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Effect of Thermal-Shock and Autoclave Treatment on the Microstructure of Al_2O_3–ZrO_2 Composite

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Abstract: Al_2O_3–ZrO_2 composites prepared from calcined technical alumina and monoclinic zirconia showed typical microstructural evolution in repeated thermal-shock cycling tests. Circular stress contours were seen after the 5th cycle and microfissures appeared after 20 cycles. However, the composites retained 240–470 kg/cm^2 strength after 20 cycles. Both ZrO_2 and Al_2O_3 were hydrolysed on autoclave treatment. © 1996 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

Zirconia–alumina composites (ZAC) have excellent strength, toughness and thermal-shock resistance properties.[1,2] Room temperature applications in the form of abrasives,[3] cutting tools, ball bearings,[4] as well as high temperature applications, e.g. metal pouring nozzles, furnace construction materials,[5] are of significance. The zirconia dispersed phase may be present in the monoclinic or tetragonal form. The former phase contributes to microcracking toughening[6] and the latter phase is responsible for the stress-induced transformation-toughening effect.[7] During cooling from sintering temperature or on quenching of the composite, stresses and strains develop in the material because of the t → m ZrO_2 transformation and also the thermal expansion mismatch[8] between alumina and zirconia. As a result, the strength, toughness[8] and thermal-shock resistance of the composite increase. On repeated thermal cycling, microcracks and fissures develop.

Zirconia is susceptible to water and degrades by a multi-step process comprising chemisorption of water, hydroxylation, transformation of ZrO_2 and formation of cracks.[9,10] Incorporation of alumina or mullite or other solutes into zirconia suppresses its hydration-related degradation.[11–14]

The effect of repeated thermal-shock cycling on the strength and microstructure of two Al_2O_3–ZrO_2 (Y_2O_3) composites and the effect of hydration by autoclave treatment on these composites are presented in this article.

2 EXPERIMENTAL

Alumina, zirconia(m) and yttria were the raw materials. Two batch compositions were prepared from them (Table 1). Batches were wet ground in a pot mill for 30 h, dried and sieved. Bars of dimensions 78 × 18 × (4–5) mm^3 were prepared by uniaxial pressing at 650 kg/cm^2 followed by isostatic pressing at 3165 kg/cm^2 pressure. The samples were fired in an oil fired furnace at 1580–1600°C and soaked for 1.5 h.

The surface of the sample was ground with SiC powder (180–600 mesh), and annealed at 1140°C for 30 min.

The bars were subjected to repeated thermal cycling between 1200°C and room temperature in drought-free atmosphere. In each cycle the sample was held for 30 min at 1200°C before being quenched. The strengths of the samples were measured in an Instron machine before and after the thermal-shock test.

Table 1. Batch compositions

Raw material	Sample AZ1 (wt%)	AZ2 (wt%)
Al_2O_3	84.0	69.0
$ZrO_2(m)$	14.5	29.5
Y_2O_3	1.5	1.5

Fractured and polished surfaces of samples were etched by 20% HF at room temperature and seen under a scanning electron microscope. The powdered samples were subjected to X-ray diffraction analysis (XRD).

The bar samples were autoclaved at 170°C under 7 kg/cm^2 steam pressure for 10 and 20 h, respectively. These were visually examined, ground to −200 mesh (B.S.S.) powder, diluted with KBr, pressed into discs and their IR spectra were recorded.

3 RESULTS AND DISCUSSIONS

The crystalline phases in the as-fired samples, those subjected to 15 thermal-shock cycles and those after 10 h of autoclaving were identified by the XRD technique. The results are shown in Table 2 and Fig. 1. Comparison of the heights of peaks at 74.4 Å and 73.7 Å for ZrO_2 (t) and ZrO_2 (m), respectively, revealed that thermal-shock cycling caused almost complete transformation of tetragonal zirconia to the monoclinic variety. In the autoclaved samples, conversion of m → t form, occurred to a different extent. At the end of 10 h autoclave treatment, AZ1 contained (m) ZrO_2 as the major phase and (t) ZrO_2 as the minor, whereas AZ2 contained (t) ZrO_2 and (m) ZrO_2 in almost equal proportion. In all the samples α-Al_2O_3 was detected (by 42.4° 2θ /2.08 Å peak) in correct proportions with the batch compositions.

