

The characterization of ceramic bodies produced from plasma dissociated zircon

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Several studies have been made of the mechanism of the reaction between zirconia and silica using plasma dissociated zircon (DZ) as the source of zirconia and of the silica. The suggestions have been made that the formation of a ceramic body from milled DZ proceeds at significantly lower temperatures than it does with the mixed oxides for reasons largely connected with the intrinsically near-perfect mixing, and that the implications could have some commercial importance. The re-association and dissociation reactions are very complex in nature and the completion, or otherwise, and the re-association to zircon is not necessarily reflected in the mechanical properties of the ceramic body; purely textural considerations may be more relevant.

1. Introduction

Examination of several forms of plasma dissociated zircon (DZ) has revealed certain common features: the zircon crystal is separated into discrete sub-micrometre sized grains of monoclinic zirconia fully wetted by an amorphous silica matrix of a foam-like texture where the plane surfaced domains of intimately intergrown zirconia and silica are bounded by thin amorphous silica films. Some recent work [1] described how this texture could arise from a liquid-liquid immiscibility which develops during supercooling of the melt. Other evidence has indicated that similar microstructural features are common to DZ produced in a variety of plasma furnaces [2]. The complex temperature, electrical and thermodynamic regimes found in many plasma devices have been explored by several authors. Sheer and Korman [3], in particular, have carried out detailed investigations of processes wherein the feedstock is introduced directly into the plasma conduction column. This is not the regime we believe is operative in this case: the feedstock probably never penetrates the plasma

core and the effects obtained are predominantly "thermal" in origin rather than "plasma".

The objectives of the present work were to determine the characteristics of bodies made from milled DZ ("Dizirc"*) and to compare them with those which would have been expected to arise from the normal reaction between zirconia and silica, to set these characteristics within the context of the more common ceramic materials and to examine the part played by the silica component of the DZ.

2. Details of the experiments

2.1. Characterization of the components used

The DZ was first characterized by the method of grain counting described in an earlier paper [4]: 98.7 per cent of the volume of the sample was shown to consist of the fully dissociated spheroids (the Type III grains), the total volume of zircon in the sample was 1.0% and the degree of dissociation was 99.0%.

Several kilos of this DZ were dry-milled and

*"Dizirc" is a registered Trade Name, the property of Keeling & Walker Limited, which refers to several patented applications of comminuted DZ.

sieved with the intention of producing a particle-size distribution reasonably compatible with those of the other powders involved in the programme of experiments. A determination of the particle-size distribution, using a "Sedigraph 5000", gave values for "Dizirc" of 50% of the particles of size less than 10 micrometres in length and 10% of the particles of size less than 1 micrometre in length.

In order to remove the silica phase in the dissociated product from the furnace a quantity of the DZ was leached repeatedly with an equivalent quantity of hot aqueous caustic potash, washed with water, hydrochloric acid, again with water, and finally rinsed several times with methanol to reduce the possibility of serious hydrophilic aggregation occurring during drying. The zirconia remaining had a particle size distribution measured using the "Sedigraph 5000" of 5% of the particles of size less than 3 micrometres and 25% of the particles of size less than 1 micrometre. This oxide was reacted with various forms of silica at a range of temperatures using conventional ceramic techniques. Measurements of density, modulus of rupture and modulus of elasticity were performed on test pieces made from the several compositions. Similar measurements were made on test pieces produced from "Dizirc", both modified either by addition of lead bisilicate or iron oxide, and unmodified.

Three silicas were used: a fused amorphous variety supplied by Thermal Syndicate Ltd (particle size distribution: 50% less than 6 micrometres and 20% less than 1 micrometre); a ground silica flour (quartz) supplied by Glassrock Products Inc. (particle size distribution: 50% less than 7 micrometres and 7% less than 1 micrometre); a fumed amorphous silica supplied by Cabot Carbon, which was, of course, of a much finer average particle size than either of the other silicas. The lead bisilicate was supplied by Podmore and Sons Ltd (particle size distribution: approximately 50% less than 15 micrometres); and iron oxide, a colour grade ferric oxide, was supplied by Pfizer (particle size distribution: about 90% less than 1 micrometre).

