JOURNAL OF MATERIALS SCIENCE 27 (1992) 1762–1766

Studies on plasma dissociation of Indian zircon in a specially developed plasma reactor

U. SYAMAPRASAD, S. BHATTACHARJEE, R. K. GALGALI, B. K. MOHAPATRA, B. C. MOHANTY
Regional Research Laboratory, Bhubaneswar 751 013, Orissa, India

Studies on the preparative and microstructural aspects of plasma-dissociated Indian zircon prepared in a specially designed plasma reactor (20 kW) are reported. The vital parameters involved in the process have been optimized for a high degree of dissociation with maximum feed rate. A near total phase separation (ZrO_2 and SiO_2) has been achieved in the plasma-dissociated zircon spheroids which constitute over 90% of the product. Microstructural studies have revealed that the spheroids are of two types with a distinct difference in the morphology of zirconia crystallites. Most of the spheroids have been found to have well-developed polygonal grains with spherulitic growth of ZrO_2 in SiO_2 glass. The rest of the spheroids consist of intergrown tabular crystals of monoclinic zirconia set in a matrix of silica. The silica present in the plasma-dissociated zircon has been amorphous and highly reactive, and is leached out using hot NaOH solution to recover fine grain zirconia.

1. Introduction

The unique properties of plasma-dissociated zircon (PDZ) have been studied by several researchers ever since its first successful preparation [1]. The increasing interest in PDZ is mainly due to its industrial potential as a convenient raw material for the preparation of zirconia and zirconia-based multiphase ceramics, besides its direct use as a good refractory and colour-making material. Several studies on the composition and microstructure [2–6] and the applications of PDZ [7–11] are available in the literature. However, very little has been reported on its preparative aspects and the plasma system in which it is prepared. Results are presented here of a study of the plasma dissociation of Indian zircon conducted in a simple and inexpensive plasma reactor developed by the authors for inflight processing of refractory powders.

2. Experimental procedure

2.1. The plasma reactor

A schematic sketch of the plasma reactor (20 kW) used for zircon dissociation studies is shown in Fig. 1. It is a non-transferred arc plasma reactor employing the principle of an extended arc [12, 13] and uses graphite electrodes. A water-cooled stainless steel chamber (height 50 cm and diameter 32 cm) with a conical bottom was used as the reactor vessel. The electrodes were arranged vertically inside the vessel as shown in Fig. 1. The top electrode (cathode) having a larger diameter (35–40 mm) than the bottom one (anode 25–30 mm), was provided with an axial hole (5–12 mm) to introduce both the plasmagen gas and the particle feed. A rack and pinion mechanism was incorporated to provide an axial motion of the top electrode for arc stabilization. A powder feeder suitable for the system with proper control over feed rate was designed, fabricated and fixed to the top end of the cathode. The plasmagen gas (argon) was introduced through a side hole provided in the "tail" of the powder feeder at an angle 45° to the vertical axis. A split pan was fixed to the bottom electrode just below the opening in the reactor vessel to collect the dissociated particles.

2.2. The feed stock

Indian zircon (MK Grade) containing 65.60% (ZrO_2 + HfO_2), 31.10% SiO_2, 0.60% TiO_2 and 0.08% Fe_2O_3 was used for the present studies. The particle size distribution of the raw material is given in Table I. The morphology of the zircon particles is shown in Fig. 2. The zircon was initially screened and particles with sizes ranging from 105–250 μm were used as the feed stock.

2.3. Plasma dissociation

The reactor was connected to a 150 V d.c. power source and the arc was initiated using argon as plasmagen gas. After obtaining a stable arc, zircon was fed into the reactor at controlled rates. The product was collected in a split pan provided at the bottom. Dissociation studies were conducted by changing various parameters: Argon flow rate 2–10 l min^{-1}; current 100–400 A; top electrode diameter 25–40 mm; axial hole diameter in the top electrode 5–12 mm; and zircon feed rate 1–10 kg h^{-1}.

