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Interfacial Reaction in Zircon–Alumina Multilayer Composites

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Abstract

The mechanism of the zircon–alumina reaction at 1600°C has been studied using a zircon–alumina multilayer composite obtained by slip casting. It has been found that in the first stage of the reaction the zircon is dissolved in a silica-rich glassy phase with the subsequent precipitation of zirconia and mullite. The role of impurities always present in the zircon powder is also discussed.

Die Reaktion von Zirkon mit Aluminiumoxid bei 1600°C wurde mit einem durch Schlickerguß hergestellten Zirkon–Aluminiumoxid Vielschicht-Verbund untersucht. Dabei hat sich gezeigt, daß sich in der ersten Stufe der Reaktion das Zirkon in einer silikatreichen Glasphase löst und sich danach ZrO_2 *und Mullit ausscheidet. Auf den Einfluß der im Zirkonpulver immer vorhandenen Verunreinigungen wird ebenso eingegangen.*

On a étudié le mécanisme de la réaction $ZrSiO_4$*–*Al_2O_3 *à 1600°C en utilisant un composite multicouche de* $ZrSiO_4$*–*Al_2O_3 *obtenu par coulage. On a établi que, dans la première étape de la réaction,* $ZrSiO_4$ *se dissous dans une phase vitreuse et qu'ensuite de la zircone et de la mullite précipitent. On discute également du rôle des impuretés toujours présentes dans la poudre de* $ZrSiO_4$*.*

1 Introduction

Mullite–ZrO_2 ceramic composites have gained importance due to their excellent properties such as high toughness,[1] high-temperature chemical stability, and very high creep resistance.[2] Because of this, mullite–ZrO_2-based composites are considered as potential candidates for high-temperature structural applications and for advanced refractories for continuous steel casting plants.[3]

Reaction sintering of a zircon–alumina mixture in the molar proportion of

$$2\,ZrSiO_4 + 3\,Al_2O_3 \rightleftharpoons Al_6Si_2O_{13} + 2\,ZrO_2$$

is now considered as an inexpensive route to produce mullite–zirconia tough ceramics.[1] Most attention has been recently paid to the kinetics of the zircon + alumina reaction, effect of additives (TiO_2, CaO, MgO) and their role in the microstructural development and final mechanical properties.[4–6] However, it is still not clear which is the mechanism through which this reaction takes place.

The aim of the present work is to study the interfacial reactions that occur in a zircon–alumina multilayer composite obtained by slip casting.

2 Experimental

The following were used as starting materials:

(i) A very fine zircon powder with 1·1 μm average particle size (Quiminsa, Spain) with the following impurities in wt%: Fe_2O_3, 0·10; CaO, 0·13; MgO, 0·04; K_2O, 0·01; Na_2O, 0·17.

(ii) Submicrometer alumina with 0·5 μm average particle size (Alcoa CT-3000-SG) with the following impurities in wt%: Fe_2O_3, 0·03; CaO, 0·02; MgO, 0·1, K_2O, u.d.; Na_2O, 0·1.

Zircon and alumina aqueous suspensions with 60 and 65 wt% solids loading respectively were performed as follows:

(i) Zircon powder + distilled water + 1 wt% deflocculant + 0·4 wt% sodium hexametaphosphate were ball milled for 4 h.

(ii) Alumina powder + distilled water + 0·5 wt% deflocculant were ball milled for 4 h.

Dolapix PC-33 (Zschimmer-Schwarz, FRG) was used as deflocculant.

After these operations, very fluid zircon and alumina slurries with pH values of 6·7 and 10·0 respectively were obtained.

Zircon–alumina multilayer green plates were obtained by sequential drain casting of zircon and alumina suspensions on plaster of Paris moulds for a fixed time of 40 s. The slip cast plates were then fired at 1600°C for 2 h. The fired specimen was cut and polished perpendicularly to the layer's direction for optical and scanning electron microscopy observation.

Thin foils adequate for the transmission electron microscopy work were conventionally prepared by ion-beam thinning (5 kV argon beams, incidence angle 30°). Coating with carbon was performed in order to avoid charging under the electron beam.

