JOURNAL OF MATERIALS SCIENCE 20 (1985) 2597–2602

The reassociation of plasma dissociated zircon

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Plasma dissociated zircon, which consists of finely divided spherulitic crystals of monoclinic ZrO_2 in SiO_2 glass, reassociates very slowly at 1500° C unless finely ground. It is suggested that this effect is due to surface nucleation control of the reaction rate. Plasma dissociated zircon in the form of a rapidly quenched coating consists entirely of tetragonal ZrO_2 crystals less than 20 nm diameter dispersed in glass. Reassociation occurs rapidly between 1300 and 1450° C because of the surface nucleation effect and enhanced zircon crystal growth rate arising from the very small diffusion distance ahead of the interface of a growing zircon crystal.

1. Introduction

Zircon ($ZrSiO_4$) may be synthesized by heating mixtures of ZrO_2 and SiO_2 powders at temperatures up to $\simeq 1675°$ C; above this temperature zircon is no longer a stable phase and it dissociates into the component oxides. Zircon may also be prepared by heating dissociated zircon below 1675° C [1].

A recent innovation in the processing of zircon involves the passage of a stream of zircon particles through a plasma reactor in which the particles rapidly melt and resolidify to form a fine dispersion of ZrO_2 in SiO_2 glass [2, 3]. The product, referred to as plasma dissociated zircon (PDZ), provides a convenient initial stage in the extraction of ZrO_2 and also has ceramic applications. The microstructure of PDZ is influenced by the cooling rate after melting which depends strongly upon the initial zircon particle size. Thus relatively slowly cooled material consists of spherulitic crystals of monoclinic ZrO_2 ($\simeq 0.1\,\mu$m crystal arm width) in SiO_2 glass whereas the most rapidly cooled material consists of extremely fine (< 10 nm) crystals of tetragonal ZrO_2 crystals in glass. A range of mixed structures between these extremes have been formed depending upon cooling conditions [4].

The first extensive study of the synthesis of zircon from the mixed component oxides and dissociated zircon was reported by Curtis and Sowman [5]. They found little difference in the rate of reaction between ZrO_2 and SiO_2 in the form of quartz, tridymite, cristobalite or glass. A sample of zircon, in the form of a milled and pressed disc, which was 90 to 95% dissociated after treatment at 1760° C, also reassociated to a similar extent to the ZrO_2 and SiO_2 powder mixtures after heating in the temperature range 1200 to 1500° C for 8 h. Other studies of the reassociation of mixtures of ZrO_2, prepared from PDZ, with quartz and cristobalite and PDZ itself [6, 7] show generally similar results to Curtis and Sowman in that appreciable reaction commences at $\simeq 1300°$ C and reaches its maximum extent at $\simeq 1500°$ C although there is considerable scatter in the reported fraction converted at intermediate temperatures.

Pepplinkhouse [7] observed that ZrO_2 prepared from two different sources of PDZ gave different results when heated as a mixture with various forms of SiO_2, but that both materials were more reactive than a precipitated form of ZrO_2. Williamson and Lloyd [6] observed that a milled PDZ was more reactive than mixtures of ZrO_2, prepared from PDZ, with various SiO_2 additions. They ascribed this effect to the nearly perfect mixing of ZrO_2 and SiO_2 in PDZ.

Several additives are known to increase the rate

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of synthesis of zircon [8]. Fe_2O_3 in particular has been found to promote the synthesis reaction and to aid sintering [9]. Small additions of ZnO also have a large effect on the rate of synthesis in the temperature range 1200 to 1400° C [7].

