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Microstructure of plasma dissociated zircon and liquid immiscibility in the ZrO_2-SiO_2 system

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The foam texture developed in plasma-dissociated zircon consists of plane surfaced interlocking grains which contain crystallites of dendritic zirconia embedded in amorphous silica. In the interstices of these grains silica has been segregated. This segregation appears to have come about mainly as the result of supercooling and liquid immiscibility. This accounts for the development of the almost pure silica phase and the formation of a zirconia-rich phase which crystallized to yield dendrites consisting of monoclinic zirconia at ambient temperature. Clear envelopes on the grains were found to consist of amorphous silica-rich material containing zirconia spherulites whose density of development is proportional to the zirconia content of the envelopes.

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1. Introduction

In describing dissociated zircon ($ZrSiO_4$) which had been liquified in a plasma furnace [1] Evans and Williamson ascribed the principal microstructure to the development of a foam texture [2] by annealing in the crystalline state. Since then consideration of the work of Glasser *et al.* [3] and Oonk *et al.* [4] suggested to us that we may be dealing with a microstructure resulting from crystallization with supercooling as well as the existence of segregation due to liquid immiscibility.

2. Microstructure of dissociated zircon

We have already described this in detail [1]. In this communication we wish to draw attention to the polygonal (foam) texture which characterized the majority of rapidly quenched dissociated zircon (DZ) produced in the AMA* plasma furnace (Figs. 1 and 2) and which is believed to be responsible for the unique properties so important in its industrial applications [5, 6]. This DZ consisted of spheroids (Fig. 3) of submicrometre to 500 μm diameter with the common size range being 25 to 250 μm. Their constituent material was so fine-grained that even when ground to thicknesses of about 10 μm it was only barely translucent. The surface had a well developed polygonal pattern (Figs. 1 and 2) with 120° triple junctions indicating the attainment of an equilibrium grain configuration. There can be great variation in the size of these polygons (Fig. 2). A minor phase was present between these grains and was particularly concentrated in the triple junctions where it tended to form concave cuspate triangles (Fig. 1) – a well known microstructure in two-phase alloys having a low dihedral angle [2]. Preliminary measurements suggested that this angle was of the order of 10 to 20°. Very thin sections show that this microstructure is present throughout the spheroids.

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Figure 1 Scanning electron micrograph of a DZ spheroid showing the foam texture, ×1 200.

The minor phase could be readily leached with dilute caustic soda which yielded an aqueous sodium silicate solution. Negligible loss of zirconia occurred during the leaching indicating that this intergranular phase was essentially silica. Point counter methods applied to scanning electron micrographs show that the minor phase occupies about 8.3% by volume (3.7% by weight) of the overall structure. In the polygons forming the major phase, branching crystallites of zirconia form an overall radial pattern (Fig. 2) suggesting nucleation at or near the centres of the polygons. These grew in a matrix of silica which can be seen more clearly in less rapidly quenched DZ [7]. The zirconia was all in the stable low temperature monoclinic form and there was no evidence of the metastable persistence of higher temperature cubic or tetragonal zirconia within the spheroids despite the high temperature obtained in the furnace and the presence of atomic nitrogen which might have stabilized the cubic form [8].

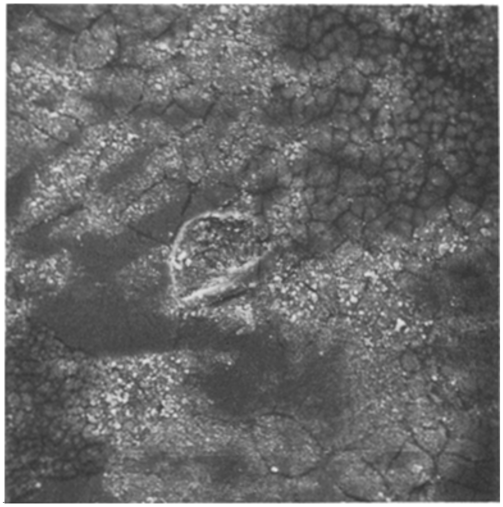

Figure 2 Scanning electron micrograph of the surface of a large spheroid showing the variable size of polygons in the foam texture, ×470.

