JOURNAL OF MATERIALS SCIENCE 12 (1977) 779–790

Composition and microstructure of dissociated zircon produced in a plasma furnace

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Examination of the dissociated zircon from a plasma furnace has revealed a number of unique properties which may make it of considerable importance to the ceramic colour, refractory and metallurgical industries. The geometry of the furnace is such that some zircon grains remained unaffected, others dissociated in the solid state producing pseudomorphs after zircon, but the majority were entirely fused and through free fall from the plasma became spheroidized. These spheroids formed over 90% of the normal product. The zirconia in the bulk of the spheroids probably first crystallized in the cubic form. It formed an anhedral, polygonal grain aggregate having typical foam texture with a siliceous minor phase in the grain interstices. A few cubes of zirconia grew on some spheroid surfaces. All the zirconia was then in the monoclinic (baddeleyite) structure. The silica was isotropic and apparently amorphous but it had anomalous properties and was probably oxygen deficient. It was highly reactive, was intergrown with zirconia in the pseudomorphs and the spheroids and also formed envelopes on most of the grains. In the few milliseconds during which the material passed through the furnace it underwent a remarkably complex crystallization and cooling history.

1. Introduction

Laboratory experiments have shown that it is possible to produce good ceramic colours from dissociated zircon (DZ) produced by the Ionarc plasma furnace and that this DZ may also have important applications in several other industries. The Ionarc furnace is a large-scale plasma device which has been in commercial operation for some years. The material leaving the plasma zone is largely molten and most of it is spheroidized by free fall through a controlled atmosphere tank on its way to the collector, in a manner analogous to the production of lead shot [1, 2]. In the Ionarc plant the DZ, consisting of an intimate intergrowth of zirconia and silica, is leached with caustic soda solution to remove the silica. The discovery that the non-leached DZ has potentially important industrial applications renders a knowledge of the nature and microstructure of this material of great practical significance.

Previous discriptions of the products are brief and largely concerned with the leached product. This paper describes our investigations into the unleached DZ produced under normal operating conditions and that produced when higher feed rates are employed. Previously it was thought that none of the zircon feedstock had survived without some partial dissociation and that the product was composed almost entirely of spheroids of DZ with a minor quantity of oval particles containing cores of zircon. X-ray diffraction has shown that the greater part of the zirconia has a monoclinic (baddeleyite) structure. It was suggested that during the dissociation of the zircon, development of the low temperature monoclinic zirconia preceded the formation of the cubic phase [3].

2. Feedstock

Both Australian and Floridan premium zircon concentrates from beach sand operations were used. Optical and chemical analyses show that these are of high purity. From the point of view of performance in the plasma, the Australian concentrate was the better. The Floridan concentrate, however, gave as good a result if the finest grained fraction, forming 1 to 3% of the concentrate, was removed. Optical examination of this fraction did not reveal any differences which could account for this lowering of the furnace performance and, as there is an equal probability of grains of all sizes being dissociated during their passage through the furnace, some other factor must be invoked to account for the deleterious influence of the finest grained zircon.

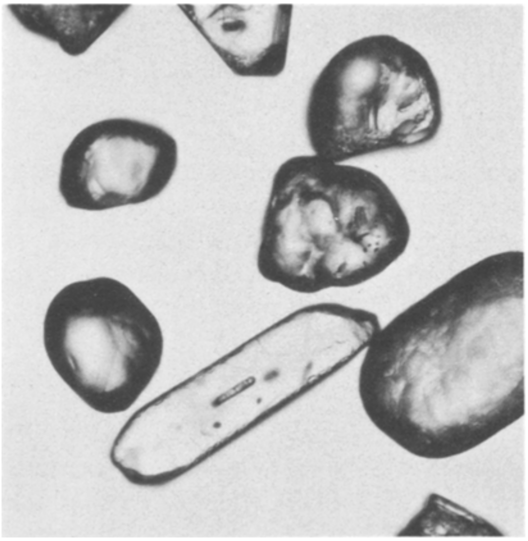

Figure 1 **Photomicrograph of Australian zircons showing well rounded grains, and subhedral to euhedral crystals, plane polarized light, X 78.**

3. Zircon dissociation

Temperatures in the furnace plasma were probably of the order of 6000° C. The majority of the feedstock was converted to spheroidal pellets of DZ showing that total melting of most of the feedstock occurred. Reference to the phase diagram (Fig. 2 [4]) suggests that this material has been heated to at least 2700° C. It must, however, be remembered that Meyer [5}, among others, has shown that the melting of compounds in a plasma is not necessarily related to the melting point.

The phase diagram shows that decomposition of zircon into zirconia and silica occurs at about 1676° C. It is important to note that this occurs in the solid state below the minimum melting point of the ZrO_2-SiO_2 system. As we will show later, some dissociation without melting takes place in the Ionarc furnace particularly at higher than normal feed rates. With falling temperature, although we are still dealing with non-equilibrium conditions, reference to the phase diagram is useful. The quenching of the plasma products prevents recombination into zircon and so we may expect the zirconia and/or the silica to be either amorphous or to have crystallized with one or more of the crystal modifications shown on the diagram. It has been suggested [3] that any appreciable silica left in the dissociated zircon after leaching with caustic soda will be in solid solution in the zirconia. However, it has been shown [4, 6] that the solid solution of silica in zirconia does not exceed 0.1%. Thus any residual silica will not be in solid solution and our work has shown that it is present as non-dissociated zircon.