Garvie [10] has prepared zircon ceramics with $\simeq 8\%$ porosity and modulus of rupture (MOR) of $\simeq 180$ MPa by sintering PDZ, milled to $\simeq 1\,\mu$m particle size, for 5 h at 1500° C. Williamson and Lloyd [6] sintered PDZ milled to $50\% < 10\%\,\mu$m at various temperatures but only observed MOR values comparable to those of Garvie after sintering for 4 h at 1700° C. This is above the dissociation temperature, however, and the product contained only 45% zircon. High MOR values (124 MPa) and high zircon contents were achieved after firing milled PDZ with an addition of 1.5 wt % Fe_2O_3 at 1500° C for 4 h. It has also been observed that high density sintered zircon ceramics can only be prepared by very fine grinding of the original zircon powder [11].

The microstructure of PDZ depends upon its thermal history [4] and would be expected to have some influence on reassociation. The present paper is concerned with this aspect of zircon formation.

2. Experimental details

Materials used were PDZ prepared at the National Physical Laboratory ($> 99\%$ dissociated) with a mean particle size of $\simeq 100\,\mu$m, laboratory prepared PDZ with particle sizes in the range 6 to 22 μm, and PDZ prepared by plasma spraying zircon particles $\simeq 20\,\mu$m diameter on to a cold substrate. Details of the microstructure of these materials are given elsewhere [4].

The progress of transformation during heating at constant rate was determined by heating samples in a Rigaku DTA apparatus at 10° C min^{-1} to various maximum temperatures up to 1500° C. Longer term heating experiments, up to 1600° C, were carried out using a Kanthal furnace with samples held in a platinum crucible.

The phase constitution of the samples was determined by X-ray diffraction using Cu$K\alpha$ radiation in a Philips diffractometer. The proportion of tetragonal and monoclinic ZrO_2 were found by comparing the integrated intensities of the (1 1 1) tetragonal peak with the (1 1 1) and (1 1 $\bar{1}$) monoclinic peaks according to [12]:

$$\%\ \text{tetragonal ZrO}_2 = $$

$$= \frac{I_{(1\,1\,1)\text{T}}}{I_{(1\,1\,1)\text{T}} + I_{(1\,1\,1)\text{M}} + I_{(1\,1\,\bar{1})\text{M}}}$$

The fraction zircon was determined by comparing the intensity of the (1 0 1) zircon peak with the sum of the (1 1 1)(1 1 $\bar{1}$) tetragonal and monoclinic ZrO_2 peaks. Calibration mixtures were prepared by grinding NPL PDZ with additions of $\sim 6\,\mu$m zircon powder. The proportion of residual ZrO_2 in reassociated PDZ samples was determined by X-ray diffraction using mixtures of zircon and ZrO_2 powders for calibration purposes.

Scanning electron microscopy of some samples was carried out using a back-scattered electron detector to provide atomic number contrast and secondary electrons to provide topographic detail.

3. Results and discussion

The phase constitution of NPL PDZ heated at 1500° C for various times is shown in Fig. 1 in the as-received condition, ground to $\sim 36\,\mu$m, and

