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Thermal shock resistance of alumina–sialon composites

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The thermal shock behaviour of pure alumina and an alumina–sialon composite was examined. The critical temperature difference of the thermal shock, ΔT_c, had a good relationship with the calculated thermal shock resistance parameter, R. The thermal shock resistance of the composite was remarkably improved by simple modification, such as oxidation at 1400 °C for 100 h. The oxide layer, with porous microstructure, consisted mainly of mullite and a small amount of alumina. The ΔT_c of pure alumina, the composite and the oxidized composite was 210, 225 and 360 °C, respectively. This improvement was considered to be due to the characteristics of the oxide layer, which had high strength as well as a low elastic constant and a low thermal expansion coefficient.

1. Introduction

Alumina-base oxide ceramics are engineering ceramics which are widely used because of their superior mechanical and chemical properties. However, high temperature application of these ceramics require improvements in their thermal shock resistance and high temperature strength. Instead of alumina ceramics, sintered alumina–sialon composites [1], which maintain high strength up to 1400 °C, are considered as candidate materials for high temperature applications. Table I compares the mechanical and physical properties of pure alumina ceramics with the representative alumina–sialon composite, which were sintered at 1700 °C in a nitrogen atmosphere.

Thermal shock failure of ceramics is one of the main factors limiting their application [2, 3]. Up to the present, considerable efforts have been made to improve thermal shock resistance from the viewpoint of structure and material [4]. There are two parameters that govern the choice of ceramics with greater thermal shock resistance. One is the thermal stress fracture resistance parameter, applied to the crack initiation problem. The thermal shock resistance parameter is represented by [2, 3]:

$$R = S(1 - \nu)/(\alpha E) \qquad (1)$$

Where S is the tensile strength of the material, ν is Poisson's ratio, α the thermal expansion coefficient, and E the elastic modulus.

The other parameter is the thermal stress damage resistance parameter, applied to the crack propagation problem. This parameter is used to prevent catastrophic crack propagation of refractory bricks. The thermal shock resistance parameter is represented by [2, 3]:

$$R'''' = EG/[S^2(1 - \nu)] \qquad (2)$$

where G is the fracture surface energy.

The purpose of the present study is to estimate the thermal shock resistance of the alumina–sialon composite and to improve its resistance to fracture initiation. To avoid the initiation of thermal stress fracture, a low elastic modulus and high strength are required. Therefore, the composite was modified by heat treatment at 1400 °C for 100 h. The surface oxidation layer with micropores is expected to protect the inner ceramics from thermal stress fracture.

2. Experimental procedure

Five kinds of samples, shown in Table II, were prepared. Highly pure and fine Al_2O_3 powder (Taimei Kagaku Co., Ltd, Japan, TM-D) was used for an

TABLE I Comparison of the mechanical and thermal properties of pure alumina ceramics and alumina–sialon composite [1]

	Pure alumina	Composite
Composition (%)		
alumina	100	68
sialon	–	32
Density (g cm^{-3})	3.94	3.60
Elastic modulus (GPa)	330	275
Poisson's ratio	0.22	0.23
Vicker's hardness (GPa)	15.80	17.20
K_{IC} (MPa m$^{0.5}$)	3.50	4.30
Bending strength (MPa)		
At 20 °C	255	460
At 1200 °C	155	335
At 1400 °C	140	300
Oxidation weight gain 1400 °C, 150 h (mg cm^{-2})	–	0.5
Thermal expansion coefficient RT – 1000 °C (10^{-6} K^{-1})	8.3	6.6
Thermal diffusivity (10^{-6}m^{2}s^{-1})	8.9	4.6
Relative dielectric constant	9.7	8.9

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TABLE II Preparation conditions of samples

Sample	Material	Conditions
A	pure Al_2O_3	1400 °C, 2 h, in air
B	pure Al_2O_3	1600 °C, 4 h, in air
C	composite	1600 °C, 2 h, in nitrogen gas
D	composite + oxidized surface	1600 °C, 2 h, in nitrogen gas + 1400 °C, 100 h, in air
E	oxidized composite	1600 °C, 2 h, in nitrogen gas + 1500 °C, 100 h, in air

TABLE III Density and strength of specimens

Sample	Density ($g\,cm^{-3}$)	Mean strength (MPa)
A	3.98	578
B	3.97	357
C	3.55	439
D	3.49	499
E	2.75	131