The crystal modification of zirconia stable above the dissociation temperature is tetragonal and this phase exists up to about 2370° C when it is believed to invert to a cubic modification [6]. The work on which this suggestion is based was

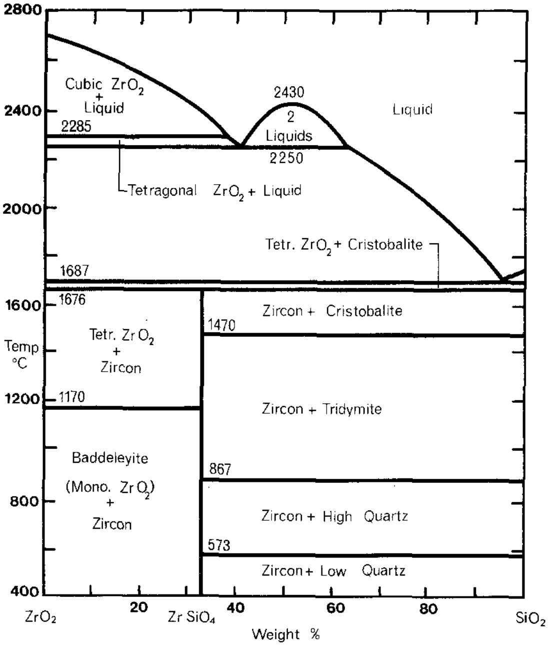

Figure 2 Phase diagram for the ZrO_2-SiO_2 system, after Butterman and Foster [4].

severely criticized by Weber [7] who expressed considerable doubt as to whether pure stoichiometric cubic zirconia can exist at all, unless stabilized by the presence of impurities such as several mol% magnesia. Optical examination of some commercially produced material, said to be lime-stabilized cubic zirconia, has shown that it is anisotropic and cannot, therefore, be cubic. Garvie [8] held that it is impossible to draw a reasonable phase diagram for the Zr–O system without introducing a tetragonal–cubic inversion at the stoichiometric composition. These points are important as Charles *et al.* [9] reproduced an X-ray powder photograph of cubic zirconia produced in their plasma torch, and Wilks *et al.* [3] claimed that cubic zirconia is present in DZ produced in the Ionarc furnace. Although we have evidence that at least some of the Ionarc zirconia originally crystallized with a cubic structure and presumably most of it crystallized with this or a tetragonal structure, X-ray and optical examination of a large number of samples of the Ionarc material has failed to produce any evidence of the presence of cubic zirconia. The zirconia is now totally of the the monoclinic (baddeleyite) crystal structure. The powder photograph mentioned above [9] appears to be identical with that of baddeleyite, and the optical evidence [3] for the presence of an isotropic phase is probably a grain-boundary effect produced by the great difference in refractive indices of the baddeleyite and the immersion medium.

Cubic zirconia has a fluorite structure and the tetragonal and monoclinic modifications have structures related to the fluorite structure. Neither the cubic nor the tetragonal forms can be retained on quenching [8]. The crystallography of tetragonal zirconia is not at all well known, but from work reviewed by Weber [7] it would seem to have a tabular habit. Natural monoclinic zirconia normally has a prismatic or tabular habit. The inversion from monoclinic to tetragonal zirconia occurs over a temperature range of about 100° C being virtually complete at about 1100° C and is accompanied by marked hysteresis [7, 8] and a considerable volume change. The downward transformation occurs over a lower temperature range with volume expansion. This phase change has been studied [7] using metallographic techniques and a microscope heating stage. The inversion on heating led to the rapid formation of platelet subgrains within the monoclinic grains. This subgrain texture did not disappear on cooling through the inversion range. The aggregates of monoclinic crystallites faithfully preserved the grain outlines of the higher temperature phase. This pseudomorphism of a high temperature phase by a lower one is common in artificial and natural substances and it also often happens that dissociation or reaction products may mimic a former phase in this way. Such phenomena are present in the DZ despite its very rapid crystallization and quenching.

Predictions from the phase diagram as to the nature of the solid silica in the DZ are difficult. It could crystallize as cristobalite or tridymite, both of which can exist metastably at room temperature. On the other hand, in the absence of suitable volatiles to aid crystallization, silica normally solidifies as a glass.

4. Nature of the furnace products

4.1. General remarks

Previously, only very brief descriptions of the furnace products (DZ) have been published [1–3]. The principal grains were described as spheroidal particles composed of an intimate mixture of zirconia and amorphous silica. The very ready leachability of the silica has been ascribed to its amorphous and strained nature. The spheroids were recorded as having a similar size range to that of the zircon feedstock and the larger ones as sometimes containing inclusions of non-dissociated zircon. Higher feed rates were said to lead to the development of larger spheroids due to the greater degree of collision in the plasma arc. No free grains of zircon were detected and therefore no consideration was given to the possibility that some zircon might pass through the furnace without suffering any dissociation whatsoever.

Our work has shown that some entirely non-dissociated zircon grains are always present in the DZ and in the following sections these are referred to as type I grains or particles. The present examination has also shown that, whilst a very small amount of zircon is present in some of the spheroids, most of the zircon particles present within dissociation products are relicts of zircon grains which were dissociating in the solid state within particles that remained solid during their entire passage through the furnace. These are termed type II grains. As recognized by previous writers, the bulk of the feedstock melted in the furnace and most, but not all, of this molten material was spheroidized by free fall before reaching the collector. The solidified products are referred to as type III grains. There is evidence that appreciable amounts of silica were vaporized and possibly some of the zirconia. The density of the DZ varies with the zircon content. Well dissociated samples give values between 3.78 and 3.86.

4.2. Grain size

Microscopic observations show that the furnace product is always coarser grained than the zircon feedstock and that faster feed rates lead to the development of coarser particles. This size increase is due to a greater increase in the number of irregularly shaped masses of agglutinated particles of all types rather than to a general increase in spheroid size. Quantitative comparisons of this grain size change are difficult in view of the disparate shapes of feedstock and product. Perhaps the most valid way of comparing the two is by measuring their equivalent spherical diameters by Coulter counter analysis. This was done for four samples of Floridan zircon feedstock and their products. In two of these furnace runs about 1.5% of the finest grained fraction of the feedstock had been removed. The analyses confirmed that a considerable grain size increase occurred but indicated that many more analyses would have to be carried out before concrete conclusions are reached. The results for two pairs of feedstock and product are shown in Fig. 3. As a result of the coarsening of grain size the curves for the furnace products lie to the left of those for the feedstock and it can be seen that the amount of shift is greater when the finest grained zircon fraction is not removed from the feedstock. The results for the other two pairs gave similar results.