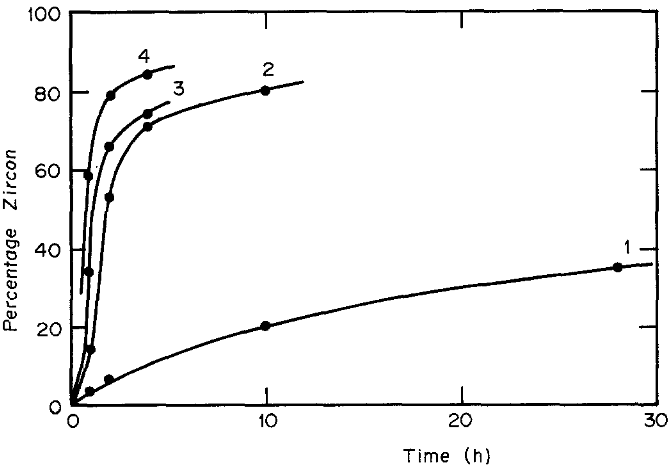
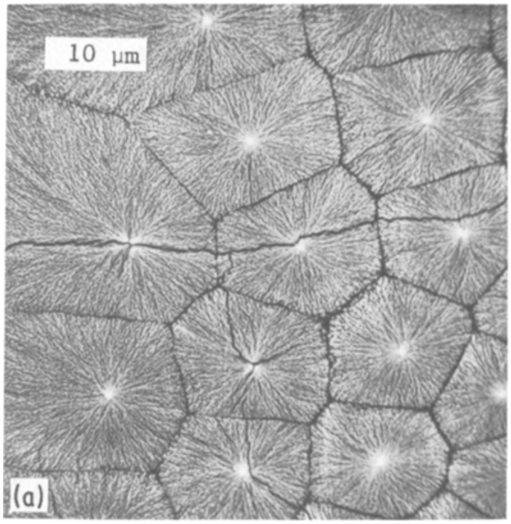
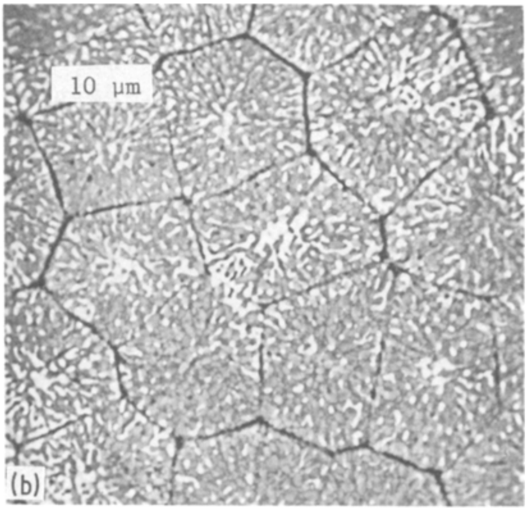


Figure 1 Percentage zircon as a function of time at 1500° C for NPL PDZ: (a) as-received; (2) ground to $-36\,\mu$m; (3) ground to $-36\,\mu$m pressed compact; (4) ground to $-36\,\mu$m, mixed with 1% zircon ($-6\,\mu$m) pressed compact.





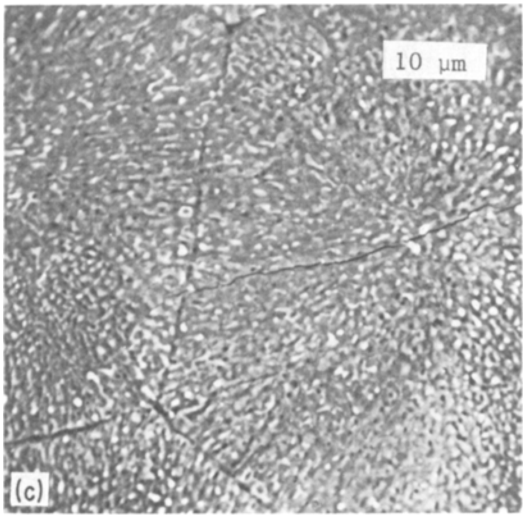


Figure 2 Scanning electron micrographs, back-scattered electron images, of NPL PDZ heated at 1500° C for various times. (a) 1 h, (b) 24 h, (c) 4 days. White = ZrO_2; grey = zircon; black = SiO_2 or cavities.

ground to ~36 μm with a small addition of 6 μm zircon. These results show a very large increase in the rate of reassociation on grinding with a further increase with the addition of zircon. Crystallization of the SiO_2 glass phase to cristobalite was also observed at temperatures greater than 1300° C. After heating for a long period to give complete zircon formation gave a structure containing no cristobalite but $\simeq 7\%$ residual ZrO_2. This indicates a weight loss of $\simeq 3\%$, as SiO_2, from the zircon during plasma dissociation.

