

Letters

Thermal expansion of zircon–alumina materials prepared by reaction sintering

It is well known that zirconia undergoes a displacive transformation from the monoclinic to the quadratic phase on heating at temperatures between 1000 and 1200°C. The structure change is associated with a volume decrease (about 9%) and renders the material useless as a high temperature structural ceramic since it causes cracking. Moreover, even when a ceramic product contains a small quantity (a few per cent) of zirconia, one can frequently observe failure of the products due to the above mentioned volume change. That is why zirconia is used for practical applications in the stabilized cubic phase or in materials with microstructures which are capable of accommodating the sudden volume change in some way.

In our studies on the zirconia–alumina [1, 2, 3] system prepared by reaction sintering, it has been noted that the thermal expansion of samples containing up to 32 wt% zirconia did not present any discontinuity between 1000 and 1200°C. The present letter reports the results obtained. Arguments are presented which indicate the relationship between thermal expansion and the content of zircon, zirconia, alumina, mullite and porosity. Special emphasis is placed on microstructural aspects inherent in reaction sintering.

The reaction between zircon and alumina follows the equation: $2\text{ZrSiO}_4 + 3\text{Al}_2\text{O}_3 \rightarrow 2\text{ZrO}_2 + 3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$. It has been established [1] that the reaction proceeds through the formation of non-crystalline mullite, the amount of which can be as much as 15% depending on the temperature and on the initial molar ratio of the reactants ($\text{ZrSiO}_4\text{--Al}_2\text{O}_3$).

Details on solid state reactions [1] in the zircon–alumina system as well as reaction sintering [2] and reaction hot pressing [3] procedures and mechanisms have been reported elsewhere.

Mixtures of zircon–alumina (containing from 0 to 73.6 wt% of alumina) have been reaction sintered at 1600°C for 5 h. Mixtures of zirconia–alumina (from 0 to 100 wt% ZrO_2) and of zirconia–mullite (from 0 to 100 wt% ZrO_2) have also been fired at 1600°C for 5 h. Moreover, samples of zircon–alumina (2 moles of ZrSiO_4 ,

3 moles of Al_2O_3) have been reaction hot pressed at 1600°C for 2 h at a pressure of 0.5 MNm^{-2} . Cylindrical samples (5 cm in diameter and 4 cm (L_0) in length) have been shaped in all the fired materials and linear thermal expansions ($\Delta L/L_0$) have been recorded using a Leitz dilatometer from room temperature up to 1400°C. The amount of phase present after firing, in each sample, has been measured using room temperature X-ray diffraction. Moreover, all samples were submitted to high temperature X-ray diffraction analysis (from room temperature to 1400°C) using a high temperature Seifert diffractometer. Porosity was measured by water displacement. Studies on the microstructure were performed by scanning electron microscopy (SEM) (Cambridge S600) using fractured pieces of the fired samples.

The results of reaction sintered and reaction hot pressed zircon–alumina and zirconia–alumina and zirconia–mullite samples are presented in Table I and Figs 1 and 2.

On the thermal expansion curves, the difference between the linear thermal expansion coefficients, α , of each sample containing monoclinic and quadratic phases at the transition temperature, has been measured and called the thermal expansion discontinuity, $\Delta\alpha$.

It can be seen that the thermal expansion discontinuity, $\Delta\alpha$, of reaction sintered and hot

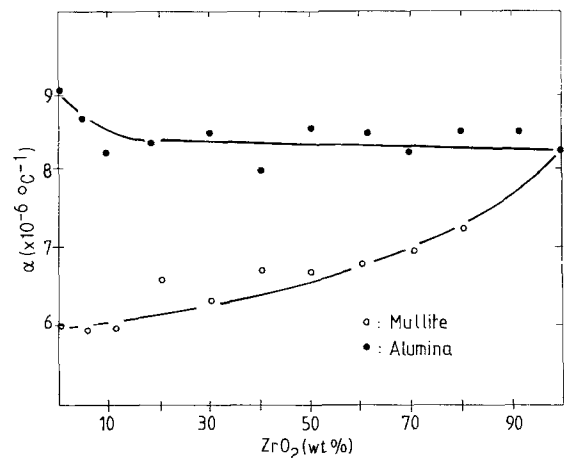


Figure 1 Evolution of the linear thermal expansion coefficients against content of zirconia for sintered zirconia–mullite and zirconia–alumina materials.