4.3. Type I grains

Totally non-dissociated zircon was present in all the forty-two samples of DZ which we examined. Grain counts indicated that at a feed rate of 180 kg h^{-1} of Floridan zircon feedstock the DZ then being produced normally contained 0.5 to 1 vol% type I grains. With higher feed rates the content of type I grains increased, and at 270 kg h^{-1} they sometimes formed up to 11 vol% of the DZ. These grains still had the typical shape of the detritic zircon of the feedstock as can be seen in Fig. 4 and their optical properties were not affected. The only new feature which these zircons possessed is a much better development of the prismatic

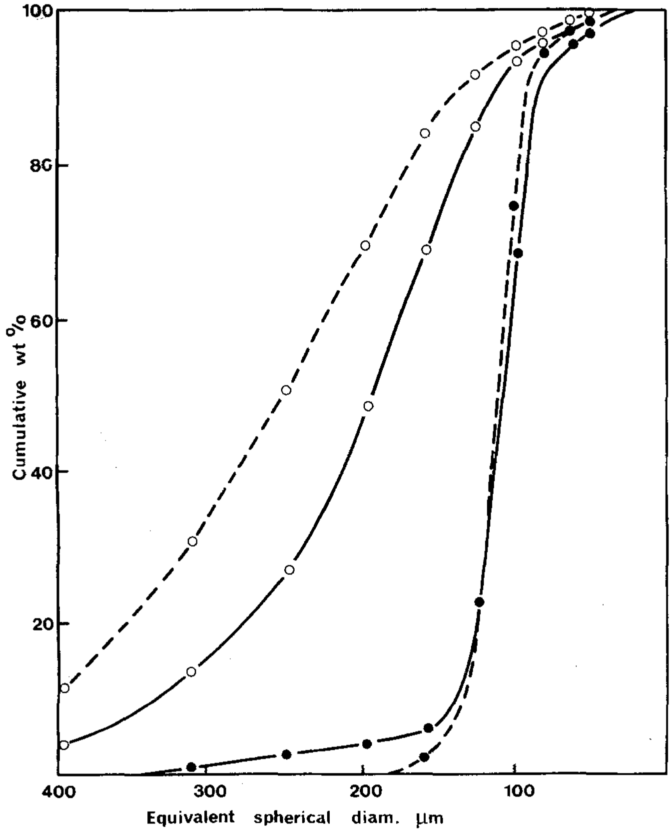

Figure 3 Cumulative percentage grain size curves for two samples of Floridan zircon feedstock (●) and the DZ (○) produced from them. The solid lines are for ordinary concentrate. The dashed lines represent a sample from which about 1% of the finest grained fraction had been removed. Feed rates for both samples were 180 kg h^{-1} and all grain size measurements were made on a Coulter counter.

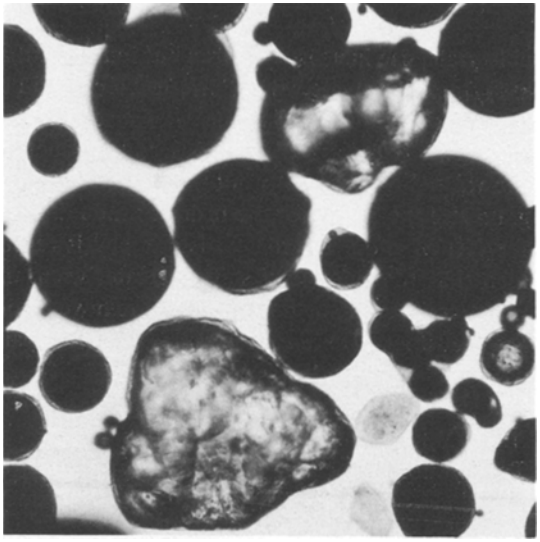

Figure 4 Non-dissociated zircon grains with thin coatings of silica, type III spheroids (some with visible silica coatings), and two discrete particles of silica, batch 6, plane polarized light, × 110.

cleavage, a characteristic of heated zircons [10, 11]. Type I grains constituted about 65 vol% of the residual zircon in the furnace product.

As mentioned in Section 2 the furnace performance of the Floridan feedstock was improved by removal of its finest grain fraction and it has been suggested [3] that, when present, these fine-grained zircons tend to vaporize in the plasma giving rise to an unproductive withdrawal of available enthalpy from the plasma. We have therefore measured the grain size distributions of type I grains in two samples of DZ and compared them with those of the feedstock used in their manufacture. In both cases the finest grain fraction had not been removed from the feedstock. For the first comparison, both the long and intermediate diameters of the grains were measured. The results have been plotted as cumulative curves (Fig. 5). The curves for the feedstock and the DZ are almost identical and suggest that the same grain size populations are present in both. To test this suggestion statistically, t-tests were used. Comparing the long diameter measurements, a t value of 0.62 was obtained and for the intermediate diameters, $t = 0.49$. Neither of these values is significant at the 0.05 level. In the second comparison only long diameters were measured. Once again the t value was well below that indicating significance at the 0.05 level. Thus there is no evidence in either case to suggest that the two samples came from different populations and it must be concluded that for this feedstock all grains of zircon, no matter what their size, stand an equal chance of being dissociated when they are fed into the furnace.