2.2. The compositions tested

Nine formulation varieties were prepared:

- (1) DZ oxide + quartz;
- (2) (DZ oxide + quartz) + 1.5% iron oxide;
- (3) DZ oxide + fused amorphous silica;
- (4) (DZ oxide + fused amorphous silica) +

1.5% iron oxide;

(5) DZ oxide + fumed amorphous silica;

(6) (DZ oxide + fumed amorphous silica) + 1.5% iron oxide;

(7) "Dizirc";

(8) "Dizirc" + 1.5% iron oxide;

(9) "Dizirc" + 1.0% lead bisilicate.

2.3. The power preparation

DZ oxide (124 g) and silica (60 g) were wet-milled together in a 1 litre porcelain ball mill for 2 hours, using 550 g of high-purity alumina grinding media and 400 ml of industrial alcohol as the milling agent. Mixes of "Dizirc" with lead bisilicate or iron oxide were made in the same way.

On completion of the milling the slip was separated from the grinding media and the alcohol was evaporated leaving a form of dried cake which was granulated by passing through a No. 22 BS sieve. After granulation, the binder, 2 wt % of Carbowax 4000, was added predissolved in chloroform which was then removed from the powder by evaporation. The dried cake was granulated, again by passing through a No. 22 BS sieve, to give the powder which was subsequently dry-pressed at 204 MN m⁻². The fabrication route adopted in the present work is one commonly used in powder technology and is commercially attractive because of its simplicity. There is, however, scope for more costly and sophisticated refinements which would probably result in higher values of both modulus of rupture and modulus of elasticity.

2.4. The test procedures

2.4.1. Sample preparation

The firing temperatures used were 1300°C, 1400°C, 1500°C, 1600°C and 1700°C. Batches of test pieces which were fired at one of the lower temperatures (1300°C, 1400°C or 1500°C) were produced in an electrically heated furnace. The rate of firing was 25°C h⁻¹ with a 4 h soaking period at the peak temperature. The test pieces for treatment at 1600°C and 1700°C were fired in a gas heated furnace. Test pieces were fired on separate bats, a different composition to each bat, using setting powder of the same composition as the specimen under examination.

Since accuracy of shape and a good surface finish are important in the test pieces submitted for modulus of elasticity measurements, these test pieces were diamond machined using a Jones

and Shipman surface grinder to produce square sections with flat parallel end faces. The formulations based on DZ oxide and both fused and fumed silicas were damaged during this machining, but it was possible to produce test pieces of good surface finish and accuracy of shape from those based on "Dizirc". It was not necessary to machine the modulus of rupture test pieces since the "as-fired" test pieces were of adequate quality.

For modulus of rupture measurements the test pieces were pressed from the various powders using a 50 mm × 6 mm rectangular bar die. In all cases, except where fumed silica was involved, the compaction pressure used was 204 MN m⁻². Great difficulty was experienced in fabricating test pieces containing the fumed silica, mainly because the test pieces collapsed on removal from the die. This was attributed to the very high compaction ratio of the ultra-fine particle size powder; this is a common feature of powder technology which can sometimes be overcome by granulating. A granulation procedure was applied, with limited success, producing only the smaller size test piece.

2.4.2. Measurement of physical properties

The procedure adopted was to first prepare batches of test pieces of each formulation fired at 1500° C. The results indicated that the formulation containing "Dizirc" and iron oxide possessed some convincing ceramic properties, but the values obtained with the other compositions were lower indicating that much less sintering had occurred in these formulations at this temperature. Indeed, no measurements could be made of the physical properties of many of the specimens fired to 1300° C or even to 1400° C.

2.4.2.1. Measurements of the modulus of rupture.

Since all ceramics are fundamentally brittle materials no attempt was made to determine strength by the method of applying a direct tensile load. The technique usually used for brittle materials is to subject specimens to cross breaking imparting both tensile and compressive loads, and yielding the value termed the "modulus of rupture". The instrument used in these experiments was a standard Hounsfield tensometer. The test piece (of size 5 mm × 5 mm) was placed on two supports of circular cross section 6 mm diameter, the links of support being 38 mm apart. The load was applied by means of a stirrup midway between the supports, the contacting edge being rounded to

a diameter of 6 mm. The lines of support and the edge of the stirrup were at right angles to the length of the test piece. Where possible ten bars of each composition were tested.