The chemical analysis of the samples was achieved on a JEOL 200 CX (side-entry configuration) microscope, equipped with an ultra-thin window detector and a TRACOR analysis system (energy dispersive X-ray).

3 Results and Discussion

The SEM micrograph of Fig. 1 shows the microstructure of the obtained multilayer composites.

In Fig. 2 the SEM micrograph of the reacted interface together with the TEM-EDX quantitative microanalysis quoted at different distances of the interface are shown.

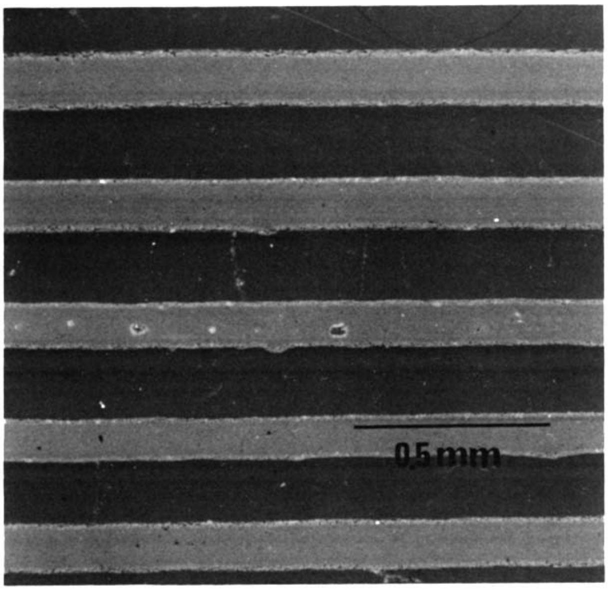
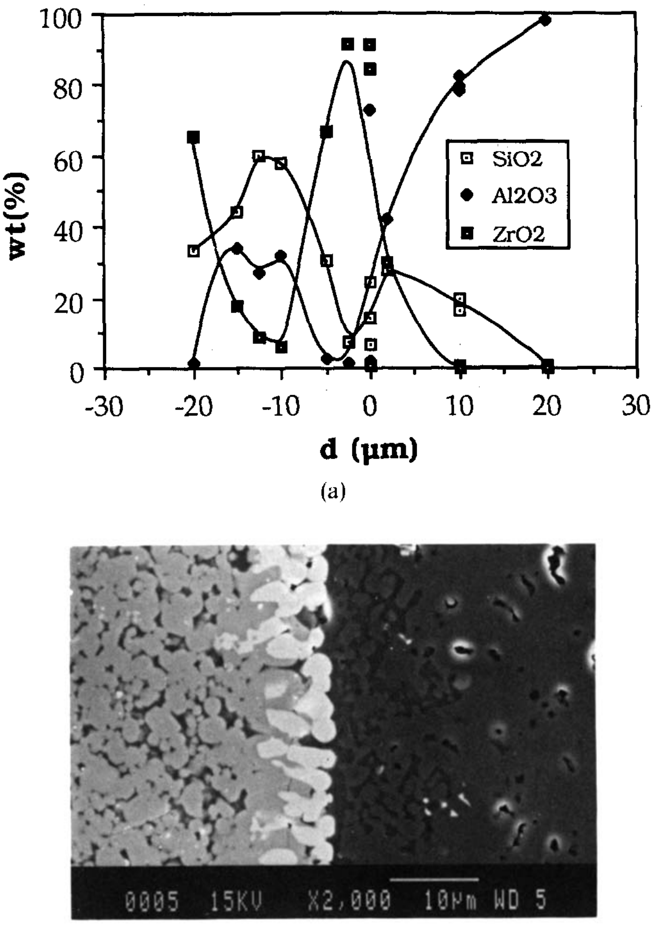


Fig. 1. SEM micrograph showing the general microstructure of the fired multilayer composite (alumina = dark, zircon = clear).



(a)

(b)

Fig. 2. SEM micrograph of the reacted interface together with the TEM-EDX microanalysis plot.