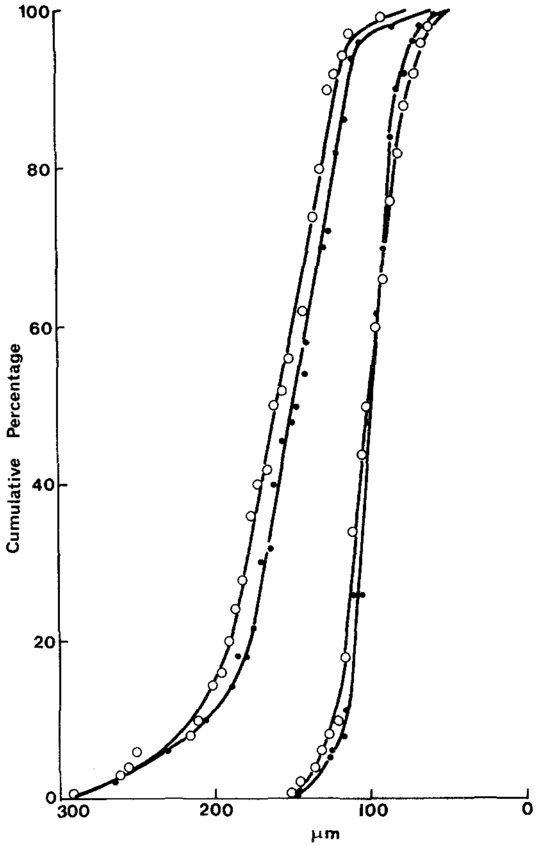

Figure 5 Cumulative percentage grain size curves for the long (left) and intermediate (right) diameters of zircon grains in batch 10 (●) and Floridan feed stock (○) used for its manufacture.

4.4. Type II grains

These are grains of zircon which have partially or wholly dissociated without any evidence of melting. The dissociation products have grown in the solid state replacing the zircon grains and mimicking their shape, i.e. in mineralogical terminology, forming pseudomorphs of the zircon grains. At the same time they have developed textures identical to those formed by similar solid state reactions within igneous and metamorphic rocks and which are well known to petrologists. All degrees of dissociation were present in these pseudomorphs from incipient development of zirconia and silica to complete replacement of the zircon grains. Fig. 6 shows a type II grain in which, although about two thirds of the zircon has dis-

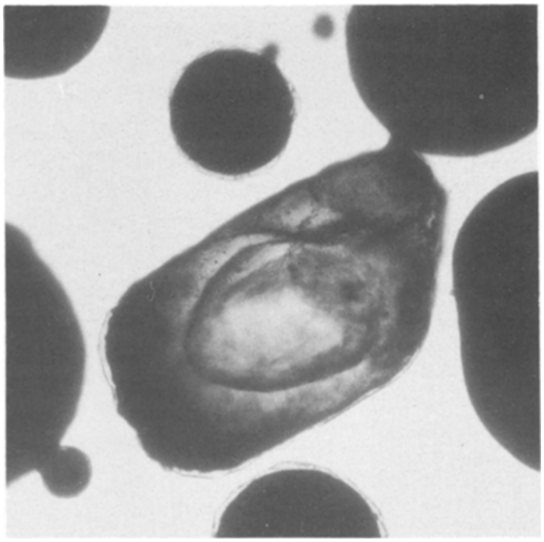

Figure 6 Type II grain showing pseudomorphism of the zircon grain from which it formed and a kernal of unaltered zircon. Type III particles are also present. Note partial development of clear envelopes of silica on some of the grains. Batch 18, plane polarized light, × 150.

sociated, the original outlines of the detrital zircon grain are fully preserved.

In his study of the high temperature behaviour of zircon, Hanna [11] found that with prolonged heating the dissociation of zircon begins on the surface, extends inwards and the zircon grains become opaque. We found a similar growth of the dissociation products, but no evidence of opacity of any part of the relict zircon. In the type II grains much of the zirconia nucleated on the zircon grain boundaries and grew inwards from these, but the development of zirconia was not always entirely by inward growth. Zirconia growth was also nucleated along cracks and cleavages within the zircon grains developing fibrous aggregates producing an overall texture similar to that of partially serpentinized olivines.

X-ray powder photographs of concentrates of type II grains carry strong zircon lines. The remaining lines matched exactly with natural baddeleyite indicating that no other crystalline phases were present. Optical studies confirmed the X-ray results. The material possessed the yellow to brown pleochroism of baddeleyite, had inclined extinction and strong birefringence. When it has grown inwards from the zircon grain surfaces the crystals can be over 50 μm long. Many were curved, showed undulose extinction and must have been a state of strain. Type II grains usually make up 2 to 8% of the DZ when normal feed rates are used. When the feed rate is increased their proportion can be as high as 35%. We have not found any textural or other evidence of the former existence of the higher temperature phases of zirconia in these grains nor any evidence of melting.

Optically the silica in these grains appeared to be isotropic. X-ray diffraction examination has not revealed the presence of cristobalite or any of the other silica polymorphs. The silica must be largely or wholly amorphous.

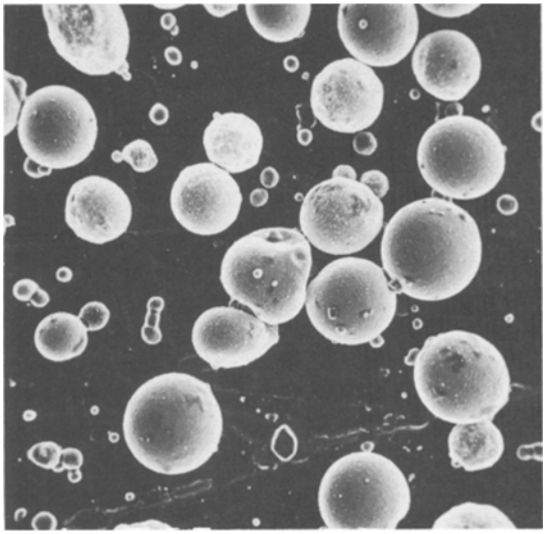

Figure 7 Scanning electron micrograph of type III spheroids with some type II grains. Batch 5, × 51.

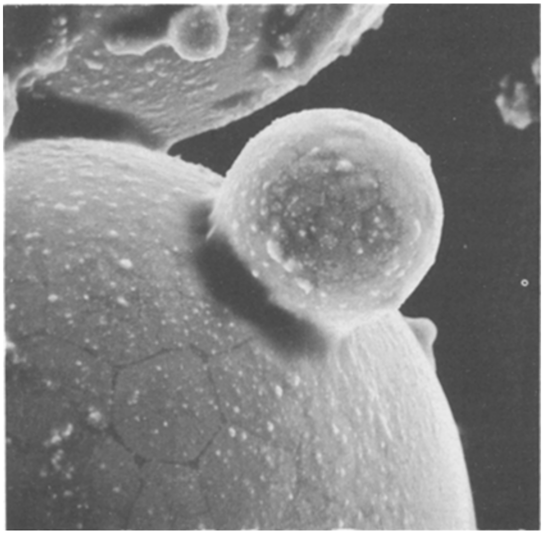

Figure 8 Scanning electron micrograph of type III spheroids showing the polygonal surface pattern. Batch 18, × 483.