TABLE I Thermal expansion discontinuity (between 1000 and 1200° C), linear thermal expansion coefficient (up to the change), composition (wt %) and volume porosity (P_V vol %) of reaction sintered, sintered and reaction hot pressed samples

Sample	Thermal expansion discontinuity $\Delta\alpha$ ($10^{-6} \text{ }^\circ\text{C}^{-1}$)	Linear thermal expansion coefficient α ($10^{-6} \text{ }^\circ\text{C}^{-1}$)	ZrSiO ₄ (wt %)	Al ₂ O ₃ (wt %)	Mullite (wt %)	ZrO ₂ (wt %)	P_V (vol %)
1*	0.	4.6	95.0	0	2.0	3.0	23
2	1.0	5.1	80.0	0	14.9	9.1	22
3	1.8	5.3	69.1	0	19.4	11.5	23
4	2.0	6.0	52.1	2.0	28.5	17.4	26
5	1.2	6.0	28.0	8.0	42.2	22.8	32
6	0	6.3	4.0	8.1	55.3	32.6	33
7	0	6.0	0	14.0	55.3	30.7	33
8	0	6.3	0	24.5	50.0	26.1	33
9	0	6.3	0	52.0	32.0	16.0	33
10†	0	9.0	—	100	—	0	≈ 30
	0	8.6	—	95	—	5	≈ 30
11	0.7	8.3	—	90	—	10	≈ 30
12	1.4	8.4	—	80	—	20	≈ 30
13	2.5	8.4	—	70	—	30	≈ 30
14	3.9	8.1	—	60	—	40	≈ 30
15	4.4	8.5	—	50	—	50	≈ 30
16	5.2	8.5	—	40	—	60	≈ 30
17	6.1	8.3	—	30	—	70	≈ 30
18	6.9	8.5	—	20	—	80	≈ 30
19	8.2	8.5	—	10	—	90	≈ 30
20	9.0	8.3	—	—	—	100	≈ 30
21	0	6.0	—	—	100	—	≈ 30
22	0	6.0	—	—	95	5	32
23	0	6.0	—	—	90	10	32
24	0.4	6.6	—	—	80	20	28
25	0.4	6.4	—	—	70	30	31
26	1.8	6.7	—	—	60	40	25
27	1.5	6.7	—	—	50	50	27
28	3.2	6.8	—	—	40	60	25
29	5.0	7.2	—	—	20	80	20
30‡	0	6.3	10	8.2	51.8	30	0

*Samples 1 to 9 are reaction sintered.

†Samples 10 to 29 are sintered.

‡Sample 30 is reaction hot pressed.

pressed zircon—alumina sample is very small, if not zero, even for large amounts (32 wt % in Sample 6) of zirconia. $\Delta\alpha$ is much more important in sintered zirconia—alumina and increases gradually with zirconia content whereas in the zirconia—mullite samples, $\Delta\alpha$ remains quite low even up to 40 wt % zirconia. Some similar features with reaction sintered zircon—alumina samples are then seen (see Fig. 2).

Using high temperature and room temperature X-ray diffraction it has been checked that none of the other phases (alumina, zircon, mullite)

present in the various studied materials stabilize the quadratic or cubic zirconia phase at room temperature. The results of Table I also show that the influence of porosity is of little importance, if any, on the disappearance of $\Delta\alpha$ in the reaction sintered and reaction hot pressed materials.

From Table I it can be seen that the $\Delta\alpha$ values of reaction sintered zircon—alumina materials are very small. As the degree of reaction between zircon and alumina increases, the mullite phase content becomes more and more important. The analysis of micrographs obtained by SEM of

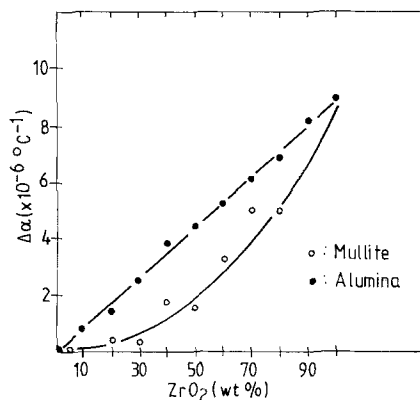


Figure 2 Evolution of the thermal expansion discontinuity values against content of zirconia for sintered zirconia–mullite and zirconia–alumina materials.

fractured surfaces of reaction sintered materials shows that zirconia grains are spherical and dispersed in the mullite phase (let us note that the volume of mullite produced is approximately four times greater than the corresponding zirconia one). Fig. 3 represents a micrograph in which one can see the dispersion of zirconia grains in the mullite phase. This microstructure shows a large number of spherical holes due to the loss of zirconia grains because of the volume difference between quadratic and monoclinic zirconia (this easy loss of zirconia has made the use of polished surfaces for microscopy examinations impossible).

This particular microstructure i.e. dispersion of spherical zirconia grains in the mullite matrix, is totally different from that found in the sintered zirconia–mullite and zirconia–alumina materials.

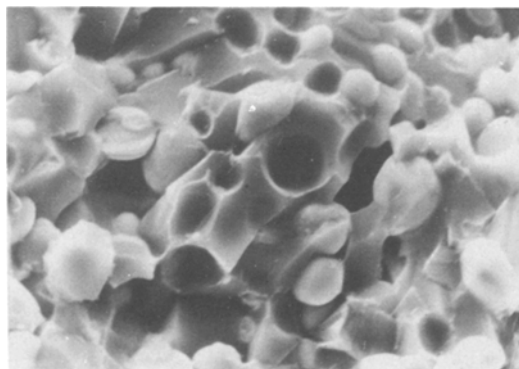


Figure 3 SEM micrograph of a reaction sintered material.