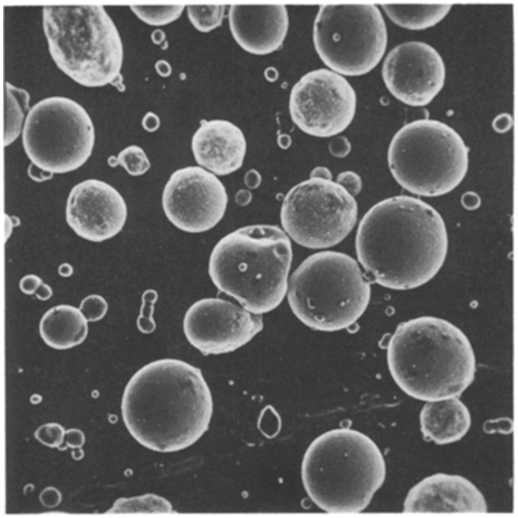

Figure 3 Scanning electron micrographs of DZ spheroids. (Two partly dissociated grains are present), ×51.

There are at least two possible mechanisms by which this foam texture might have evolved. First there may have been segregation in the solid state during rapid auto-annealing, second there may have been separation of the minor phase due to liquid immiscibility. With regard to the first possibility it is pertinent to note that the DZ after being subjected to temperatures of 6000° C or so is quenched to 60° C in about one sec. It seems unlikely to us that the foam texture could have developed in the solid state in such a short time. The second possibility is examined in the next section.

3. Phase relationships and immiscibility in the ZrO_2–SiO_2 system

The phase diagram published by Butterman and Foster [9] is shown in Fig. 4. It depicts a small area in which two liquids are developed at temperatures well above those at which monoclinic zirconia is stable. Earlier [3] it had been suggested that an immiscibility gap should occur near the ZrO_2 end of the system. Neither this suggestion nor the equilibrium phase diagram can be used to account for the silica-rich phase developed in the DZ foam structure. Oonk *et al.* [4] have recently analysed data for selected binary silicate systems showing immiscibility. These data can be used to derive parameters which, together with a knowledge of the ionic size and formal charge of the second

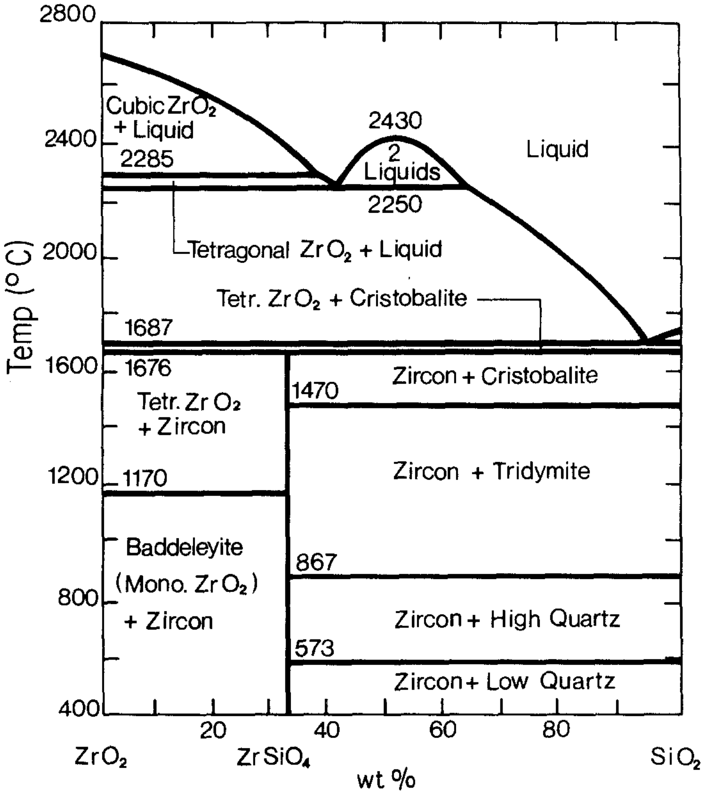

Figure 4 Phase diagram for the ZrO_2–SiO_2 system, after Butterman and Foster [7].