Al_2O_3 source, which can be sufficiently densified at 1400 °C. The starting powder composition of the composite was Al_2O_3:Si_3N_4:AlN = 80:17.5:2.5 (wt %). Thirty two per cent sialon coexisting with alumina was produced by this composition in the sintered body [1], and some of its properties are presented in Table I. Fine powder Si_3N_4 (Ube Industries, Ltd, Japan, SN-E10) and AlN (Tokuyama Soda Co., Ltd, Japan, F-grade) were used as starting materials. The powders were mixed for 20 h in a polyethylene container using nylon-coated iron balls and ethyl alcohol as a mixing fluid. The resultant slurry was dried and then sifted. The sifted powder was compacted to 60 × 50 × 8 mm by die pressing, followed by cold isostatic pressing under at 300 MPa.

Al_2O_3 was sintered for 2 h in air under two temperature conditions (samples A and B). The composite was put in a hexagonal boron nitride container and sintered in a nitrogen atmosphere (sample C). The machined composite specimens for the bending test were heat-treated at 1400 °C for 100 h in air (sample D). Completely oxidized composite specimens were prepared for characterizing the oxide layer. Thin composite specimens (4 × 0.5 × 40 mm) were heat-treated at 1500 °C in air for 100 h.

The density of the sintered specimens was measured by the Archimedes method. Rectangular bars of 3 × 4 × 40 mm were cut from the sintered specimen for the bending test and the thermal shock test. The bars were finished with a 600-grid diamond wheel along the longitudinal direction, and the edges were bevelled. Four-point bending strength was measured for ten bars of each sample at room temperature. The inner and outer spans were 10 and 30 mm, respectively, and the cross head speed was set at 0.5 mm min^{-1}.

A thermal shock test was carried out for samples A, C and D. Three to five test bars for each sample were held in a furnace for 30 min and dropped into the water bath which was maintained at 20 °C. The cracks caused by thermal stress were optically examined with a dye penetrant. The bending strength was measured after the thermal shock test.

3. Results

The densities and the mean strengths are shown in Table III. Sample A had a strength of 578 MPa, which was much higher than those of sample B and higher also than those of ordinary alumina-base ceramics sintered at about 1600 °C. Sample B was considered to have been over-fired, and its strength was decreased by grain growth.

The oxidized sample D was 10% stronger than sample C. The strength of sample E was about one third of that of the composite.

Fig. 1 shows scanning electron microscope (SEM) images of a section of sample D. The oxide layer, with numerous micropores, was about 50 μm thick and was uniformly produced on the composite. The grain and pore sizes of the completely oxidized sample E were about ten times larger than those of sample D, because sample E was heat-treated at a temperature 100 °C higher than sample D.

Fig. 2 shows the residual room temperature strength after the thermal shock test. The ΔT_c was determined as 210 °C from Fig. 2a, and it agreed well with the reported one [5]. The ΔT_c of the composite was 225 °C, as can be determined from Fig. 2b, and the residual strength strongly scattered near the ΔT_c. Thermal shock resistance was drastically improved in the case of sample D, and its ΔT_c was determined as 360 °C from Fig. 2c.

The specimens whose strength decreased after the thermal shock test corresponded to those with macrocracks caused by thermal stress, which were optically observed using a dye penetrant. Sample D had high strength and superior thermal shock resistance compared with ordinary alumina-base ceramics.

4. Discussion

4.1. Features of the oxidized surface

The oxide layer was found to be composed mainly of mullite and a small amount of α-alumina by the X-ray diffraction method. It was considered that oxidation of the composite produced 76 wt % mullite and 24 wt % alumina. The theoretical density of this mullite-base oxide could be calculated at 3.32 $g\,cm^{-3}$. The density of sample E was calculated to be 82.8% of the theoretical one. The open porosity measured by the Archimedes method for sample E was 1%. Therefore, numerous pores were considered to discontinuously exist in the oxidized specimen.

4.2. Strength of the oxidized surface layer

The strength of the oxide layer of sample D could not be measured in the present study, because it required 2000 h at 1400 °C to completely oxidize a 0.5 mm thick composite [1].