From these figures it is clear that the Al^{3+} diffuses into the zircon layer up to ≈20 μm from the interface, while Si^{4+} diffuses into the alumina layer up to a similar distance.

An intergranular glassy phase is observed at both sides of the interface. Coarse grains of zirconia (2–5 μm) are located at the zircon interface. In this region (0–5 μm) a depletion of SiO_2 and Al_2O_3 concentration occurs.

TEM micrographs corresponding to − 10 μm and + 10 μm regions (Fig. 2) are shown in Fig. 3.

In the − 10 μm micrograph, grains of zircon partially dissolved can be observed as well as dendrites of zirconia precipitate from the glass during cooling. In the TEM micrograph corresponding to + 10 μm region a grain of mullite between alumina grains was detected.

These results suggest that in the present case the zircon grains are dissolved in a silica-rich glassy phase. This glassy phase, which is due to the

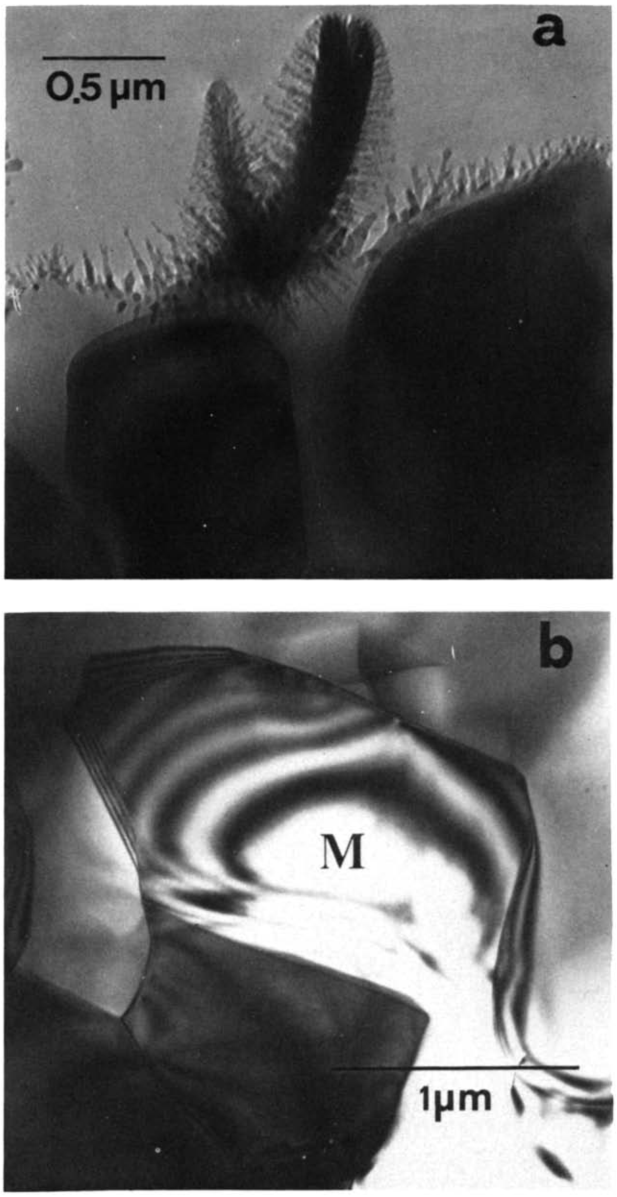


Fig. 3. TEM micrographs corresponding to (a) $-10\,\mu$m and (b) $+10\,\mu$m regions (M = mullite).

impurities already present in the starting powders, affects the mechanism of the process. As it is well known the glassy phase is a sink of impurities. These impurities act as glass network modified ions decreasing the viscosity of the glass and consequently enhancing the mass transport.