metal ion, enable the shape of the immiscibility region to be calculated as a function of temperature. The curves obtained are very similar to those which can be drawn by extrapolating the two liquid field of Butterman and Foster [9] to obtain the modified phase diagram shown in Fig. 5. If we follow a liquid of zircon compostion down to the immiscibility curve on this diagram we can then estimate the *approximate* proportions of the two immiscible liquids which would be produced. The estimate can be made by applying the figure of 3.7 wt% for the silica-rich phase, in which case the conjectural construction of Fig. 5 predicts an effective quasi-equilibrium fictive temperature of 1900° C and a silica content of 77 wt% for the minor phase. Previous work [1, 7] shows this to be too low in SiO_2. Somewhat better agreement can be obtained by assuming a fictive temperature of 1700° C, in which case the SiO_2 content of the minor phase would be 85%, but its proportion would increase to $\sim$12%. We think that much of the difficulty in reconciling the results is caused by uncertainties in the phase diagram [9]. For example, Oonk *et al.* [4] have shown that immiscibility curves in liquid silica-metal oxide systems lie towards the silica side of the diagram. Using Fig. 5 and assuming super-cooling due to the very rapid quenching, we suggest that prior to crystallization there was a separation into two immiscible liquid phases whose compositions followed the left-hand and right-hand boundaries of the immiscibility curve with crystallization taking place after immiscibility had led to the development of foam texture. This explanation accounts for the development of the silica-rich phase, the formation of a zirconia-rich phase, and the unimpeded rapid crystallization of zirconia from a ZrO_2-rich liquid precursor. The dendritic form of the zirconia crystallites results from their growth with strong super-cooling.

In the preparation of zirconia for some industrial processes the silica-rich phase is leached with caustic soda. If this phase solidified at about 15 to 1600° C it would contain about 10 to 15 % of ZrO_2 leading to a slight loss of zirconia during leaching. The silica-rich phase, however, only forms about 3.7% of the spheroids which means that the zirconia loss will be around the 0.5% level – a negligible amount which is in keeping with the losses encountered in commercial operation.