4.5. Type III grains

4.5.1. General description

Most of the totally dissociated zircon was in the form of spheroids (Fig. 7). Over 90% of these had diameters between 25 and 250 μm. The overall range was submicrometre to 500 μm. Not all the dissociated zircon was in the form of spheroids. Some was present as irregularly shaped particles and some as cement in agglutinated masses. Some agglutinated masses formed by the freezing of molten spheroids in contact with each other, others consisted of mixtures of all the various particles described in this paper cemented together by dissociated zircon (Figs. 8 and 9). These agglutinated masses could be over 2 mm in length. They were generally very porous.

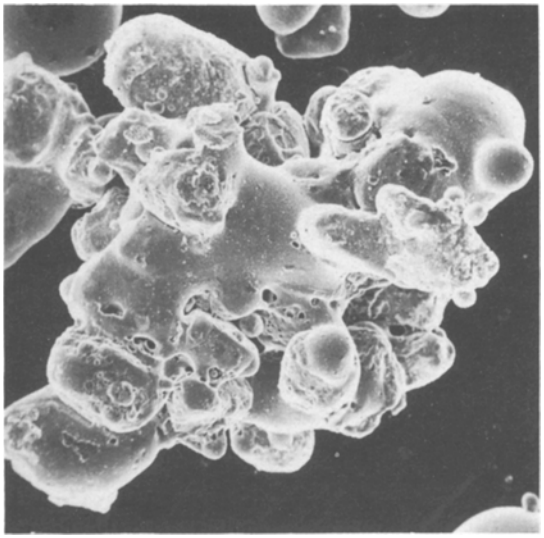

Figure 9 Scanning electron micrograph of an agglutinated mass of types III, II and I material. Batch 6, × 48. Note highly porous nature.

4.5.2. The spheroids

These appeared to be of two main types. The most common one consisted of such fine-grained material that even when ground to thicknesses of about 10 μm it was only barely translucent. The surface had a well developed polygonal pattern (Figs. 8 and 10) with 120° triple junctions indicating considerable grain growth and the attainment of an equilibrium grain configuration after solidification. There can be great variation in the size of these grains (Fig. 11). A minor phase was present between these grains and was concentrated particularly in the triple junctions where it tended to form concave cuspate triangles – a well known microstructure in two-phase alloys having a low dihedral angle [12]. Preliminary measurements suggested that this angle was of the order of 10 to 20°. The high degree of opacity in these spheroids made it difficult to detect this microstructure in thin sections of standard (30 μm) thickness. However, by grinding down the edges of the mounts to about 10 μm, this texture could be faintly seen. Fig. 12 shows the development of the polygonal texture within a spheroid. Scanning electron

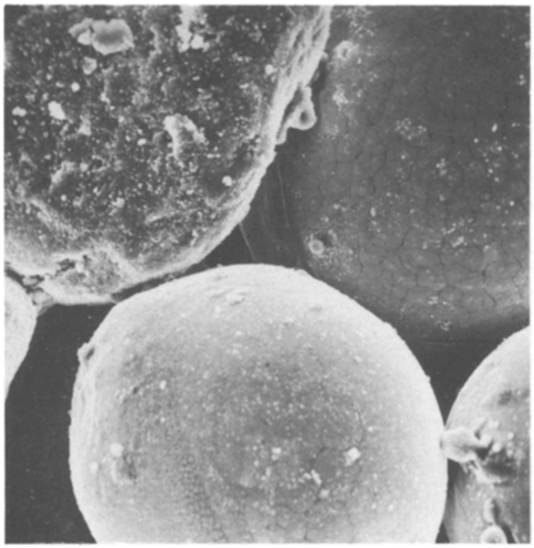

Figure 10 Scanning electron micrograph of several type III spheroids and a type II grain. Note the polygonal surface pattern on the spheroids. Batch 18, × 188.

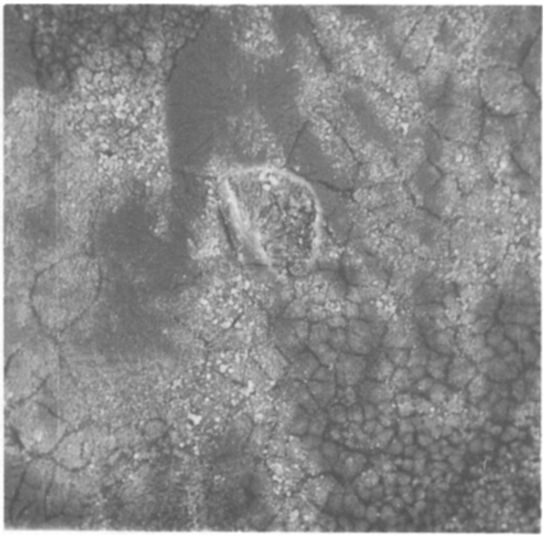

Figure 11 Scanning electron micrograph of the surface of a large type III spheroid showing the polygonal pattern. Batch 7, × 470.

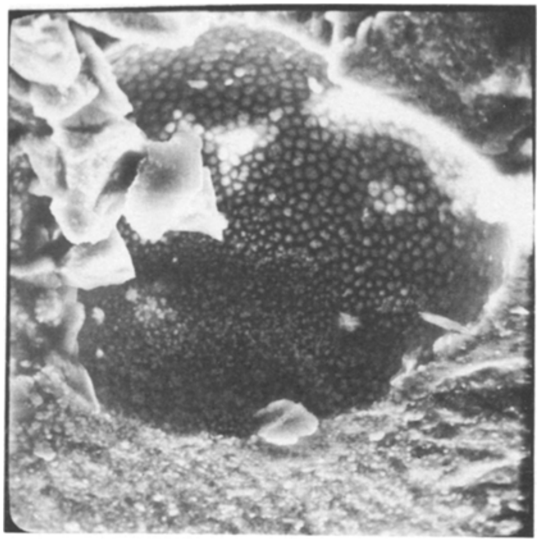

Figure 12 Scanning electron micrograph showing the development of polygonal texture within a spheroid, × 950.

micrographs have also revealed that, like the irregularly shaped type III grains, these spheroids were porous (Fig. 13). Thin sections showed that zircon inclusions were rare.