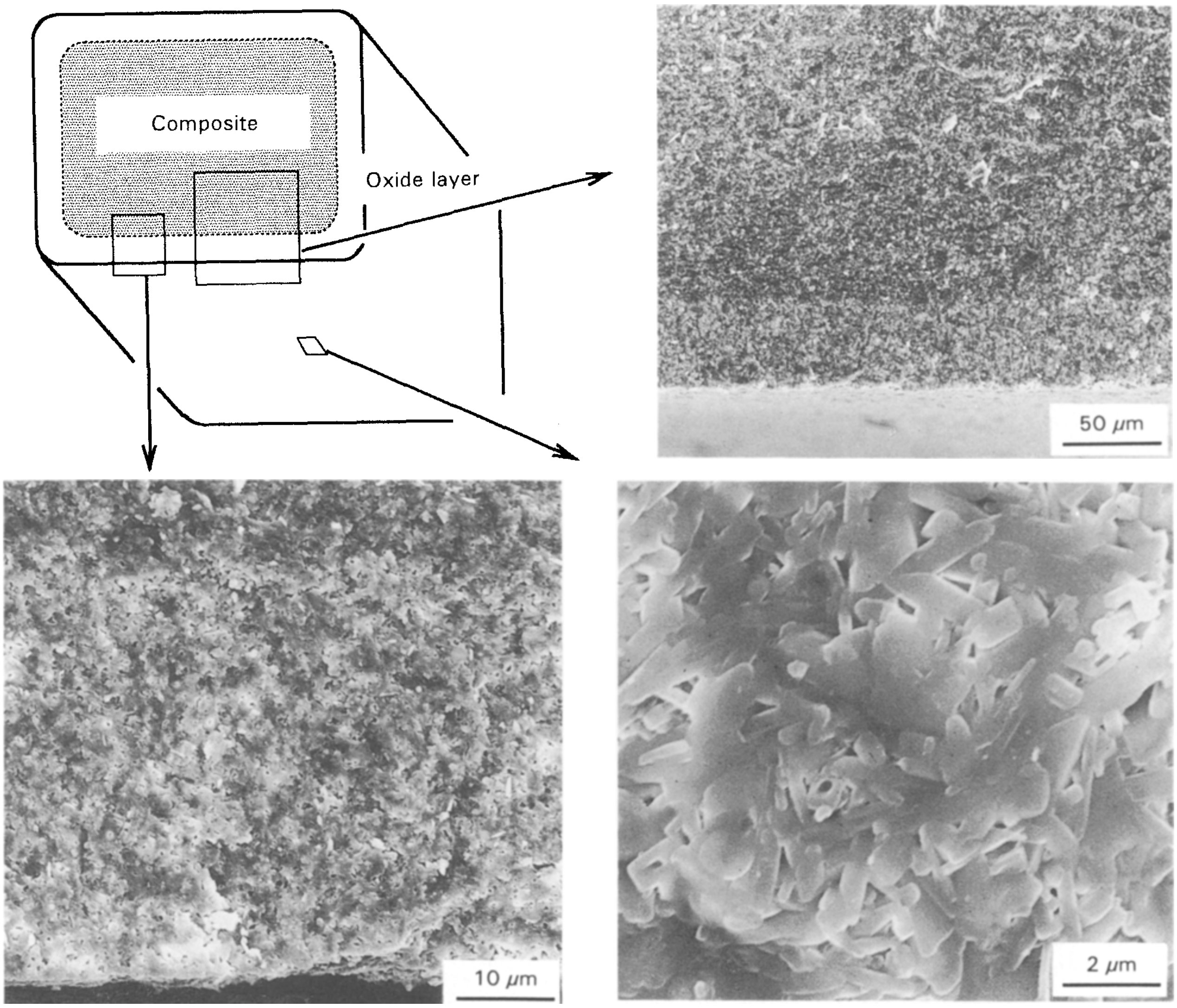

Figure 1 SEM images of the oxidized composite.

The strength of ceramics is usually related to the grain size as expressed by Orowan's equation:

$$S = k\,d^{-1/2} \qquad (3)$$

where S is the strength of the material, d the grain size, and k is constant. Using this equation and grain size observation, the strength of the surface oxide layer of sample D was estimated to be more than three times greater than that of sample E. It could be comparable to the strength of the composite.

Sample D was stronger than sample C. There are two important factors to consider in explaining the increase in strength by oxidation of the composite. The first factor is the production of a surface layer stronger than the composite. This is reasonable from the above discussion. The second factor is the surface compressive stress generated during cooling after heat treatment. The thermal expansion coefficient of mullite ($5 \times 10^{-6}\,K^{-1}$) is smaller than that of the composite ($6.6 \times 10^{-6}\,K^{-1}$). However, it is difficult to estimate the residual stress of the porous oxide layer. The contribution of the surface compressive stress was considered to be small, because the low elastic modulus oxide layer might be too thick to transfer the stress.