0022–2461

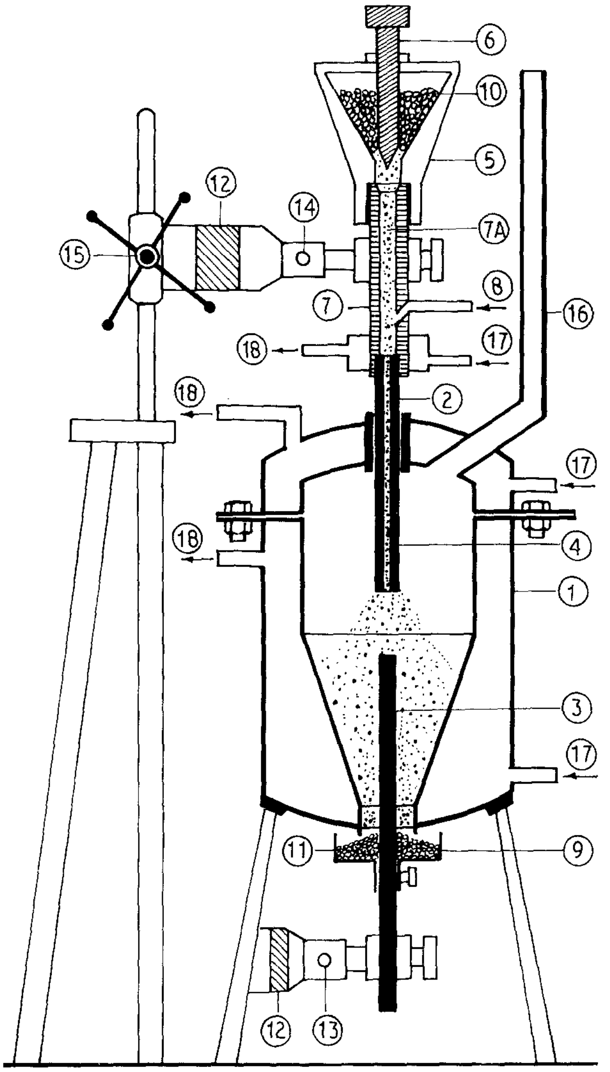

Figure 1 Schematic sketch of the plasma reactor (20 kW, d.c.) used for zircon dissociation studies. 1, Reactor vessel; 2, cathode; 3, anode; 4, axial hole in cathode; 5, powder feeder, 6, feed control screw; 7, feeder tail; 7A, axial hole; 8, gas inlet; 9, split pan; 10, feeder powder; 11, processed powder; 12, electrical insulation; 13, positive power terminal; 14, negative power terminal; 15, rack and pinion assembly; 16, exhaust; 17, water inlets; 18, water outlets.

TABLE I Particle size distribution of Indian zircon (MK grade)

Sieve size (μm)	(wt %)
+355	0.50
−355 +250	16.06
−250 +150	56.68
−150 +105	25.52
−105 +90	0.29
−90	0.06

2.4. Characterization of PDZ

The product collected from the reactor contained some graphite particles. These were removed by flotation technique using pine oil in water medium. The degree of dissociation was estimated by determining the weight loss of the sample product after leaching out both SiO_2 and ZrO_2 in warm HF (undissociated zircon does not dissolve in HF). The undissociated grains from the reactor product were removed by employing a tabling technique. The phases present in the feed stock and the product were identified by an automated X-ray diffractometer (Philips ADP 1700) using CuK_α radiation. The microstructural examinations were conducted using an optical microscope and scanning electron microscope (Jeol 35 CF).

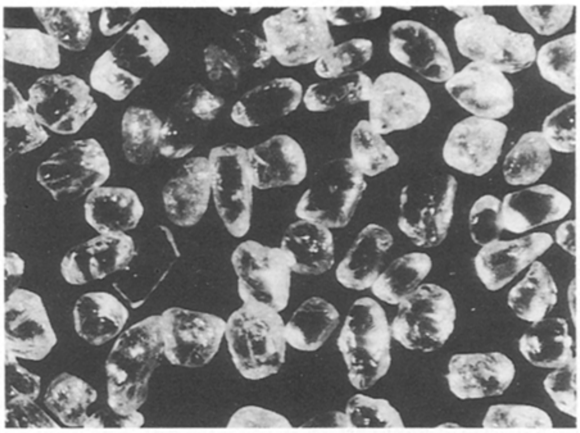

Figure 2 Morphology of Indian zircon particles (sizes 105–205 μm).