When the glassy phase is saturated in ZrO_2, ZrO_2 grains precipitate. Then, more alumina is dissolved in the glass until it reaches the mullite composition; at this point the mullite crystals precipitate. This sequence is in quite good agreement with the SiO_2–Al_2O_3–ZrO_2 equilibrium diagram proposed by Pena and De Aza.[7] That is, there is no initial dissociation of zircon followed by a reaction of the silica with the alumina particles to give mullite, as suggested by Wallance *et al.*[8] and Cambier *et al.*[9]

Commercial zircon fine powders (such as the ones used in this work) contain alkaline ($\approx 0{\cdot}18$ wt%) and alkaline earth ($\approx 0{\cdot}2$ wt%) cations. These impurities cause a decrease in the temperature of the zircon + SiO_2 + mullite eutectic (1595°C) of the SiO_2–Al_2O_3–ZrO_2 system[7] as well as a decrease in the viscosity of the corresponding liquid. Both facts can explain the experimental observations of Wallance *et al.*[8] through which at 1575°C the reaction between alumina and zircon proceeds through the formation of what they call 'non-crystalline mullite' plus ZrO_2 and subsequent formation of crystalline mullite.

The mullite nucleation from the aluminium silicate glass developed during the reaction sintering of zircon and alumina mixture is strongly dependent on the nature of the cation present in it. For instance, in the case of CaO- and MgO-containing compositions,[10] nucleation periods of approximately 15 h and 6 h respectively were observed at 1425°C, while in the case of TiO_2-containing compositions[8] no nucleation period was observed at 1550°C. Consequently, mullite and zirconia were detected together at any reaction time. This fact is in agreement with the results reported by Stokiey[11] for aluminosilicate glasses. He observed that the presence of TiO_2 caused crystallization of crystalline phases in such glasses.

4 Conclusions

The reaction between alumina and zircon at 1600°C takes place through the following sequence:

(i) Dissolution of zircon in a silica-rich glassy phase.
(ii) Precipitation of zirconia particles.
(iii) Dissolution of alumina in the glass until it reaches the composition of mullite.
(iv) Precipitation of mullite crystals.

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References

1. Moya, J. S., Reaction-sintered mullite–zirconia and mullite–zirconia–SiC ceramics. In *Proceedings of the 1st International Workshop on Mullite*, November 1987. American Ceramic Society.

2. Torrecillas, R., Rahalj, S., Gros, H., Fantozzi, G., Moya, J. S., de Aza, S. & Rodriguez, M. A., High-temperature mechanical properties of mullite–ZrO_2 reaction-sintered composites. Paper to be presented at the 11th Riso International Symposium on Metallurgy and Materials Science, September 1990, Denmark.
3. Chakraborti, D. P., Nandi, P., Tiwari, L., Mukhopadhyay, M. S. & Chatterjee, K. C., Microstructural development and improvements in mechanical properties of reaction-sintered alumina–zircon composites. In *UNITECR '89 Proceedings*, ed. Trostel. American Ceramic Society, 1989, pp. 1652–62.
4. Pena, P., Miranzo, P., Moya, J. S. & de Aza, S., *J. Mat. Sci.*, **20** (1985) 2011– .
5. Miranzo, P., Pena, P., Moya, J. S. & de Aza, S., *J. Mat. Sci.*, **20** (1985) 2702– .
6. Moya, J. S., Miranzo, P., Pena, P. & de Aza, S., In *Processing of Advanced Ceramics*, ed. J. S. Moya & S. de Aza. Sociedad Española de Cerámica y Vidrio, Madrid, 1986, pp. 121–33.
7. Pena, P. & de Aza, S., *J. Mat. Sci.*, **19** (1984) 135–42.
8. Wallance, J. S., Petzow, G. & Claussen, N., Microstructure and property development of in-situ reacted mullite–ZrO_2. In *Advances in Ceramics*, Vol. 12, 1984, pp. 436–42.
9. Cambier, F., Baudin, C., Pilate, P. & Leriche, A., *Brit. Ceram. Trans. J.*, **83** (1984) 196–200.
10. Moya, J. S., Miranzo, P. & Osendi, M. I., *Mat. Sci. Eng.*, **A109** (1989) 139–45.
11. Stokiey, S. D., Glastech. Ber. 32K, *5th International Congress on Glass*, Verlag der DKG, Frankfurt M., 1959, pp. V/1–8.