4.3. Comparison between the thermal shock resistance parameter, R and ΔT_c

Thermal shock resistance parameters for alumina and the composite were calculated by means of Equation (1) using the values of α, ν and E listed in Table I. The strength represented by the bending strength (Table III), instead of the unknown tensile strength, was used in the calculation and yielded R values of 165 and 186 K for samples A and C, respectively.

The ΔT_c of samples A and C was 210 and 225 °C, respectively, and thus correlates well with the calculated thermal shock resistance parameter,. R. The properties of the oxide layer of sample D are not yet known. However, the R of sample D was expected to have a high value because it contained the following superior properties:

1. High S: the surface layer may be as strong as the composite.
2. Small α: α of mullite is $5 \times 10^{-6}\,K^{-1}$.
3. Small E: E of mullite (230 GPa) is smaller than that of the composite and is further decreased by the porous structure of the oxide layer.

5. Conclusions

The thermal shock behaviour of pure alumina and an

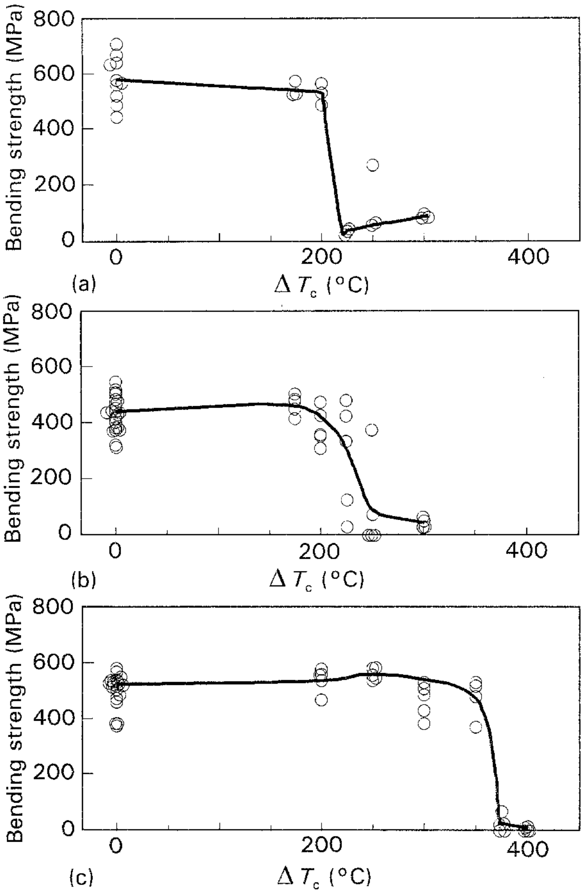

Figure 2 Residual strength of specimens after thermal shock testing for (a) alumina, (b) composite, and (c) oxidized composite.

alumina–sialon composite were examined. ΔT_c had a good relationship with the calculated thermal shock resistance parameter, R. The composite was heat-treated at 1400 °C for 100 h in air to improve thermal shock resistance. The composite surface was uniformly oxidized to give 50 μm thick oxide layer. The oxide layer had a porous microstructure, and consisted mainly of mullite and a small amount of alumina. The ΔT_c of the pure alumina, composite and oxidized composite was 210, 225 and 360 °C, respectively. It is noteworthy that the thermal shock resistance of the composite was remarkably improved by simple modification, such as oxidation. This improvement was considered to be due to the characteristics of the oxide surface layer, which had high strength, a low elastic constant and a low thermal expansion coefficient.

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References

1. K. TAKATORI, *J. Mater. Sci.* **26** (1991) 4484.
2. D. P. H. HASSELMAN, *Bull. Amer. Ceram. Soc.* **49** (1970) 1033.
3. J. NAKAYAMA, in "Fracture mechanics of ceramics", Vol. 2, edited by R. C. Bradt, D. P. H. Hasselman and F. F. Lange (Plenum Press, New York, 1974) pp. 759–778.
4. E. H. LUTZ, M. V. SWAIN and N. CLAUSSEN, *J. Amer. Ceram. Soc.* **74** (1991) 19.
5. T. K. GUPTA, *ibid.* **55** (1972) 249.

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