3. Results and discussion

3.1. Performance of the plasma reactor

The performance of the reactor was found to be excellent with respect to arc stability, particle flowability and effective injection of particles into the hot zone of the plasma. The arc stability was greatly increased with a remarkable reduction of noise when the feed material was introduced. Because the particles are fed along the axis of the electrode, most of them follow a trajectory close to the hottest zone in the plasma, thereby easily attaining the required high temperature. The dissociated droplets then undergo a very rapid cooling while they leave the plasma zone and thus prevent possible reassociation of the products of dissociation. This is evident from the fact that above 90% of the zircon feed could be dissociated in a single pass through the reactor.

3.2. Optimization of process parameters

The performance of the reactor and the quality of the dissociated zircon were found to depend greatly on the process parameters, namely the arc current, argon flow rate, diameters of the cathode and anode and axial hole diameter of the cathode. A number of experiments were conducted to optimize these parameters for obtaining a high degree of dissociation with maximum zircon feed rate, keeping the power level within 20 kW. For higher arc currents (200–400 A), it became necessary to use a higher diameter cathode (35–40 mm) to avoid excessive heating of the nozzle tip. The diameter of the bottom electrode (anode) was kept smaller (25–30 mm) to prevent any possible accumulation of fused zircon particles over its surface. It was found that very low argon flow rates of 2–3 $l\,min^{-1}$ were sufficient to stabilize and expand the arc to several times its normal length when a cathode hole diameter of 5 mm was used. Although the quality of PDZ prepared under this condition was excellent, the feed rate of zircon could not be increased beyond 2.5 kg h^{-1}. Higher feed rates under this condition resulted in some fused agglomerates together with the dissociated spheroids. This may be attributed to an increased collision rate of the molten particles near the cathode tip because of the decreased interparticle distance. On the other hand, when the diameter of the cathode hole was increased beyond 10 mm with a corresponding increase in the argon flow rate, a marked reduction in the degree of dissociation was observed due to the lack of sufficient temperature. The highest zircon feed rate of 4–5 kg h^{-1} at about 20 kW power was achieved with a degree of dissociation of 91%. The optimum range of parameters for 20 kW power are: cathode diameter 35–40 mm, cathode hole diameter 8–10 mm, operating voltage 55–65 V, current 300–350 A and argon flow rate 10 l min^{-1}.

3.3. Characterization of PDZ

Thermal dissociation of zircon ($ZrSiO_4$) occurs because the free energy of formation of this compound from the component oxides reaches zero at about 1600 °C [14]. The generally accepted phase diagram of the ZrO_2–SiO_2 system [15] shows that the dissociation of $ZrSiO_4$ into ZrO_2 and SiO_2 occurs at 1676 °C. In plasma, most of the feed stock undergoes total melting and this occurs above 2700 °C as in the phase diagram. A near total phase separation is possible because of the ultrafast quenching and the high difference in the melting points of the component oxides (about 1000 °C). Fig. 3a and b show the X-ray diffraction (XRD) patterns of Indian zircon and the dissociated zircon, respectively. The disappearance of tetragonal $ZrSiO_4$ peaks and the presence of monoclinic ZrO_2 peaks in Fig. 3b confirm the dissociation. The absence of any SiO_2 peaks indicate the amorphous nature of the SiO_2 phase.

A photomicrograph of typical dissociated zircon spheroids is shown in Fig. 4. The degree of dissociation (expressed as 100 wt% zircon in PDZ) at a feed rate of 4–5 kg h^{-1}, was found to be 91%. The spheroids were coarser than that of the feed stock and showed a lower specific gravity. The specific gravity values of the feed stock and spheroids were 4.6 and 3.8 g cm^{-3}, respectively. This is due to the porous nature of the spheroids and the presence of blow holes, as revealed by the scanning electron micrograph (described in the following section). An easy separation of the spheroids from the undissociated zircon particles was possible because of the lower specific gravity value and the spheroidal shape. The spheroids free from graphite and undissociated zircon were treated with NaOH solution of different concentrations and temperatures to study the chemical activity of free SiO_2 present in the spheroids. It was possible to leach out SiO_2 with 50% NaOH solution around 140 °C to recover zirconia, high-valued product. The zirconia thus obtained was monoclinic with an average particle size of about 0.2 μm.