2.4.2.2. Measurement of the modulus of elasticity.

This was determined by the resonant frequency technique [5].

2.4.2.3. Measurement of the density.

This was determined according to the recommendations of [6]. This is a method which involves a weighing of the suspended bar in water after preparing it by drying at 110° C and subsequent evacuation at a pressure not greater than 666.5 Pa.

2.4.2.4. Measurement of the extent of zircon conversion.

This was measured by X-ray diffraction analysis for zircon at 3.29 Å, 2.34 Å and 2.05 Å using a Philips PW 1010 generator, 1050 goniometer and 1051 electronics: all the formulations prepared were tested after firing at the five temperatures whether bodies were successfully formed or not.

3. Results

Table I sets out the effect of firing temperature on the modulus of rupture, the modulus of elasticity, the density and the extent of zircon conversion for the nine formulations prepared. The data are set out graphically in Figs 1 to 11.

4. Discussion

Many studies have been made of both the dissociation and re-association of zircon. Table II, largely extracted from a review by Ramani *et al.* [7], illustrates how widely the impressions gained have varied. Starting with monoclinic zirconia and silica powders of greater than 99% purity several investigators have produced at least a partial conversion to zircon, generally at temperatures in the range 1500 to 1750° C, although some workers have quoted lower temperatures. Curtis and Sowman [8] determined the low-temperature limit of synthesis to be about 1320° C and the rate of synthesis to increase rapidly as the temperature increased from 1430° C to 1540° C; they also declared that the crystal form of the silica had no influence on the course of the synthesis. Their experiments on re-association after dissociation showed that it was very dependent on the rate of cooling after the disassociation: the faster the rate

TABLE I Effect of firing temperature on modulus of rupture, modulus of elasticity, density and the extent of zircon conversion for the nine formulations prepared

Composition	Firing temperature (° C)	Density (kg m ⁻³)	Conversion to Zircon (wt %)	Modulus of elasticity (× 10 ⁹ N m ⁻²)	Modulus of rupture (× 10 ³ N m ⁻²)
DZ oxide + quartz	1300	*	8	*	*
	1400	*	24	*	*
	1500	2417	37	8.2	10.70
	1600	2450	52	16.2	16.51
	1700	3353	42	56.4	51.37
DZ oxide + quartz + iron oxide	1300	*	45	*	*
	1400	*	68	*	*
	1500	3599	62	123.4	65.09
	1600	3693	82	136.2	67.08
	1700	3491	74	65.5	43.78
DZ oxide + amorphous silica	1300	*	54	*	*
	1400	*	75	*	*
	1500	2685	55	28.2	19.09
	1600	2892	57	43.6	27.49
	1700	3660	62	*	64.45
DZ oxide + amorphous silica + iron oxide	1300	*	67	*	*
	1400	*	77	*	*
	1500	3734	67	139.5	62.55
	1600	3904	72	159.5	74.34
	1700	3492	67	56.2	28.36
DZ oxide + fumed silica	1300	*	13	*	*
	1400	*	37	*	*
	1500	2197	62	5.10	10.56
	1600	2310	57	8.55	11.28
	1700	3492	57	61.9	24.51
DZ oxide + fumed silica + iron oxide	1300	*	67	*	*
	1400	*	77	*	*
	1500	3098	77	*	19.63
	1600	*	*	*	*
	1700	*	*	*	*
"Dizirc"	1300	*	2	*	*
	1400	*	32	*	*
	1500	3173	77	46.3	20.81
	1600	3559	67	90.1	45.85
	1700	3539	45	124.2	145.80
"Dizirc" + iron oxide	1300	3007	82	31.0	78.63
	1400	4157	87	184.3	96.62
	1500	4293	70	204.4	123.70
	1600	4344	62	216.0	107.19
	1700	3539	62	106.4	86.50
"Dizirc" + lead bisilicate	1300	*	11	*	*
	1400	*	51	*	*
	1500	2896	65	19.9	12.40
	1600	3335	84	61.9	27.50
	1700	3866	15	122.2	123.29

*The body produced could not be measured for mechanical properties after firing at the temperature stated.