The minor phase in these spheroids could be readily leached with dilute caustic soda which yielded a product of sodium silicate. A negligible loss of zirconia occurred during the leaching indicating that this intergranular phase was essentially silica. The development of the two-phase microstructure in the bulk of the dissociated zircon must account, at least in part, for the facility with which silica is leached from this material for, as Smith [12] has pointed out, the development of this texture implies that the interstitial minor phase has a connectivity throughout what is essentially a compact crystalline aggregate, thus providing a continuous channel for the flow of liquid in such systems. The caustic soda solution therefore comes into rapid contact with all the grains and is able to leach out the remaining silica present within these grains.

Figure 13 A broken type III spheroid showing its highly porous nature. SEM, × 950.

Thin sections and scanning electron micrographs of broken spheroids suggested that every spheroid contained some rounded cavities (vesicles). These varied from pores which occupied up to half the volume of the spheroid down to pores of micrometre size. The pores resembled very closely the vesicles (gas holes) commonly developed in lava but the size of some of these, compared with the volume of the spheroid in which they occur, suggested that they represented trapped gas rather than gas which came out of solution during the solidification of the dissociated zircon. The trapped gas could have been argon, nitrogen, silicon monoxide or zirconia. We consider that silicon monoxide may have been an important component, as we have found thin layers of silica lining a number of these cavities.

The second type of spheroid was translucent to transparent in thin section and consisted of bladed or tabular crystals up to 60 μm long. These had a high relief, were pleochroic with yellow-brown to dark brown colours and showed slightly inclined or straight extinction. They thus possessed the optical properties of baddeleyite [13, 14]. Tiny zircon inclusions were common in this spheroid type. These zircons were usually highly angular suggesting that they were fragments of zircons which shattered in the furnace and they may have acted as nucleating surfaces for the growth of baddeleyite. These spheroids were normally not porous.

4.5.3. Phases present in the type III grains

Examination of the polygonal grains showed that recrystallization had occurred within these with the development of a radial arrangement of tiny crystallites (Figs. 8 and 11). This suggested that a phase change had occurred within these grains. X-ray diffraction examination produced no evidence of the metastable persistence of cubic or tetragonal zirconia. It was all then in the stable low temperature monoclinic form. Thus the question regarding the nature of the original crystal structure of the polygonal grains is not readily resolved. In Section 3 we have referred to the controversy in the literature as to whether pure stoichiometric cubic zirconia can exist and we expressed our doubts concerning claims that it was present metastably in the quenched products of two plasma furnaces. Nevertheless, it is probable that the zirconia produced by Charles *et al.* [9] and in the Ionarc furnace crystallized originally as the cubic polymorph. Our evidence for this statement is the discovery of a few cubes adhering to spheroids in leached DZ (Fig. 14). Presumably the growth was epitaxial which suggests that the polygonal grains originally had a cubic structure. Consideration of the high temperatures obtaining in the furnace (Section 3) favours the supposition that the polyhedra were originally cubic. A tendency for the development of the cubes as hopper crystals and other irregular forms suggests deposition from the vapour state [15] on what must have been solid spheroids. The rarity and small size of these cubes also favours deposition from vapour since the degree of supersaturation necessary for their nucleation would not often be achieved and there would be little time available for the long-distance diffusion of material to the crystal faces during their growth.

The silica in the spheroids appeared from optical, DTA and X-ray studies to be entirely amorphous. It was the major or sole component of the minor phase present between the polygonal grains. It was extraordinarily reactive in that it could be completely leached from the type III grains by 5% NaOH solution at about 80° C in under 2 h.

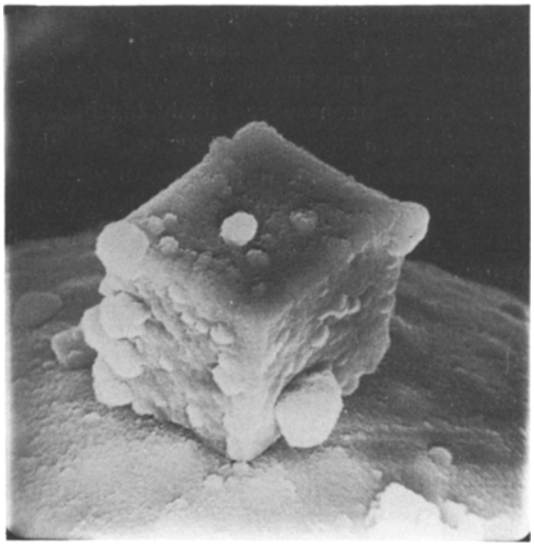

Figure 14 SEM of a cube of zirconia which grew on the surface of a spheroid. The length of the crystal edge is about 10 μm.

5. Silica grains and envelopes

Silica was extensively vaporized during the dissociation process [1]. Some of this free silica passed out with the exhaust gases, the rest formed thin, normally colourless silica envelopes on all the particle types in the product and also rounded grains of discrete silica. Examples of these envelopes can be seen in Figs. 4, 6 and 15. The thickness ranged up to 20 μm. These envelopes could be readily stained with methylene blue which indicated that they must possess microporosity. Experiments with large numbers of particles indicated that all took up methylene blue on some portions of their surface even though no envelope could be seen at × 1000. This suggested that silica was present at least in part on the surface of every grain.