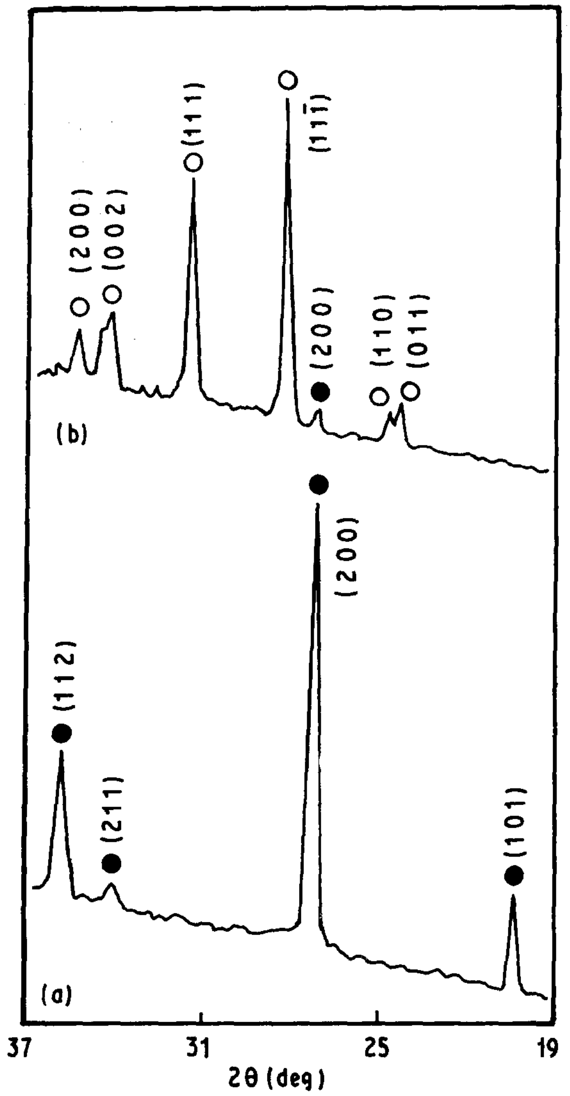

Figure 3 XRD patterns of (a) Indian zircon and (b) plasma-dissociated Indian zircon. (●) $ZrSiO_4$, (○) ZrO_2.

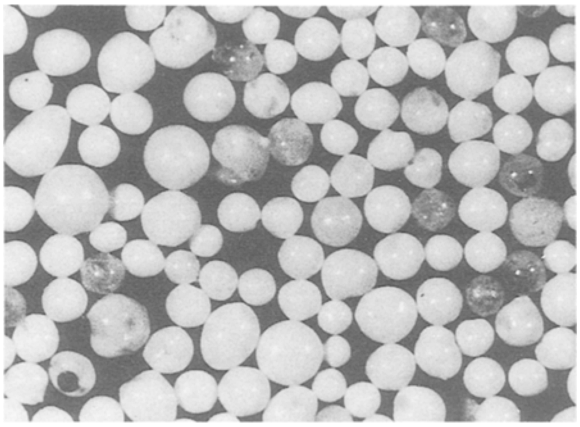

Figure 4 Photomicrograph of plasma-dissociated zircon (sizes 105–250 μm).

Scanning electron microscopic examination of PDZ spheroids, cracked PDZ spheroids and partially leached PDZ spheroids revealed that the spheroids were of two types with distinct difference in their microstructures. The surface of the majority of the spheroids (Type I) had well-developed polygonal

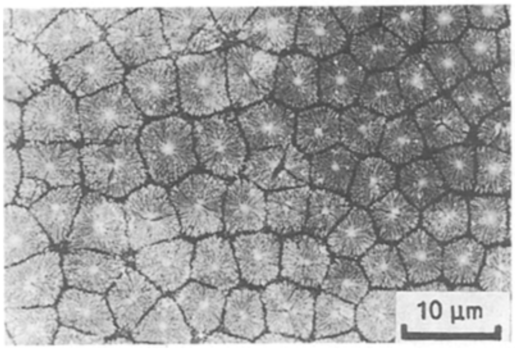

Figure 5 SEM microstructure of the surface of plasma-dissociated zircon spheroid (Type I) showing well-developed polygonal grains. Here zirconia has a spherulitic growth (white) in silica matrix (dark).