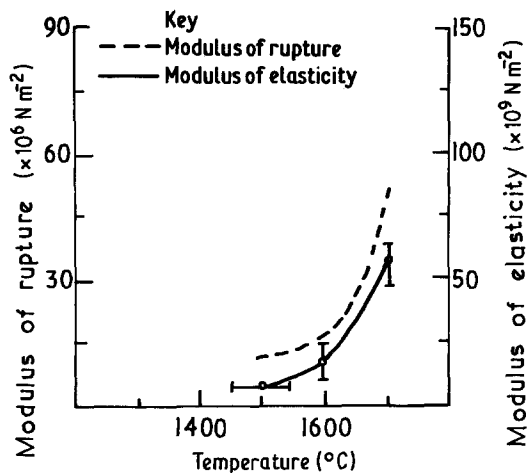


Figure 1 The variation of modulus of rupture and the modulus of elasticity with firing temperature for DZ oxide and quartz.

of cooling the less was the degree of re-association. Stott and Hilliard [9] claim that complete re-association could only be achieved by reheating at 1500°C for seven days followed by cooling for three days, although, others, such as Bartlett [10], give very much shorter times. It has been observed that the rate of synthesis of zircon by re-association was accelerated at temperatures of above 1300°C by the presence of some oxide additives such as Fe_2O_3 , MnO_2 , CaO and NiO [11].

From the physical property results given in Table I several observations which bear on this reaction can be made. The DZ oxide-silica formulations without added iron oxide all behave similarly (the slow reaction of the fumed variety

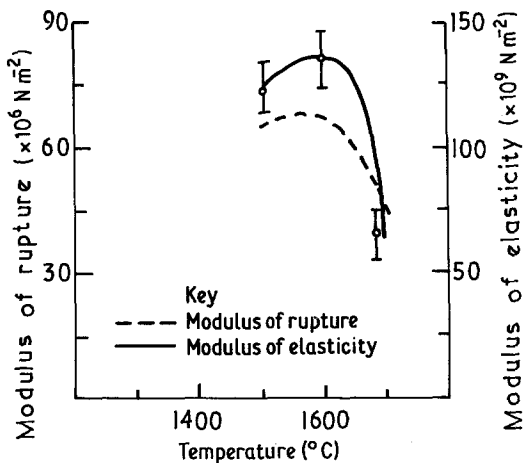


Figure 2 The variation of modulus of rupture and the modulus of elasticity with firing temperature for DZ oxide with quartz with iron oxide.

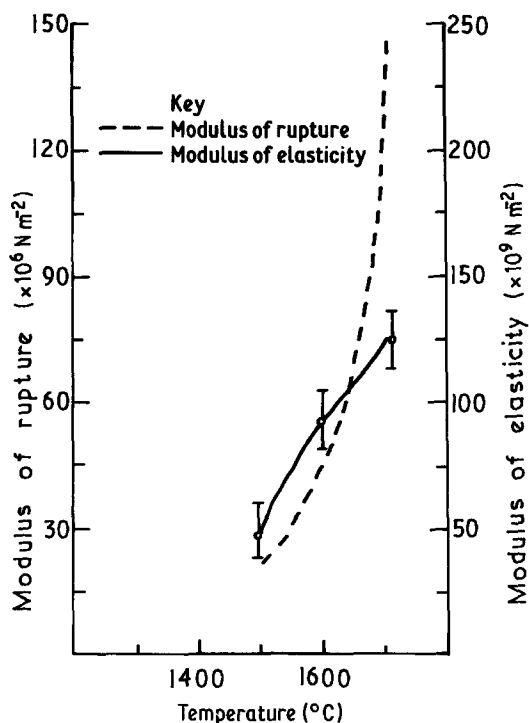


Figure 3 The variation of modulus of rupture and the modulus of elasticity with firing temperature for "Dizirc".