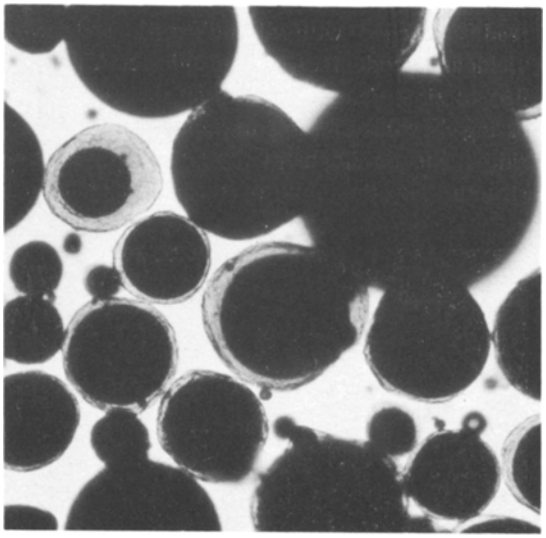

Figure 15 Type III spheroids with films of silica. Batch 6, plane polarized light, × 140.

The silica envelopes were rapidly leached with dilute caustic soda solutions. They were usually isotropic but some show very weak birefringence. X-ray diffraction and DTA investigations gave no tridymite peaks. This suggested that the silica was amorphous in keeping with the findings of Bonet *et al.* [16]. However, refractive index measurements of the silica envelopes gave an average value close to 1.471. This figure is a little lower than the average index of natural tridymite and considerably lower than those of quartz or cristobalite [13]. It does however give a good fit with the values of artificial tridymite (1.469 to 1.473) and is above that of pure silica glass (1.458) [17]. The high refractive indices of this silica may be due to the fact that the vaporized silica dissociated forming silicon monoxide and that, when this condensed, silica W [18] was formed, it in turn formed an amorphous or poorly crystalline silica with somewhat different properties from ordinary amorphous silica. All our leaching experiments have shown that this silica and that within the spheroids is far more reactive and more readily leachable than ordinary amorphous silica. Heating experiments on finely ground DZ in air indicated that oxygen was taken up by the DZ. This may have been because the silica was oxygen deficient, which may account for its reactivity and anomalous optical properties.

6. Quantitative study of the dissociated zircon

6.1. Method

Grain counts using a point counter were carried out on over thirty samples of dissociated zircon. The results of typical grain counts are given in Table I. Particles only present in trace amounts have been omitted. Type II grains were classified into four categories (a to d) according to whether they were one quarter dissociated, a quarter to three quarters dissociated, over three quarters dissociated or wholly dissociated. Investigations by geologists [19] using this method of grain analysis have proved that it gives a very accurate measure of the composition of sands.

6.2. Results and discussion

The principal object of this part of the investigation was to determine what variations occurred in the composition of the DZ, as it had become apparent that some furnace batches had a better colour-making performance than others. It soon became clear that a major factor in the performance of derivatives of the DZ during colour-making tests was the zircon content. Attention was therefore focused on this constituent in an attempt to determine its wt% as accurately as possible in all samples.

For this purpose, the densities of the different constituents are required to convert the figure for vol% into wt%. The value of 4.6 was used for zircon. The mean density of type III spheroids was found to be 3.54 which has been used in these calculations as the mean density of the zirconia—

TABLE I Grain counts, silica contents and other data for DZ samples

Batch no.	Feed rate ($kg\,h^{-1}$)	Type I (vol%)	Type IIa (vol%)	Type IIb (vol%)	Type IIc (vol%)	Type IId (vol%)	Type III (vol%)	Zircon (vol%)	Zircon (wt%)	Silica analyses (wt%)	Silica (calculated) (wt%)
1	180	0.5	ttr.	0.4	0.3	1.5	97.3	0.7	0.9	1.5	0.4
2	270	1.9	2.4	1.8	3.8	7.9	82.2	5.3	6.8	3.4	3.2
3	180	1.7	0.4	0.3	0.4	5.4	91.8	2.2	2.8	1.3	1.3
4	235	3.0	2.0	1.5	2.6	9.8	81.1	5.8	7.4	3.5	3.9
5	235	4.4	2.0	2.3	4.1	7.6	79.6	7.8	9.9	5.5	4.6
6	180	0.7	0.2	0.5	0.2	1.2	97.2	1.1	1.4	1.5	0.7
7	260	10.9	6.2	3.0	2.1	18.1	59.7	18.4	22.6	9.2	9.9
8	295	8.3	3.8	2.1	2.2	15.0	68.6	12.9	16.2	6.0	7.3
9	270	10.5	4.8	3.5	3.8	12.8	64.6	16.8	20.8	9.8	9.2
10	270	10.2	5.4	2.2	2.4	22.6	57.2	16.4	20.4	9.5	9.1
11	270	6.0	2.2	1.9	2.6	12.2	75.1	9.1	11.5	5.4	5.3
12	180	2.1	0.5	0.8	1.2	3.0	92.4	3.1	4.0	2.0	1.9
13	180	2.9	0.7	0.6	1.3	3.5	91.0	3.9	5.0	2.3	2.4
14	180	1.5	0.7	0.5	1.1	3.4	92.8	2.5	3.2	3.3	1.5
15	270	8.1	4.2	2.0	2.6	11.3	71.8	13.0	16.3	7.7	7.4
16	180	4.1	0.9	0.8	1.6	4.5	88.1	5.4	6.9	3.8	3.3
17	180	2.8	0.7	0.7	1.6	5.1	89.1	3.9	5.0	2.9	2.4
18	180	4.0	1.0	1.6	2.0	7.4	84.0	6.0	7.7	3.4	3.6
19	180	0.2	0.1	0.1	0.5	1.6	97.5	0.3	0.4	–	–
20	180	0.5	0.2	0.3	0.3	2.3	96.4	0.9	1.2	–	–
21	180	0.9	0.5	0.5	0.8	1.6	95.7	1.7	2.2	–	–
22	180	1.1	0.3	0.5	1.2	3.7	93.2	1.8	2.3	–	–

2000 grain intersections were counted for each sample, using a $\frac{1}{3}$ mm interval and traverses 0.75 mm apart.

silica material in the types II and III particles. Assuming that only a negligible amount of zircon is present in the type III material (this was confirmed by X-ray studies), the total vol % zircon for each sample was calculated and from this the wt %, see Table I.