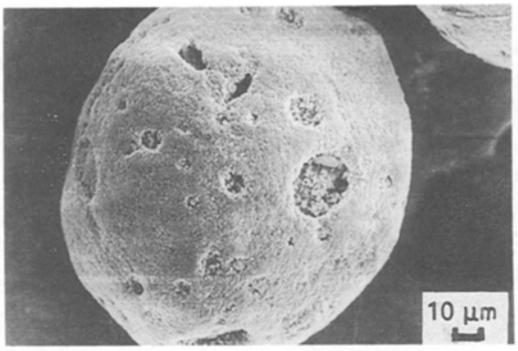

Figure 8 A partially leached plasma-dissociated zircon spheroid revealing the porosity and blow holes.

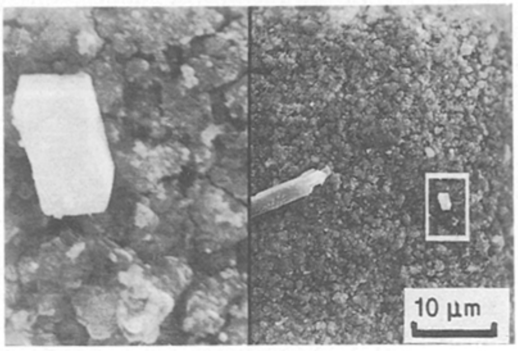

Figure 9 A well-developed monoclinic zirconia crystal observed in a Type II spheroid.

grains with 120° triple junctions (Fig. 5). In these spheroids monoclinic zirconia showed a spherulitic growth in the SiO_2 matrix. The mean diameter of the ZrO_2 crystallites is about 0.1 µm. SEM examination of the blow holes in the cracked Type I spheroids also revealed that a similar two-phase microstructure was present in the bulk of the spheroids. The other type of spheroid (Type II) consisted of intergrown tabular crystals of monoclinic ZrO_2 grown in a matrix of SiO_2. This has been observed in a few of the spheroids partially leached in hot NaOH solution (50%). A clear distinction between the two types of spheroids is displayed in Fig. 6 in which ZrO_2 crystals are clearly visible on the surface of Type II spheroids. In Fig. 7, growth of tabular crystals of monoclinic ZrO_2 (length 10–20 µm) is shown. The porous nature of the spheroids and the presence of blow holes are shown in Fig. 8. An enlarged view of a monoclinic ZrO_2 crystal observed in a partially leached Type II spheroid is shown in Fig. 9.

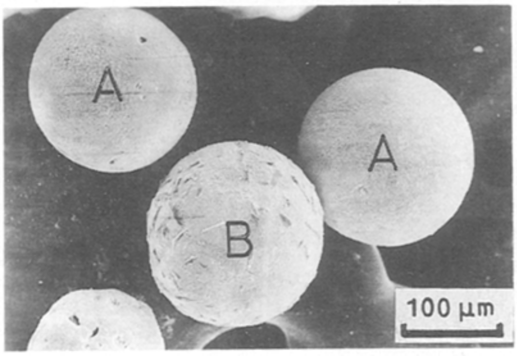

Figure 6 Partially leached plasma-dissociated zircon spheroids showing the distinction between Type I(A) and Type II (B).

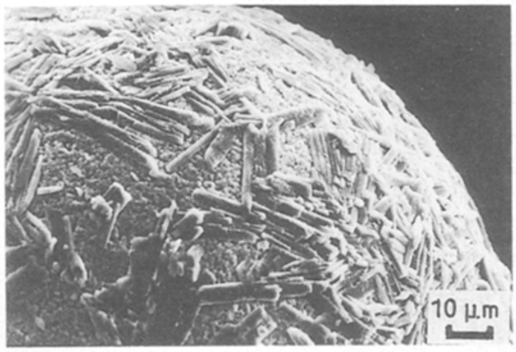

Figure 7 Tabular growth of monoclinic zirconia crystals on the surface of a partially leached Type II spheroids.