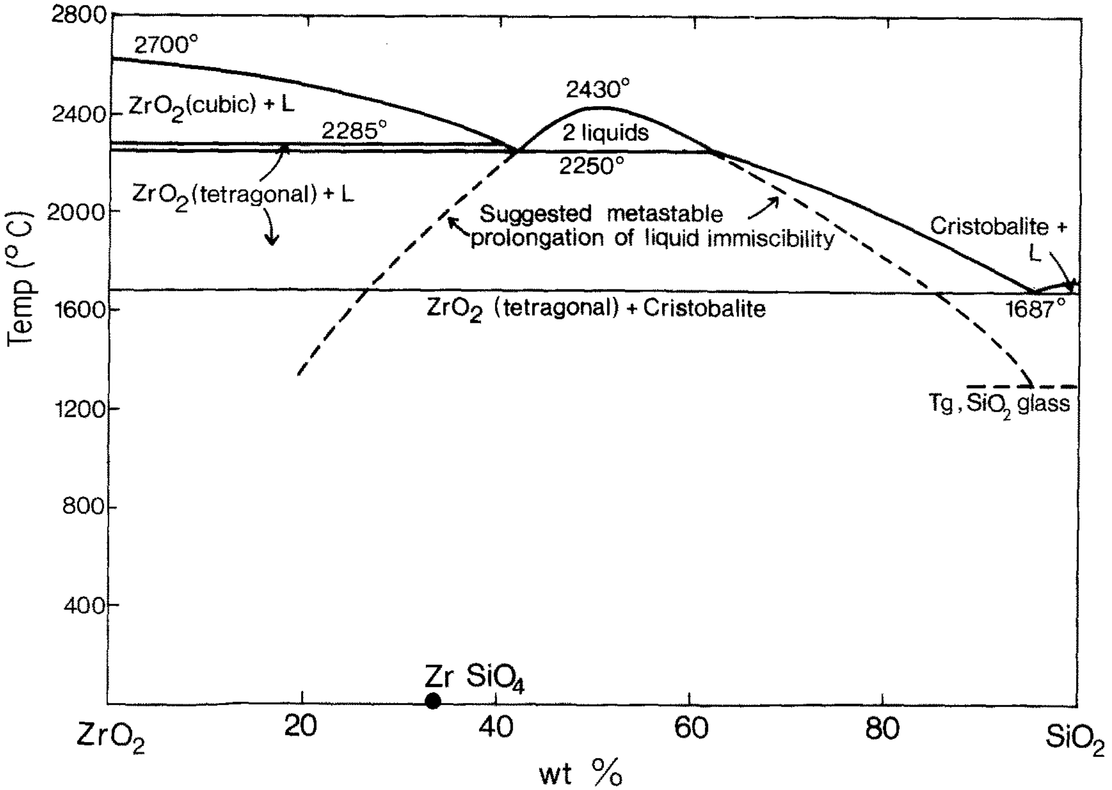

Figure 5 Modified phase diagram for the ZrO_2–SiO_2 system. The thermodynamically stable liquidus and solidus are taken from [7]. Pecked lines suggest the metastable extension of the immiscibility region to lower temperatures, as inferred in the present study. The glass transformation temperature, Tg, is for pure SiO_2.

4. The silica-rich envelopes

The internal structure of DZ grains, which characterizes the bulk of the product, has been described. Each grain is, however, also surrounded by a continuous thin shell which from its low refractive index is presumed to be rich in SiO_2. This shell material, which is best developed on type III grains, was concentrated by crushing DZ in an agate mortar under alcohol and sedimenting the less dense shell portions directly on to carbon-membrane electron microscope grids. These were subsequently examined using CORA, a transmission electron microscope equipped for morphological studies as well as electron diffraction and chemical analysis from regions as small as 800 to 1000 Å.

In addition to type I, II and III grains, two other morphologies were observed amongst the less dense fraction. These are shown in Fig. 6. The more perfect spherulites ranged between 200 and 2000 Å in diameter. They were non-crystalline. An analysis of five spherulites gave Zr (as wt% ZrO_2) contents between 0.3 and 1.4% with a mean of 0.9%: the balance was SiO_2. They are believed to be silica "smoke" which condensed directly from the vapour. The second type of morphology was more irregular and represents polygonal fragments of silica-rich shells. Fig. 7 shows the appearance of part of a shell at high magnification. The fragments gave

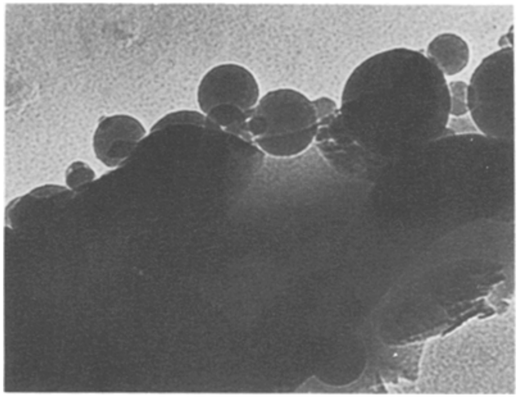

Figure 6 Transmission electron micrograph of DZ shell and silica "smoke", ×205 000.

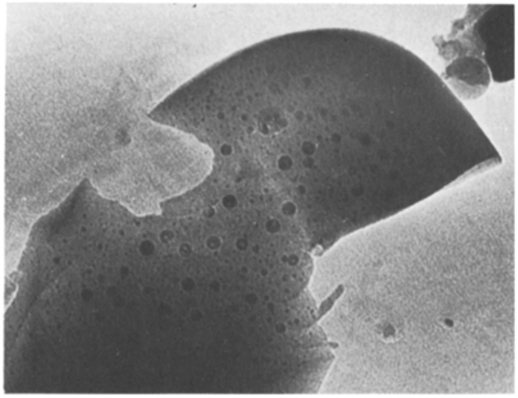

Figure 7 Transmission electron micrograph of DZ shell showing zirconia spherulites, ×205 000.