Polished section micrographs of the samples, AZ1, before thermal-shock, after 5 and after 20 thermal-shock cycles are shown in Fig. 2(a)–(d). The bright phase is ZrO_2, dark phase is pore and the alumina matrix is grey coloured. After 5 cycles, a peculiar feature of circular contour formation around pores was observed, these happened to be stress contours. The thermal expansion mismatch between α-Al_2O_3 (8.1–$9.1\times10^{-6}/°C$) and (t) ZrO_2 ($a_t = 11.6\times10^{-6}/°C$, $c_t = 16.8\times10^{-6}/°C$) aggravated the stress and caused contour formation. Pores served as sink for absorption of stress and strain. The effect of thermal-shock in the initial few cycles probably gave rise to this type of spherulite formation as a result of the accumulation of stress around pores before being absorbed there. The contrast of the stress contours was better revealed in the back-scattered image (Fig. 2(c)), compared with the secondary electron image (Fig. 2(b)). This suggested that the scattering of electrons was affected by stress contours. Stress/strain contours other than circular geometry were also shown by Wunderlich and Rühle,[15] as well as by Claussen and Jahn.[16]

Table 2. Crystalline phases in as-fired, quenched and autoclaved samples

Conditions	Samples AZ1	AZ2
As-fired	(t)-Z^H A, (m)-Z^T	(t)-Z^M A, (m)-Z^L
Quenched	(m)-Z^H (t)-Z^L A	(m)-Z^H (t)-Z^L A
Autoclaved (10 h)	(m)-Z^H (t)-Z^L A	(m)-Z^M (t)-Z^M A

Z, ZrO_2; A, Al_2O_3; H, High conc.; M, Medium conc.; L, Low conc.; T, Trace; (t), Tetragonal; (m), Monoclinic.

On further thermal cycling, the stress exceeded the stability limit and got released with the formation of microcracks. Consequently, microfissures were evident after 20 cycles (Fig. 2(d)). It was shown earlier[2] that pore size increased with the progress of thermal-shock cycling and pseudoplasticity developed in the samples.

The autoclaved samples were free from crazes and cracks. The infrared spectra of the ground material (AZ1 and AZ2) are shown in Fig. 3(a) and (b). There are peaks at 460 cm^{-1} for ZrO_2, at

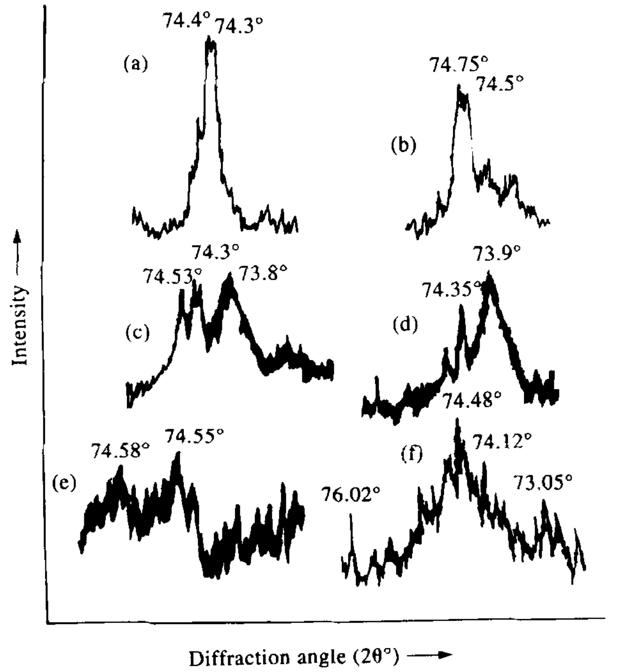

Fig. 1. High angle XRD peaks of samples: as-fired (AZ1 = a, AZ2 = b); quenched for 15 cycles (AZ1 = c, AZ2 = d); autoclaved for 10 h (AZ1 = e, AZ2 = f).

