the final zirconia particle size can be calibrated. This is especially important if PDZ is afterwards leached in an alkali solution (NaOH) or hidrofluorhidric acid (HF) with the objective of obtaining monoclinic zirconia powders with different and controlled size.
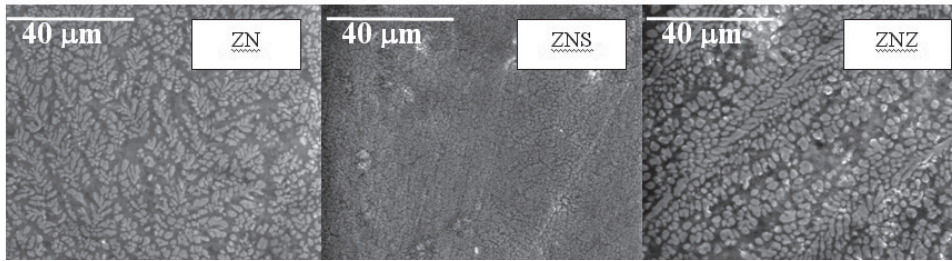
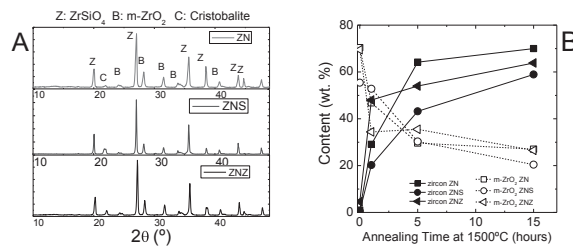Figure 2: SEM image of the three plasma processed Material (x3000)

Figure 3: (A) XRD patterns of the annealed samples (15 hours) and (B) Rietveld quantification for the annealed materials as function of the annealing time at 1500ºC.

As mentioned, in order to establish the thermal stability of the processed materials, samples were submitted to an annealing thermal treatment at 1500ºC for different temperatures during 15 hours. Figure 3A shows the XRD patterns of the long time annealed samples (15 hours). The sharpness of the diffraction peaks was notably increased with these thermal treatments, showing the increase in the crystallinity. Zircon was progressively recombined as the annealing treatment increased. No important non crystalline phases were detected; hence the Le Bail method was not applied to these samples. Finally, it is important to point out that the amount of t-ZrO_2 was in all cases very low. Although zircon was recombined, up to more than the 75 wt.% some monoclinic zirconia was still present accompanied by Cristoballite (SiO_2).

The results of the quantitative analysis of the annealed materials are shown in figure 3B, from these it is clear that the recombination of the m-ZrO_2, in similar in the three batches studied, the recombined zircon is not complete and maximum for the stoichiometric sample (Zn) and as expected smaller in the samples with additive (ZnS and ZnZ). 20-30 % of zirconia is retained in all the cases. However, at short annealing times (1 hour) ZnZ material presented the higher recombination proportion. This might be explained by the fact that microstructure characteristic size of this material is ten times smaller.

4. Conclusions

Plasma dissociated zircon (PDZ) were processed, both structural and microstructural characterization was carried out by means of X ray diffractions and Rietveld method complemented by Scanning Electron Microscopy with EDX local chemical analysis. Furthermore, the resulting amorphous silica was also evaluated by the Rietveld method. Particularly, this was carried out by a modelled phase method within the Rietveld method presented by Le Bail.

A complete dissociation was achieved in all cases, with rounded (dendritic-spherulitic) zirconia grains imbibed in a fused silica (non crystalline) matrix. The monoclinic zirconia grains size was between 0.5 and 10 microns.

The proposed processing route showed to be suitable to obtain PDZ, with the mentioned microstructure. The addition of microsilica resulted in an important decrease of the zirconia grains size while the zirconia addition had the opposite result, showing that within this range the final zirconia grains size can be selected with this processing variable.

The higher zirconia content in the fused liquid at plasma temperature increased the viscosity of the liquid from which the spherulytic zirconia grains crystallize showing that it is a diffusion limiting mechanism.

A thermal annealing (15 hour at 1500ºC) treatment was completed in order to establish the thermal stability to the thermodynamically favoured recombination, demonstrating that for this condition a certain grade of recombination was achieved, 20 % of zirconia was retained and no important amorphous silica phase was detected by XRD. Moreover, this behavior was not influenced by the Zr:Si ratio. The recombination was hardly influenced by the additives; and it showed to by faster for smaller particle size PDZ. No important amount of t-ZrO_2 was retained. This was observed in both in the annealed samples and the PDZ.

Finally the proposed XRD analysis demonstrated to be suitable to evaluate both, the crystalline phases and the amount of amorphous silica present in this kind of materials.

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