Scanning electron microscopy at various stages of the reassociation, at 1500° C, of as-received PDZ (Fig. 2) shows the persistence of the original spherulitic microstructure for a considerable time. The phases can be distinguished by use of the back-scattered detector, thus ZrO_2 is white, zircon grey and SiO_2 black. The structure of a sample heated for 24 h at 1500° C, to give complete reaction, shows small regions of residual ZrO_2 in a zircon matrix (Fig. 3a) with some black regions which could be residual SiO_2 or cavities. Examination of the same area using secondary electrons (Fig. 3b), however, shows that the interspherulitic black regions observed using the back-scattered detector are cavities. An estimate of the volume change occurring during the reassociation of monoclinic ZrO_2 and SiO_2 glass, based on the densities of the three phases shows that a small volume decrease ($\simeq 2.5\%$) would be expected on formation of zircon and this shrinkage is probably the origin of the cavities.

Samples heated to give partial reassociation and formation of cristobalite show the presence of large cracks across the PDZ spheres (Fig. 2b which are probably associated with stresses arising from the volume change accompanying the β to α transformation during cooling.

Constant heating rate experiments, using unground laboratory-prepared PDZ of various particle sizes, showed that the rate of zircon formation increased as the powder particle size decreased and, consequently, the proportion of tetragonal ZrO_2 increased (Fig. 4). These data were limited, however, because of the unknown loss of SiO_2 from the spheroidized particles during processing. Thus the 6 μm powder was brown in colour and examination by optical microscopy showed that it

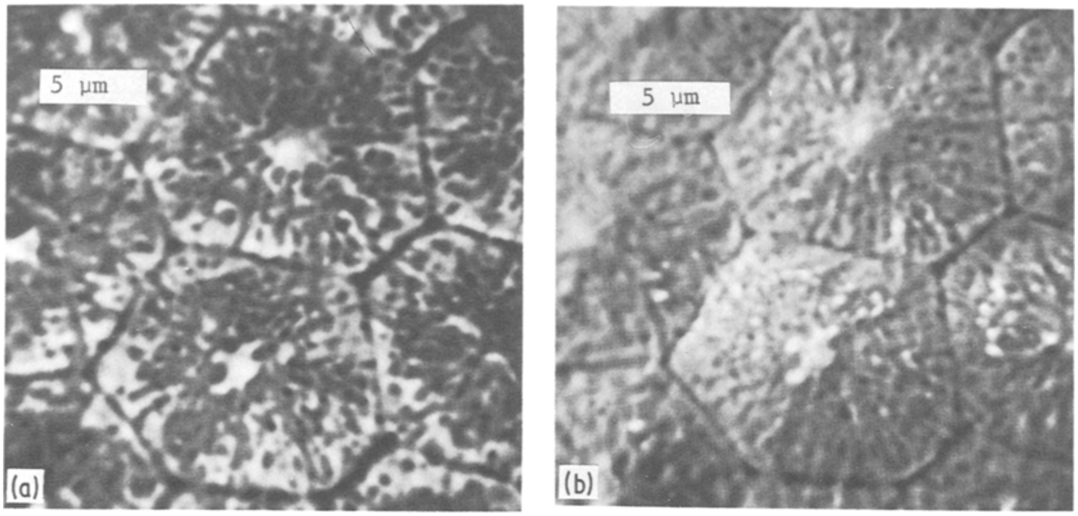


Figure 3 Scanning electron micrographs of NPL PDZ heated to 1500° C for 24 h. (a) Back-scattered electron image. (b) Secondary electron image.

contained a considerable proportion of dark, fluffy material in addition to the spherical dissociated particles. This dark powder was almost certainly SiO produced by vaporization under the reducing conditions used during dissociation [4]. The observation of cristobalite in this material after heating to temperatures between 1200 and 1600° C supports the above suggestion and the results are consistent with reassociation of the PDZ spheres, oxidation and crystallization of amorphous SiO to cristobalite, and little reaction between the cristobalite formed from SiO and residual ZrO_2 in the particles. Assuming approximately 50% of the SiO_2 is lost from the 6 μm particles as SiO gives internally consistent results and indicates that reassociation within the particles commences at $\simeq 1100°$ C and is complete at $\simeq 1300°$ C.