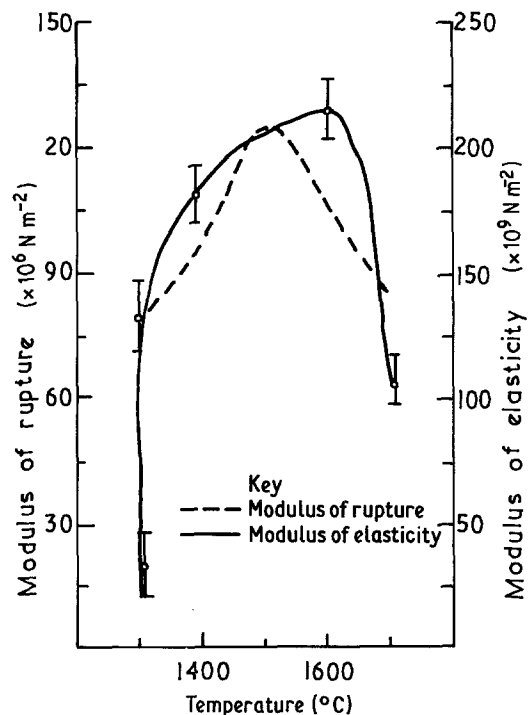


Figure 4 The variation of modulus of rupture and the modulus of elasticity with firing temperature for "Dizirc" with iron oxide.

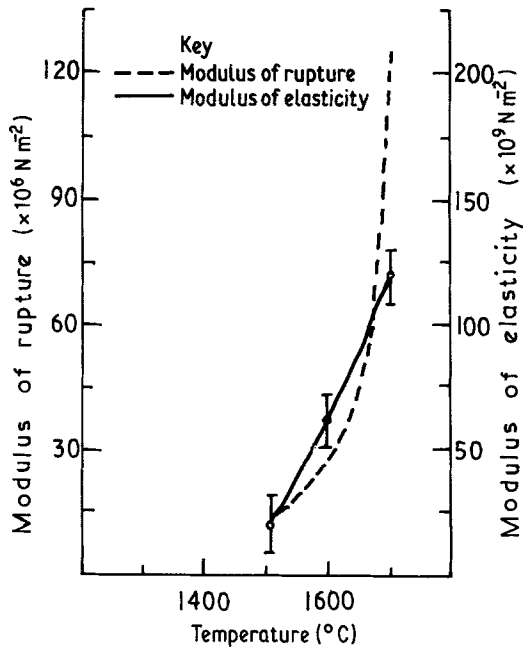


Figure 5 The variation of modulus of rupture and the modulus of elasticity with firing temperature for "Dizirc" with lead bisilicate.

may be due to the difficulty of achieving good mixing and good particle to particle contact between the constituents). Density, modulus of elasticity and modulus of rupture values show little increase with temperature from 1500°C to

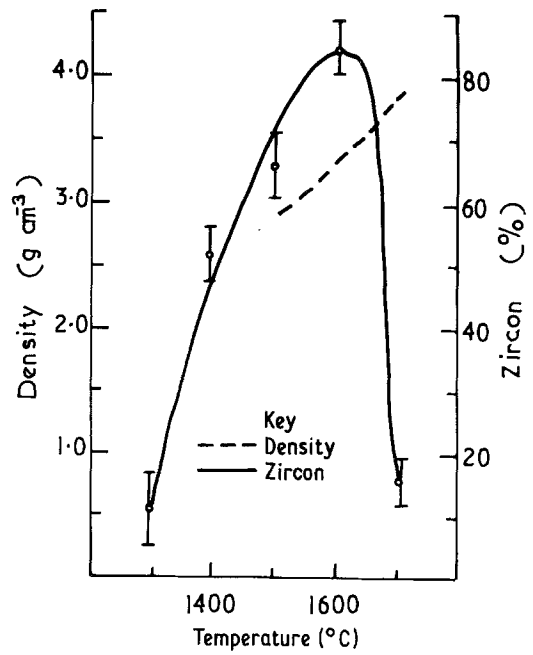


Figure 7 The variation of density and conversion to zircon with firing temperature for "Dizirc" with lead bisilicate.

1600°C, but there is a sudden increase in all three properties when the firing temperature is raised to 1700°C (Fig. 1).