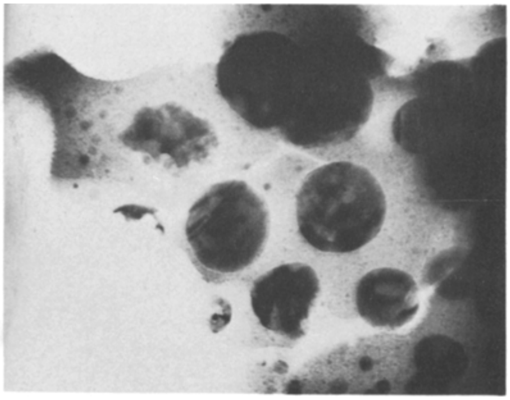

Figure 8 Transmission electron micrograph of DZ shell showing zirconia spherulites developing faceted morphology, ×328 000.

broad, weak diffraction haloes characteristic of glass on which are superimposed crystalline diffraction spots. These were indexed fully for one specimen and were found to be entirely consistent with spacings calculated for a cubic or pseudocubic ZrO_2. It must be noted that the zirconia in these envelopes only represents an infinitesimally small proportion of the total zirconia in the DZ, which is normally monoclinic. A total of 16 fragments, believed from their morphologies to be from shells, were analysed. Fifteen had ZrO_2 contents ranging between 2.4 and 7.2 wt% ZrO_2; the sixteenth had $ZrO_2 = 14.2\%$, and was probably contaminated. The shells show evidence of internal structure in the development of dark spherulites. At the lowest ZrO_2 contents, the spherulites are comparatively uncommon but gradually increase in abundance as the bulk ZrO_2 content rises. As these dark regions are frequently only 100 to 200 Å in size, they are included in the analysis. If the spherulites are ZrO_2 rich, the surrounding matrix must therefore be reasonably pure SiO_2 and it is unlikely to contain more than 1 to 2% ZrO_2.

The silica envelopes are believed to arise by condensation from the vapour on to liquid DZ droplets. Their high SiO_2 content is explained by the higher vapour pressure of "SiO_2" relative to those of Zr vapour species at temperatures obtained near the plasma core. During cooling, ZrO_2 becomes progressively less soluble until it nucleates and crystals grow. Some detail is lost in making photographic reproductions, but the negatives show clearly that the larger of the spherulitic growths are beginning to show a transition to polygonal morphology. These are shown in Fig. 8.

5. Conclusions

It is suggested that the more probable explanation of the development of foam texture in plasma-dissociated DZ, with the development of a high silica interstitial phase, is that the segregation of these two phases was due to liquid immiscibility coupled with supercooling. The development of supercooling would be favoured by the very rapid quenching of the molten DZ. The grains are surrounded by a silica-rich shell, probably condensed from the vapour, which contains $<7.2\%$ ZrO_2; the ZrO_2 has segregated to form small (100 to 500 Å) crystallites.

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References

1. A. M. EVANS and J. P. H. WILLIAMSON *J. Mater. Sci.* 12 (1977) 779.
2. C. S. SMITH *Met. Rev.* 9 (1964) 1.
3. F. P. GLASSER, I. WARSHAW and R. ROY, *Physics Chem. Glasses* 1 (1960) 39.
4. H. A. J. OONK, T. J. VAN LOO and A. A. VERGOUWEN *ibid.* 17 (1976) 10.
5. J. P. H. WILLIAMSON and A. M. EVANS, *Trans. J. Brit. Ceram. Soc.* 78 (1979) 68.

6. *Idem, ibid.* **78** (1979) 73.
7. A. M. EVANS and J. P. H. WILLIAMSON, *J. Mater. Sci.* **14** (1979) 680.
8. N. CLAUSSEN, R. WAGNER, L. J. GLAUCKLER and G. PETZOW. *J. Amer. Ceram. Soc.* **61** (1978) 369.
9. W. C. BUTTERMAN and W. R. FOSTER, *Amer. Mineral.* **52** (1967) 880.

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