X-ray diffraction showed that the plasma-sprayed zircon deposit consisted entirely of tetragonal ZrO_2 and glass. Cristobalite was not detected after heating to 1500° C, indicating that reassociation

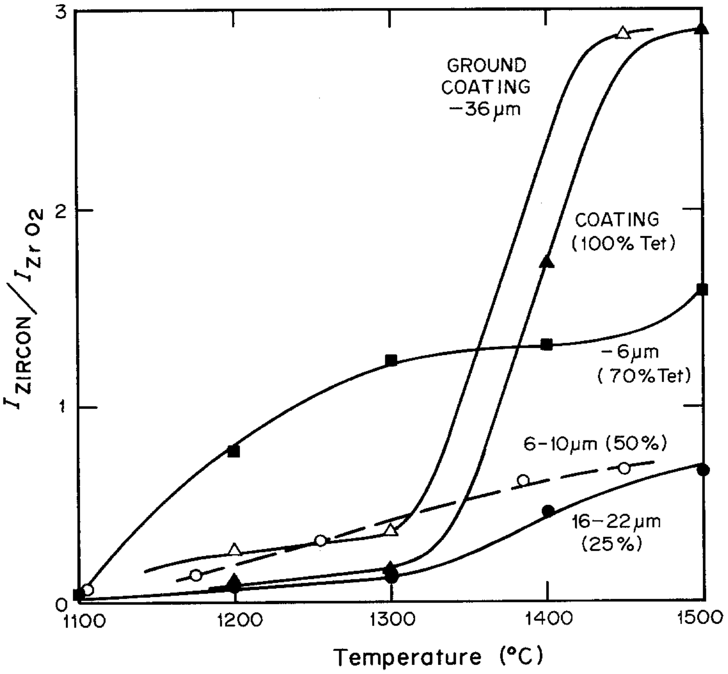


Figure 4 Ratio of integrated intensities of zircon (1 0 1) XRD peak to sum of (1 1 1) tetragonal and monoclinic ZrO_2 peaks. Laboratory prepared PDZ coating and powders of various particle sizes after heating at a rate of $10° C min^{-1}$. Percentage ZrO_2 as tetragonal form in the as-prepared condition shown in brackets.

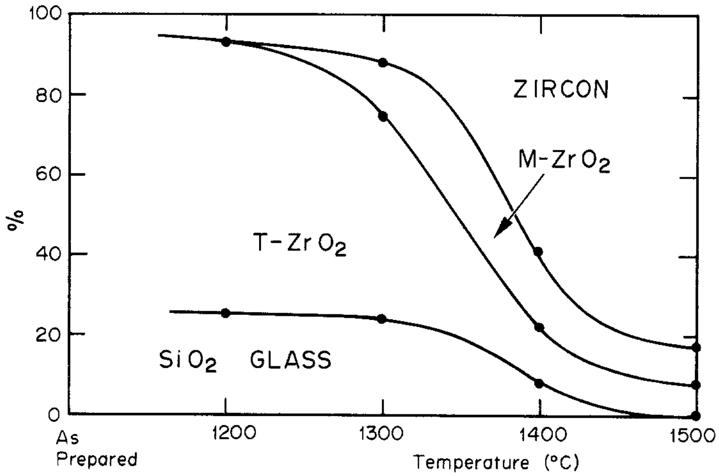


Figure 5 Percentages of SiO_2 glass, tetragonal ZrO_2, monoclinic ZrO_2 and zircon as a function of temperature at a heating rate of 10° C min^{-1}. Plasma sprayed deposit.

was complete. However, the residual ZrO_2 of $\simeq 10\%$ suggests a loss from the original zircon of $\simeq 5$ wt % in the form of SiO_2 during spraying. The phase constitution of the deposit, after making allowance for SiO_2 loss, is shown in Fig. 5 as a function of maximum temperature reached at a heating rate of 10° C min^{-1}. This shows some zircon formation at 1200 to 1300° C with rapid reassociation at higher temperatures and complete reassociation at $\simeq 1450$° C. Monoclinic ZrO_2 was observed after heating to 1300° C and above. Vibratory milling of the sprayed deposit for 30 min resulted in transformation of part of the tetragonal zirconia to the monoclinic form and the proportion of zircon formed was slightly greater than the unmilled material up to 1300° C but similar results were observed at higher temperatures.