The zircon conversion figures show that the courses of the re-association and dissociation

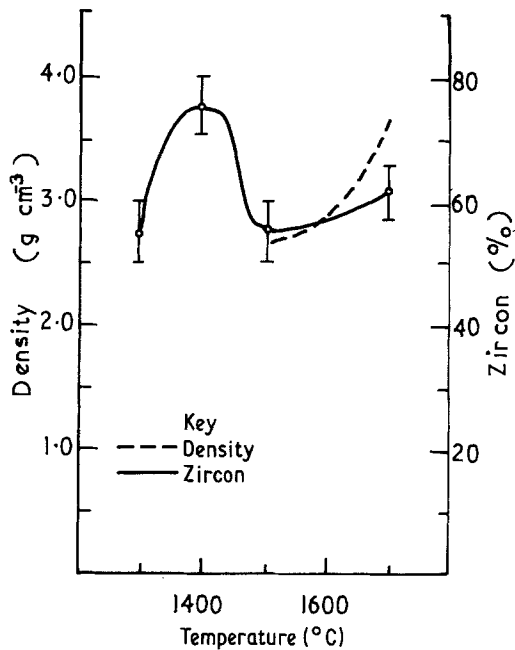


Figure 6 The variation of density and conversion to zircon with firing temperature for DZ oxide and amorphous silica.

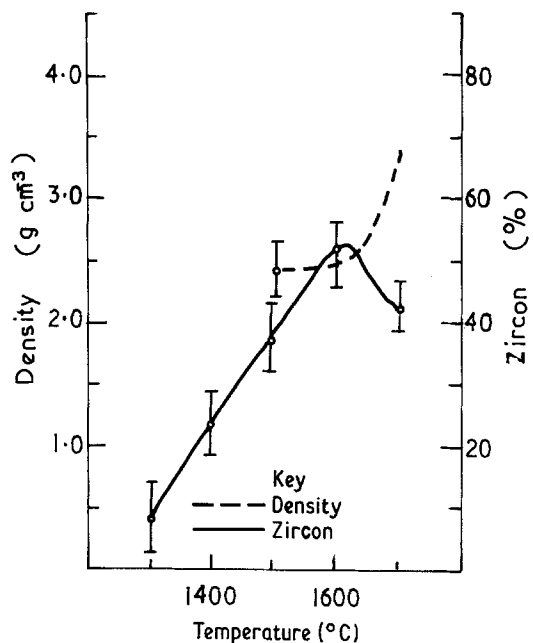


Figure 8 The variation of density and conversion to zircon with firing temperature for DZ oxide and quartz.

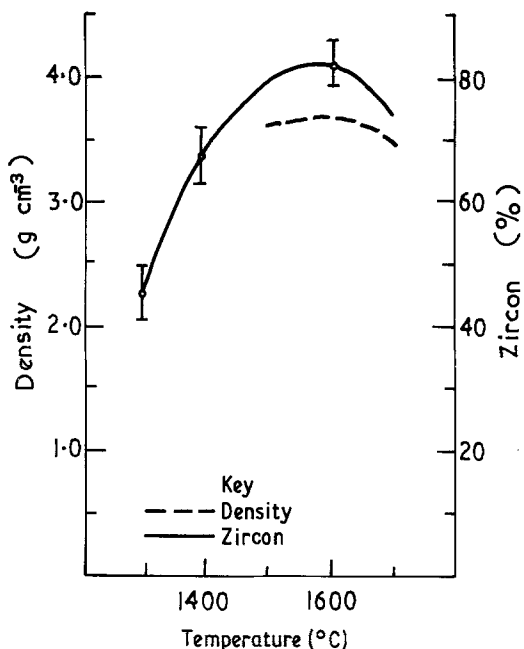


Figure 9 The variation of density and conversion to zircon with firing temperature for DZ oxide and quartz with iron oxide.

reactions are not necessarily related in any direct way to these changes in the ceramic properties. What is very noticeable is the marked reluctance of any of the DZ oxide-silica mixtures to convert completely to zircon.

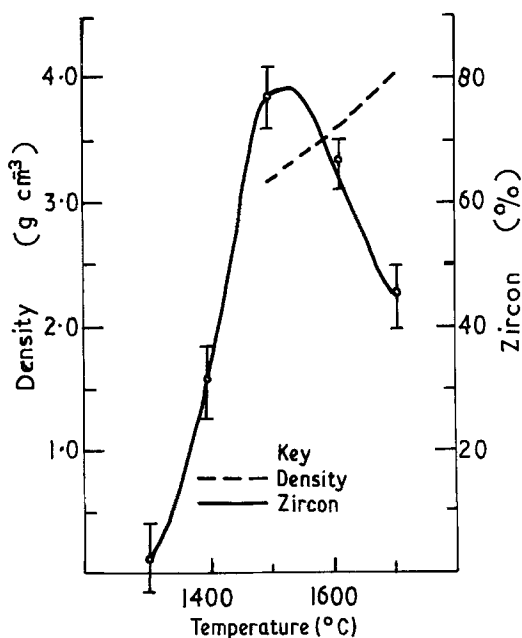


Figure 10 The variation of density and conversion to zircon with firing temperature for "Dizirc".