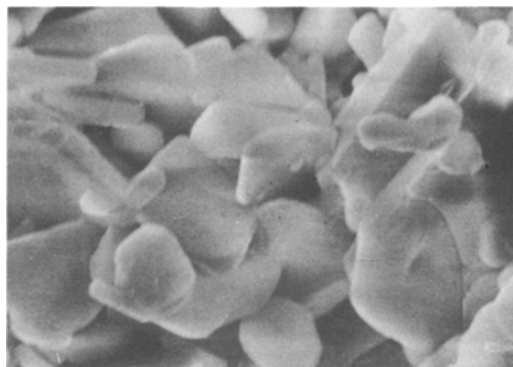


Figure 4 SEM micrograph of a sintered zirconia–mullite material.

Such a microstructure, representative of zirconia–mullite materials, is presented in Fig. 4 in which one can see that grains of zirconia and mullite are arranged contiguously. At the transition temperature a large variation in the volume of the zirconia grains induces a modification in the volume of the sintered samples whereas in the reaction sintered samples a shrinkage of the volume of zirconia can occur without modifying the volume of the samples, zirconia grains being dispersed inside the mullite phase.

This type of microstructure of reaction sintered samples has features in common with zirconia–silica–alumina fused cast materials [4] which are materials with no noticeable thermal expansion discontinuity on heating above 1100°C. One can therefore conceive that one of the potential advantages of using reaction sintering, when possible, is that this technique may produce materials with favourable microstructures as a consequence of the solid state reaction mechanisms. Indeed, in the case of the zircon–alumina system, the observed microstructure is due to the mechanisms of the reaction [1], namely, the decomposition of zircon into zirconia and silica, and the subsequent reaction of the silica and alumina to form an amorphous mullite phase with a sufficiently low viscosity to flow and completely surround the remaining zirconia grains.

Acknowledgement

The authors wish to thank Prof. R. J. Brook for a critical review of the manuscript.

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Received 29 May
and accepted 10 July 1980.

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The possibility of proof testing ceramics against thermal fatigue by mechanical stress

Proof testing is thought to be a requisite for the confirmation of reliable use of ceramics. It is therefore being practically applied to some ceramics. Recent studies on proof testing have confirmed that it is effective for soda-lime glass [1] and for silicon nitride [2]. The application, however, seems to have been limited to ceramics which are used under mechanical stress or under an atmosphere similar to the one used under testing. The proof test will be useful for ceramics under thermal shock on the assumption that the flaw sensitive to the thermal shock is identical to the one which is sensitive to mechanical stress. On this assumption, a method for mechanical proof testing against thermal fatigue failure has been proposed [3]. The assumption, however, is not always valid, because a ceramic has flaws of various types, which are susceptible to stress as well as the atmosphere.

On the assumption that the flaw sensitive to mechanical stress under ambient atmosphere is not identical to the one sensitive to other types of stress, such as, thermal stress caused by water quenching, the ceramics surviving the proof test under ambient atmosphere should include those with both a high and low thermal fatigue life after water quenching. In other words, the distribution of the thermal fatigue life of ceramics surviving the proof test will be similar to that of ceramics without the proof test.

To examine the differences between the flaw sensitive to water quenching thermal stress and that sensitive to bending stress in an ambient atmo-

sphere, the following experiments were carried out.

A soda-lime silica glass rod of diameter 4 mm, was cut into specimens of 150 mm in length. The specimen was loaded by four-point bending (Fig. 1) for 10 sec. The stress was chosen so that the survival probability was about 74% (Test I) and about 62% (Test II). The value of the stress for 74% survival was about 9.9 kg mm^{-2} and that for 62% about 10.3 kg mm^{-2} . Unloading was carried out rapidly (≤ 0.1 sec).

After testing, the specimen was cut with a diamond blade just outside the two supporting points (E and F in Fig. 1). The cut specimen was mounted onto a specimen holder, so that three-point bending stress was applied to the specimen. Thermal stress was applied by repetition of heating and water quenching (Fig. 2). The three-point bending stress was applied during the thermal cycles. The bending stress was applied in such a way that the surface of the specimen subjected to tensile stress in the proof test was, also, under tensile stress in the thermal fatigue test. The heating time was about 30 min. The time for transferring the specimen from the hot zone to water was about 1.6 sec. The heating temperature was about 190°C . For comparison, glass rods without the proof test were also examined.

The survival probability, P , was calculated by dividing the number of surviving specimens after N cycles of thermal shocks by the sum of specimens ($= 9$).

The value of P plotted against the thermal cycles, N , is given in Fig. 3. As shown in the figure, the value of P as a function of N follows the Weibull statistics for the specimens without the