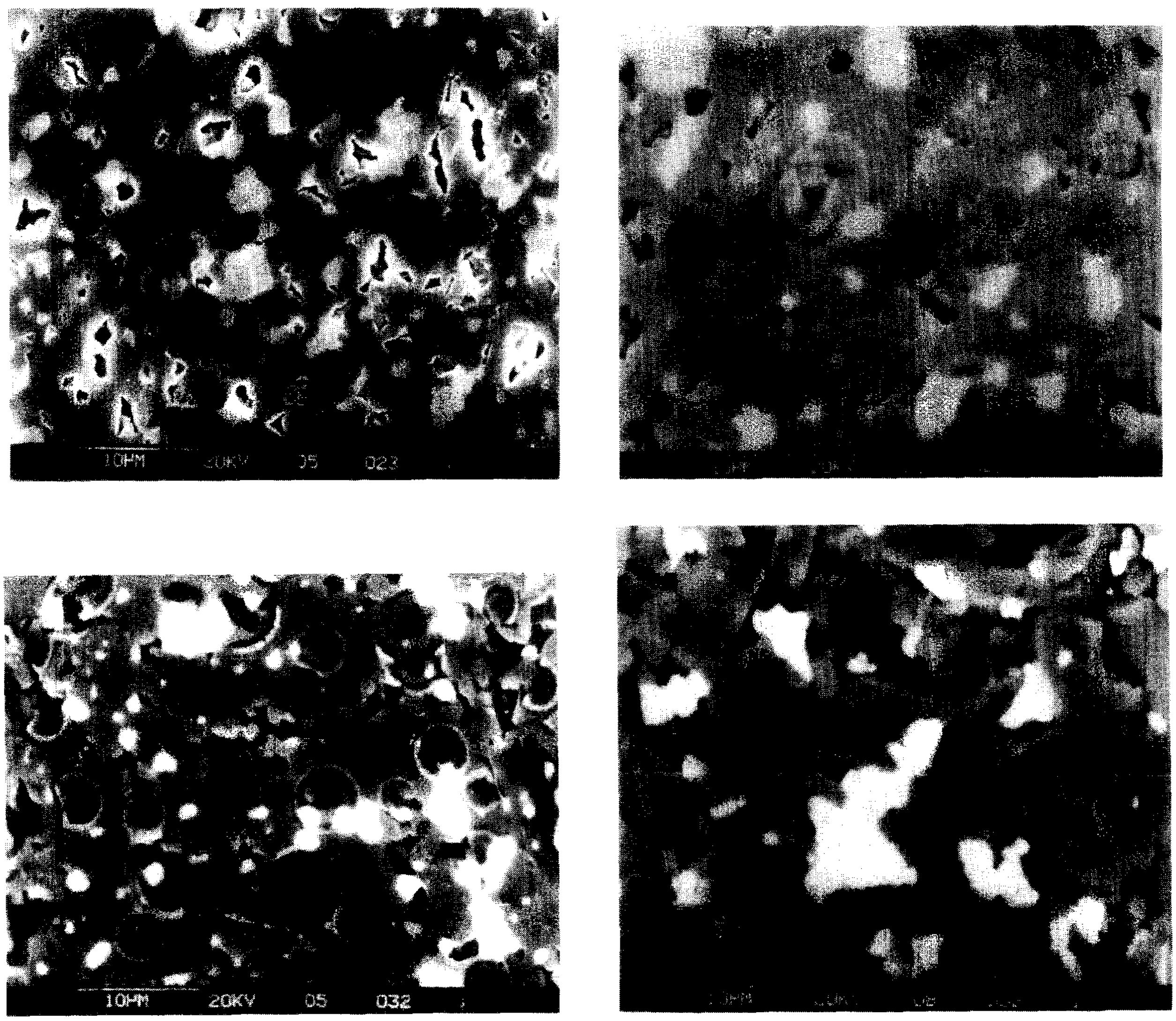

Fig. 2. SEM micrographs of AZ1 sample: (A) secondary electron image of as such sample; (B) secondary electron image of sample after 5 quench cycles; (C) back-scattered image of sample after 5 quench cycles; (D) back-scattered image of sample after 20 quench cycles.