The very slow rate of reassociation observed when the NPL PDZ particles are heated at 1500° C is surprising, considering the intimate mixing of the two components on a submicroscopic scale [4]. The very small diffusion distances involved ($\simeq 0.1\,\mu$m) suggest that the reaction rate is controlled, not by diffusion limited crystal growth but rather by nucleation of the zircon phase. This would explain the observation that the rate of reassociation is greatly increased by grinding, which would provide fracture surfaces which could act as heterogeneous nucleation sites for zircon. The observation that the process is nucleation controlled is also supported by the increased rate of reassociation of the milled PDZ with the addition of a small proportion of fine zircon powder. An additional factor may be a contribution to crystal growth rate by surface diffusion.

Similarly, the larger surface area of the fine particle size PDZ would be expected to provide enhanced nucleation rates. In these materials, however, the ZrO_2 is more finely disseminated, containing a large proportion of tetragonal ZrO_2 with crystal size <20 nm [4] and the very small diffusion distances involved in the reaction between SiO_2 and tetragonal ZrO_2 to form $ZrSiO_4$ would be expected to give a faster growth rate of the interface between zircon and the dissociated structure.

The plasma-sprayed deposit would also contain considerable internal surface, and thus more nucleation sites, because of the limited contact between solidified lamellae only a few μm thick [12]. Since this material also consisted entirely of extremely fine tetragonal ZrO_2 in glass, the crystal growth rate would be expected to be the maximum attainable in the structures examined; thus the complete reassociation by heating to 1450° C at a rate of 10° C min^{-1}. The formation of some monoclinic ZrO_2 at temperatures above 1200° C suggests that growth of ZrO_2 particles occurs, by an Ostwald ripening process, to a size greater than the critical diameter of $\simeq 20$ nm below which tetragonal ZrO_2 is stablilized [4].

The maximum rate of reassociation was observed for the 6 μm PDZ in which negligible reaction occurred on heating to 1100° C but reassociation was complete at 1300° C. This is similar to experiments using ZrO_2–SiO_2 evaporated thin films in which zircon was first observed, by electron diffraction, on heating for 5 min at 1200° C but no ZrO_2 was observed after heating for 5 min at 1300° C [13]. The thin films also had a large surface area and very fine distribution of the two components. The ZrO_2 was reported to be initially present as cubic or tetragonal but it transformed to monoclinic after heating for 2 h at 1100° C, presumably because of crystal growth to the critical size.

4. Conclusions

The rate of reassociation of plasma dissociated zircon, which consisted predominantly of monoclinic ZrO_2 spherulites in SiO_2 glass, is extremely slow at 1500° C but increases by an order of magnitude after grinding. The reason for this is probably associated with more effective nucleation of zircon at the fracture surfaces.

The reassociation of rapidly quenched PDZ, which consisted of <20 nm tetragonal ZrO_2 particles in glass, commenced at $\simeq 1200°$ C and was complete at $\simeq 1450°$ C at a heating rate of 10° C min^{-1}. The rapid reassociation of this material is probably related to surface nucleation effects as well as more rapid zircon crystal growth because of the small diffusion path in the vicinity of the growing zircon interface.

Acknowledgement

This work has been supported by the Australian Research Grants Scheme and a Monash Special Research Grant. Thanks are also due to Mr R. K. Bayliss, National Physical Laboratory, UK, for samples of PDZ.

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Received 17 August
and accepted 13 September 1984