As will be shown later, there was good agreement between the wt % zircon determined by this method and the residual silica percentage determinations [20]. As less than 0.1% silica can be present in solid solution in the zirconia, the residual silica, left after strong leaching of the DZ, must be entirely present in the non-dissociated zircon. It therefore gave a measure of the degree of dissociation of the zircon concentrate on passing through the plasma furnace as, of course, did the results of the grain counts.

Before the silica figures became available to us, it was decided to test the grain count results by quantitative X-ray diffraction measurements. Standards were prepared using Palabora baddeleyite and Floridan zircon and the heights of the two most intense reflections for baddeleyite and zircon were measured. The same peak heights were then measured for five samples of DZ. The results, together with the value for the wt % zircon obtained from the grain counts, are plotted on Fig. 16. A good correlation between the grain count and X-ray results suggested that the grain counts had a good degree of accuracy and that only negligible amounts of zircon were present in type III material. Further confirmation of the validity of the grain count results came from a second independent set of data, the figures for the chemically determined residual content in the leached DZ – Table I.

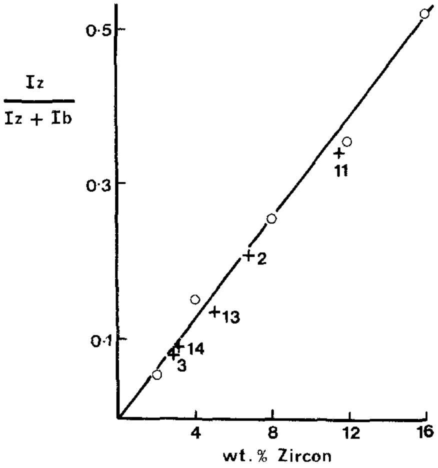

Figure 16 Plot of the ratios of the intensities of the strongest X-ray reflections for standard mixtures of zircon and baddeleyite. Batch samples for which the same ratio was obtained plotted against per cent zircon obtained from grain counts. Numbers are those of batches included in Table I.

The silica contents calculated from the grain count data showed good agreement with the chemically determined silica contents for 13 of the 18 analysed samples. Two other samples gave reasonable agreement and only three were markedly different. Of these, sample 14 was run on the diffractometer and gave a zircon content of 3.2% – a value in exact agreement with that calculated from the grain count. Such a good agreement between most of the chemical analyses and the calculated values for silica validates the grain count method of determining the zircon content of the DZ.

6.3. Degree of dissociation

The results of the previous section indicate that the degree of dissociation can be expressed as 100 – wt % zircon in the DZ, i.e. for batch 15 this would be 100 – 7.7 = 92.3%.

Quantitative knowledge of the degree of dissociation has proved to be useful in predicting the colour performance of DZ derivatives in ceramic pigment manufacturing processes.

7. Conclusions

Detailed examination of the products of the only plasma furnace which has been operated on a large scale for the production of dissociated zircon, has revealed that the degree of dissociation was never complete and at high feed rates it could be less than 80%. Some zircon grains always survived the passage through the furnace. Others underwent partial to complete dissociation in the solid state and zirconia–silica pseudomorphs of zircon were developed. These particles usually made up 2 to 8% of the product when normal feed rates were used. When the feed rate was increased, they could be as high as 30 to 35%. X-ray and optical studies showed that all their zirconia had the monoclinic structure and there was no morphological evidence that the zirconia originally crystallized as a higher temperature polymorph. It probably grew below the tetragonal inversion temperature and we presume that these particles passed through or close to the outer zones of the plasma. The intergrown silica was isotropic and presumably amorphous.

The bulk of the material melted in the plasma zone and during free fall most of it spheroidized. Irregularly shaped particles and agglutinated masses also occurred. The spheroids were composed of monoclinic zirconia (baddeleyite) and silica and appeared to be of two main types. About 80 to 90% consisted of such fine-grained material that even when sectioned to only 10 μm thick, they were barely translucent. The surface and interior had well defined polygonal patterns with 120° triple junctions indicating considerable grain growth and the attainment of an equilibrium grain configuration after solidification. A minor phase was present between these grains being concentrated in the triple junctions where it tended to form concave cuspate triangles. Later recrystallization had taken place within the grains with the development of a radial arrangement of tiny crystallites. These spheroids were highly vesicular. Zircon inclusions were rare. The other spheroid type was translucent to transparent in thin section and consisted of blades and platelets of yellow-brown pleochroic baddeleyite, up to 60 μm long. One or two tiny, angular zircon inclusions were usually present in this type.

The interpretation of the textures seen in the spheroids is of considerable interest. X-ray diffraction examination showed no evidence of the metastable persistence of cubic or tetragonal zirconia. The crystallites of zirconia, however, had replaced polygonal grains which may originally have crystallized with a cubic or tetragonal crystal structure. We believe that it was cubic, as we have found a few pseudomorphs of cubes adhering to spheroids. If the growth of these was epitaxial, then the substrate was probably cubic.

Silica in the spheroids appeared to be entirely amorphous. It was the major component of the minor phase between the polygonal grains. It also formed envelopes of varying thickness on most of the particles in the furnace products. These envelopes probably formed from condensation of silicon oxide vapour, perhaps from the monoxide.

It is clear that the dissociated zircon reacted in various ways according to the pathways followed through or around the plasma zone and in the few milliseconds between solidification and quenching it had a remarkably complex cooling history. It is also evident that complete dissociation of zircon feedstock was never achieved and so we suggest that the degree of dissociation can be defined as $100 - \text{wt}\%$ non-dissociated zircon. We have found it possible to calculate the degree of dissociation in the furnace product using grain counts.

Acknowledgements

We thank Dr P.H. Wilks for his helpful advice, for providing samples and silica analyses and for his keen interest in our investigations. We are indebted to Mr G.L.C. McTurk for taking the scanning electron micrographs and we are grateful to Mr D.J.K. German for his encouragement.

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Received 31 May and accepted 27 August 1976.