650 cm^{-1} probably caused by the Al–O–Al bond, at 1090 cm^{-1} probably the result of the Al–O–Zr coupling, at 1630 cm^{-1} for the bending vibration of OH^{-1} group and at 3500 cm^{-1} for the stretching vibration of absorbed water. After heating the autoclaved samples at 1000°C, the peaks at 1630 cm^{-1} and 3500 cm^{-1} persisted (Fig. 3(c)). But after heating at 1200°C for 1 h these two peaks at 1630 cm^{-1} disappeared (Fig. 3(d)).

Sen and Thiagrajan[17] also observed the disappearance of the 1630 cm^{-1} IR absorption peak of Al-hydroxide on heat-treatment at 1200°C, which existed, however, even at 1000°C. Actually, bauxite and gibbsite lost their hydroxyl groups between 1000 and 1100°C,[18] $Zr(OH)_4$ decomposed between 300 and 500°C and fused before 900°C. No hydroxyl group retention was possible at 1000°C for $Zr(OH)_4$. So, hydroxylation of both ZrO_2 and Al_2O_3 probably took place during autoclaving. The 1090 cm^{-1} peak in the present case was probably not caused by the Si–O–Si bond, but by the Al–O–Zr coupling.

4 CONCLUSIONS

Thermal-shock resistance and hydration resistance of alumina–zirconia composites were found to be good. The strength degraded on thermal-shock cycling even from the 3rd quench cycle and steadily decreased with the progress of quench cycles.

An interesting phenomenon of circular stress contour formation around pores was revealed after the 5th cycle in AZ1 sample. With an increasing number of cycles, the stress was released with the formation of microcracks. Microfissures developed after the 20th cycle. Despite this, the sample retained 438 kg/cm^2 load bearing capacity.

On autoclaving the samples at 170°C–7 kg/cm^2 steam pressure, hydration of both alumina and

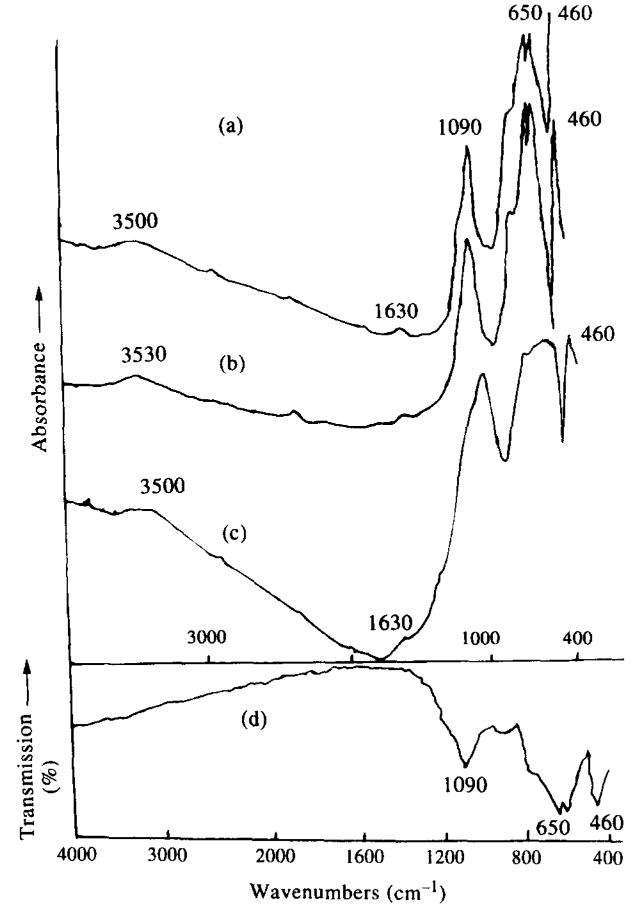

Fig. 3. Infrared spectra of autoclaved and heat treated AZ1 and AZ2 samples: (a) AZ2, autoclaved 10 h; (b) AZ1, autoclaved 10 h; (c) AZ1 autoclaved, heat treated at 1000°C, 2 h; (d) AZ1 autoclaved, heat treated at 1200°C, 1 h.

zirconia was observed and confirmed by infrared spectroscopy. The autoclaved samples were free from crazes and cracks.