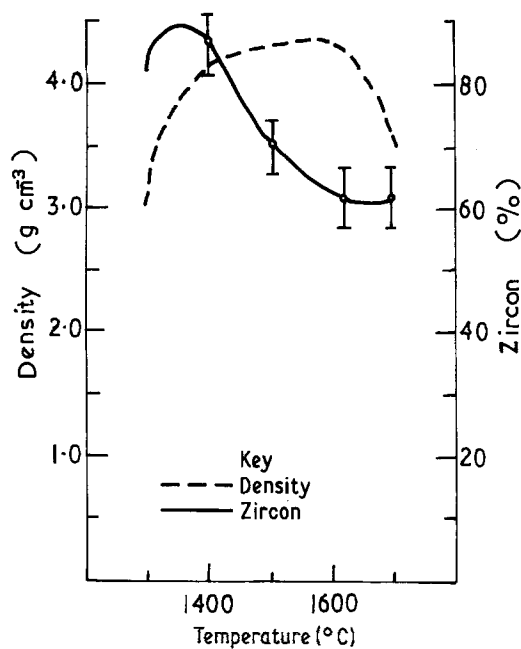


Figure 11 The variation of density and conversion to zircon with firing temperature for "Dizirc" with iron oxide.

The "Dizirc" specimens behave in a superficially similar manner to the DZ oxide-silica compositions with a large increase in the values measured after firing the 1700°C. However, the values of both properties are much higher in the case of "Dizirc" at all three temperatures than those measured for any of the DZ oxide-silica samples at the same temperature.

In the case of compositions with added iron oxide another type of pattern can be seen. Test bars made with these formulations show densities and moduli of elasticity increasing with increasing firing temperatures from 1300°C to 1600°C and then falling sharply when the firing temperature is raised to 1700°C. Moduli of rupture values show the increase in value with increasing temperature up to 1500°C and then show a fall. Test pieces made from DZ oxide and silica doped with iron oxide show the same pattern of increase in value of properties from 1500°C to 1600°C followed by a decrease at 1700°C. Once again, the property values in absolute terms are much higher in the case of formulations made from "Dizirc" with iron oxide than from DZ oxide-silica with iron oxide.

A comparison of the zircon conversion and density curves for all these samples demonstrates a much more complex situation: the only curves which are clearly related to each other are those

TABLE II Disassociation/re-association temperatures reported for zircon

Investigator	Date	Disassociation temperature (°C)	Re-association temperature (°C)	Nature of decomposition	Nature of synthesis
Washburn & Libman	1920	2550	—	Congruent melting	—
Barlett	1932	1450	1450	—	From disassociated material
Heindl	1933	1800	—	—	—
Zhirnowa	1934	2430	—	Congruent melting	—
Clark & Reynolds	1937	—	1500	—	From mixed oxides
Bauer	1939	1650	—	—	—
Kirby	1944	1900	—	—	—
Geller & Yavorski	1945	—	1700	—	From mixed oxides
Stott & Hilliard	1946	1500–1740	1500	—	From disassociated material
Geller & Lang	1949	1775	—	Incongruent melting	—
McKee & Adams	1950	1800	—	—	—
Curtis & Sowman	1953	1540	1320	In the solid state	From disassociated material
Cocco & Schromek	1957	1720	—	Incongruent melting	—
Kelor & Andreeva	1962	1800	1700–1750	—	From mixed oxides
Rosen & Muan	1965	1600–1650	—	—	—
Butterman & Foster	1967	1669–1683	—	In the solid state	—
Jones, Kimura & Maun	1967	1660	—	—	—
Qureshi & Brett	1968	1660	—	—	—
Hossain & Brett	1969	1675	—	—	—
Gokhale et al	1969	—	1155	—	From mixed oxides

for “Dizirc” and “Dizirc with lead bisilicate. This latter finding gives no support to the idea that its presence would restrain the conversion of the mixed oxides to zircon (which conversion is anyway by no means complete); nor is it likely to act as a sintering-aid since it may simply dissolve in the glassy silica phase. In fact these curves, taken together, show that the conversion to zircon with “Dizirc” peaks at a temperature nearly 200°C higher, but to final values higher than for either of the DZ oxide or DZ oxide–iron oxide pairs.