The formation of two kinds of spheroid with different microstructures can be correlated to the thermal history of the solidifying droplets which depend on the particle size and the trajectory followed by the particles in the plasma [5]. The size of the ZrO_2 crystallites observed in the Type I spheroids is much smaller than the crystals present in the Type II spheroids. This indicates that the spheroids of Type I which constitute the bulk of the furnace product have attained a higher temperature and have undergone a faster quenching rate than those of the Type II.

4. Conclusions

1. Studies on plasma dissociation of Indian zircon have been successfully conducted in a specially developed laboratory model plasma reactor (20 kW d.c.).

2. The important parameters involved in the process have been optimized to achieve a degree of dissociation of 91% with a feed rate of 4–5 kg h^{-1} at about 20 kW power.

3. The reactor is simple, inexpensive and its performance has been excellent with respect to arc stability, particle flowability and heat affection. Besides mineral dissociation it is useful for spheroidization, structural modification and synthesis of refractory powders and in-flight reduction of ore fines.

4. Microstructural studies on the dissociated spheroids have revealed that most of them have well-developed polygonal grains with spherulitic growth of ZrO_2 crystallites with a mean diameter of about 0.1 μm in a matrix of SiO_2. The rest of the spheroids contain intergrown tabular crystals of monoclinic ZrO_2 with length varying from 10–20 μm.

5. It was possible to leach out SiO_2 present in the plasma-dissociated zircon using hot NaOH solution to recover zirconia.

Acknowledgements

The authors thank Dr B. S. Acharya, CPAF Division, RRL, Bhubaneswar, for his contribution to the XRD analysis, and Professor H. S. Ray, Director, RRL, Bhubaneswar, for permission to publish this work. One of the authors (SB) would like to thank the Pool Scheme of CSIR, India, which enabled her to carry out the research.

References

1. P. H. WILKS, P. RAVINDER, C. L. GRANT, P. A. PELTON, R. J. DOWNER and M. L. TALBOT, *Chem. Engng Prog.* **68** (4) (1972) 82.
2. A. M. EVANS and J. P. H. WILLIAMSON, *J. Mater. Sci.* **12** (1977) 779.
3. *Idem, ibid.* **14** (1979) 680.
4. A. M. EVANS, J. P. H. WILLAMSON and F. P. GLASSER, *ibid.* **15** (1980) 2335.
5. R. McPHERSON and B. V. SHAPER, *ibid.* **19** (1984) 2696.
6. R. McPHERSON, R. RAO and B. V. SHAFER, *ibid.* **20** (1985) 2597.
7. J. P. H. WILLIAMSON and A. M. EVANS, *Trans. J. Brit. Ceram. Soc.* **78** (1979) 68.
8. *Idem, ibid.* **78** (1979) 73.
9. R. McPHERSON, *J. Aust. Ceram. Soc.* **17** (1981) 2.
10. R. McPHERSON, B. V. SHAFER and A. M. WONG, *J. Amer. Ceram. Soc.* **65** (1982) C-57.
11. J. P. H. WILLIAMSON and D. E. LIOYD, *J. Mater. Sci.* 16 (1981) 1264.
12. C. B. ALCOCK, A. McLEAN and I. D. SOMMERVILLE, "Report on Plasma Research", University of Toronto (1985).
13. R. K. GALGALI, U. SYAMAPRASAD, S. K. MISHRA and B. C. MOHANTY, *Trans. IIM (India)* **41** (1988) 489.
14. I. D. SOMMERVILLE, A. McLEAN, C. B. ALCOCK and C. A. PICKLES, in "Plasma Technology in Metallurgical Processing", edited by J. Feinman (ISS, Pennsylvania, 1987) p. 93.
15. W. C. BUTTERMAN and W. R. FOSTER, *Amer. Mineral.* **52** (1967) 880.

Received 7 January
and accepted 13 May 1991