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REFERENCES

1. HORI, S., KURITA, R., YOSHIMURA, M. & SOMIYA, S., Influence of small ZrO_2 additions on the microstructure and mechanical properties of Al_2O_3. In *Advances in Ceramics, Vol. 24, Science and Technology of Zirconia III*, ed. S. Somiya, N. Yamamato & H. Yanagida. American Ceramic Society, Westerville, OH, 1988, pp. 423–30.
2. MITRA, B. L., BISWAS, N. C. & AGGARWAL, P. S., Thermo-mechanical properties and microstructure of alumina–zirconia. *Bull. Mater. Sci.*, **15**(2) (1992) 131–41.
3. GARVIE, R.C., Structural applications of zirconia bearing materials. In *Advances in Ceramics, Vol. 12, Science and Technology of Zirconia II*, ed. N. Claussen, M. Rühle & A. H. Heuer. American Ceramic Society, Columbus, OH, 1984, pp. 465–79.
4. LANGE, F., Higher strength and toughness achieved in alumina–zirconia composites. *Mater. Eng.*, **93**(4) (1981) 102.
5. KOEHLER, R. K., The structure and properties of refractory ZrO_2 ceramics — II. Applied investigations. *Ceram. Int.*, **10**(2) (1984) 66–74.
6. ONO, T., NAGATA, K., HASHIBA, M., MIURA, E., NURISHI, Y. & SHIMADA, T., Internal friction, crack length of fracture origin and fracture surface energy in alumina–zirconia composites. *J. Mater. Sci.*, **24** (1989) 1974–8.
7. HOMERIN, P., THEVENOT, F., ORANGE, G., FANTOZZI, G., VENDENEEDE, V., LERICHE, A. & CAMBIER, F., Mechanical properties of zirconia-toughened alumina prepared by different methods. *J. de Physique C1*, **47**(2) (1986) 717–21.
8. BURESH, F. E., Microcrack extension in microcracked dispersion toughened ceramics. *Adv. in Ceram.*, **12** (1984) 306–21.
9. YOSHIMURA, M., NOMA, T., KAWABATA, K. & SOMIYA, S., Role of H_2O on the degradation processes of Y–TZP. *J. Mater. Sci. Lett.*, **6** (1987) 465–7.
10. YOSHIMURA, M., Phase stability of zirconia. *Am. Ceram. Soc. Bull.*, **67**(12) (1988) 1950–5.
11. HIRANO, M. & INADA, H., Fabrication and properties of yttria- and ceria-doped tetragonal zirconia/alumina composites. *Brit. Ceram. Trans. J.*, **90** (1971) 48–51.
12. MITRA, B. L., BISWAS, N. C. & AGGARWAL, P. S., Thermal and hydrothermal properties and microstructure of zirconia–alumina–mullite. *Mater. Lett.*, **14** (1992) 50–4.
13. HIRANO, M. & INADA, H., Stability under hydrothermal conditions and fracture strength of Y–TZP/spinel–alumina and Y–TZP/mullite–alumina composites. *Brit. Ceram. Trans. J.*, **89** (1990) 214–17.
14. HIRANO, M., Inhibition of low temperature degradation of tetragonal zirconia ceramics — A review. *Brit. Ceram. Trans. J.*, **91** (1992) 139–47.
15. WUNDERLICH, W. & RÜHLE, M., Critical stresses for microcracking in monoclinic zirconia. *Adv. in Ceram.*, **24** (1988) 509–15.
16. CLAUSSEN, N. & JAHN, J., Mechanical properties of sintered *in-situ* reacted mullite–ZrO_2 composites. *J. Am. Ceram. Soc.*, **63** (1980) 228–9.
17. SEN, S. & THIAGRAJAN, S., Phase transformations in amorphous $3Al_2O_3$–$2SiO_2$ system prepared by sol–gel method. *Ceram. Int.*, **14** (1988) 77–86.
18. WORRALL, W. E., *Clays and Ceramic Raw Materials*. Applied Science Publishers, London, 1975, p. 174.