The very great differences in ceramic properties may be ascribed to differences in texture. Alternatively they may be due to the formation of a new species, perhaps an iron silicate, in some texturally significant amount, which has promoted densification. Another possible mode of formation

TABLE III Modulus of rupture values for a range of different ceramics

Ceramic body	Modulus of rupture ($\times 10^9 \text{ N m}^{-2}$)
Sintered aluminium oxide	350–480
“Dizirc” with iron oxide	130–140
Electrical porcelain	115–130
Bone china	110–125
Zircon	100–115
Earthenware	55–70
High-grade refractory bricks	10–25
Low-grade refractory bricks	5–10

of these ceramics has been discussed in a previous work [12] where the suggestion was made that a eutectic may be continuously formed in which the zirconia and silica are dissolved and zircon instantly precipitated. The present evidence does not appear to favour this view. Generally, in the case of ceramic and metallic articles produced by sintering from powder, properties such as moduli of rupture and elasticity depend very much on the final density obtained. Assuming the absence of flaws and strains, an article produced from powder and fired to its maximum (theoretical) density has the highest values of mechanical strength and elasticity; well-defined relationships have been established between these properties and others, such as degree of porosity. However, these relationships seldom apply in cases where significant changes in texture arise due either to phase changes, for example the monoclinic–tetragonal phase change in zirconia, or, as in the present case, where there is re-association or disassociation. Comparison between the “Dizirc”–iron oxide bodies and the other compositions studied indicate that only in the former can promising mechanical properties be developed at relatively low, commercially attractive, temperatures. The evidence from these experiments would appear to confirm the importance of the intrinsically complete, fully wetted, mixing of the constituent zirconia and

silica in "Dizirc" to produce a satisfactory ceramic body. Some of the technological implications of these new ceramics have recently been explored by Rogers [13] and by Williamson and co-workers [12, 14].

Although more sophisticated techniques of strength measurement and of generally assessing the mechanical behaviour of ceramic materials are now being developed, modulus of rupture remains the most frequently quoted parameter for comparison. Table III compares the strength of a range of ceramics ranging from traditional earthenware bodies to sintered aluminium oxide and including "Dizirc" (with iron oxide).

Particularly during the last decade, a number of workers have determined the "work-of-fracture" of many ceramic materials. Such measurements have been carried out on DZ bodies by Garvie [15] who showed that significant improvements in this property can be attained by modifications to the texture. The associated gain in fracture toughness is a clear advantage for certain mechanical applications of these bodies, such as for extrusion nozzles, turbine components etc.

5. Conclusions

The following conclusions can be drawn from the results of this work:

(1) Using conventional ceramic techniques at moderate temperatures (up to 1500°C) the highest strength, highest density bodies were produced with "Dizirc" doped with iron oxide.

(2) None of the bodies produced from any of the DZ oxide-silica mixes at any temperature below 1700°C have mechanical properties of any interest.

(3) As a general rule the effect of the iron oxide addition is to reduce the sintering temperature of a "Dizirc" composition by approximately 200°C; the sintering temperature of zirconia-silica composition is similarly reduced by the addition of iron oxide.

(4) Whilst the presence of iron oxide appears to favour re-association in inducing the re-association reaction to occur at a lower temperature, it also appears to discourage the subsequent disassociation at higher temperatures (at about 1700°C).

(5) Lead bisilicate does not assist in the sintering

of a "Dizirc" composition; nor does it effect the conversion to zircon to any significant extent.

(6) The two forms of silica reacted with the zirconia produce bodies with differing mechanical properties, but there is no evidence to indicate the possible reasons for the differences in behaviour, since there is not a clear correlation of the values of zircon conversions with temperature.

(7) The greater reactivity of the "Dizirc" may be due simply to the nearly perfect mixing of the constituent zirconia and silica.

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