JOURNAL OF MATERIALS SCIENCE 30 (1995) 5121–5124

Fast firing of reaction-bonded aluminium oxide RBAO composites

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Al_2O_3/ZrO_2 composites have been prepared by fast firing of oxidized $Al/Al_2O_3/ZrO_2$ precursors produced by the reaction-bonded aluminium oxide (RBAO) technique. This fabrication route results in high-strength ceramics at relatively low densities. For example, after fast firing for 20 min at 1550 °C, RBAO containing 20 vol% ZrO_2 shows four-point bending strengths of > 600 MPa at a density of $\sim 95\%$ theoretical which is comparable to conventionally sintered RBAO.

1. Introduction

Nearly fully dense materials with fine microstructures and high strength can be manufactured by fast firing [1–7]. In this process, samples are inserted in a furnace preheated to the sintering temperature, held at that temperature for only a few minutes, and then rapidly cooled to room temperature. These conditions form the basis for improved materials properties and reduced manufacturing costs.

The effectiveness of the fast-firing process has been generally understood in terms of the difference in activation enthalpies of densification and coarsening at relatively high temperature [8], and transport of material by dislocation movement or plastic flow [9]. The generation of transient mismatch stresses inside the compact was recently proposed as complementary approach [7].

Very high heating rates, characteristic for the fast firing, generate large thermal stresses which can lead to thermal fracture. The maximum heating rate that a powder compact can withstand without fracturing depends on fracture strength, Young's modulus, thermal conductivity, and the linear coefficient of thermal expansion [10]. These parameters increase during sintering which, together with the presence of changing thermal gradients within the sample, make reliable calculation of the maximum possible heating rate very difficult. An additional problem arises from the fact that, in a crackless sample which was heated under the maximum heating rate and sintered, cracking can still occur during rapid cooling.

Improved thermal stress resistance of a powder compact requires an increase of its strength. It has been shown that green bodies with very high fracture strengths can be produced using the RBAO process [11]. Also, partially or fully oxidized RBAO bodies can attain strengths of 50–80 MPa, which is more than an order of magnitude higher than conventionally produced powder compacts. Therefore, RBAO processing is promising in preparing green bodies which can withstand high heating rates.

In the present work, samples fabricated by the RBAO process were sintered under extreme heating rate conditions and cooled rapidly in air. Microstructural characteristics and mechanical properties have been correlated and compared with samples of conventionally sintered RBAO.

2. Experimental procedure

Aluminium, Al_2O_3, and ZrO_2 powders were attrition milled in acetone for 7 h using 3 mm diameter TZP balls. The powders used, as well as the composition before and after oxidation, are listed in Table I. The mixture was then dried in air at room temperature and passed through a 200 μm sieve to break up agglomerates. Rectangular bars were formed by uniaxial pressing at 12.5 MPa followed by cold isostatic pressing at 300 MPa. The specimens were oxidized in air in a two-step heating cycle with heating rates of 2 °C min^{-1} (RT–400 °C) and 1 °C min^{-1} (400–1000 °C) (see also [12]). After oxidation, the samples were placed directly into the furnace which was already at the sintering temperature (up to 1700 °C). Assuming that the samples reach full temperature after 8–10 min, the effective heating rate is > 200 °C min^{-1}. After sintering for a certain period of time (1–30 min), the samples were taken out and air cooled. The free cooling to room temperature took about 10 min. The heating cycle for oxidation and fast firing is shown in Fig. 1.

After firing, specimens were ground and polished to dimensions of $3 \times 4 \times 30$ mm^3. The densities of green bodies and fast fired specimens were determined both geometrically and by Archimedes' principle. SEM investigations of polished surfaces were carried out with a Jeol SM840A microscope, and grain size was measured by the linear intercept method. Fracture strength of the samples was measured in four-point bending according to German standard DIN 51100, using reduced spans of 20 and 10 mm.

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TABLE I RBAO powder composition before and after oxidation

Material	Type and origin	Composition before oxidation (vol %)	Composition after oxidation (vol %)
Al	Alcan 105, Alcan Int., Canada	40	–
Al_2O_3	Ceralox MPA-4, Condea Chemie GmbH, Germany	40	84
ZrO_2	TZ-2Y, Tosoh Co., Japan	20	16

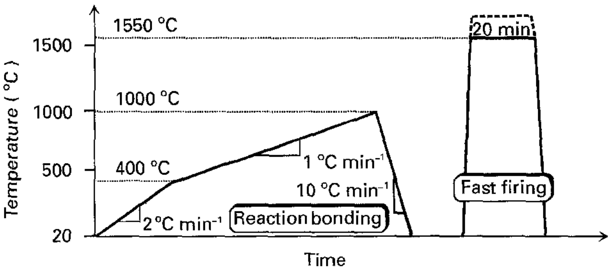

Figure 1 Two-step reaction bonding and fast firing cycle.

Phase content was characterized by X-ray diffraction (XRD) on both polished surfaces and fracture surfaces in order to detect the tetragonal (t) monoclinic (m) transformation of ZrO_2. The hardness was determined using a standard Vickers indentor with a 100 N load.

3. Results and discussion

Densities of green compacts and fully oxidized bodies attain values of 54% theoretical and 60% theoretical, respectively. The strength of oxidized bodies was 60 MPa. The sintered density for different fast-firing temperatures in Fig. 2 indicates that, for a hold time of 20 min, 1550 °C appeared to be the most suitable temperature resulting in samples with 95% theoretical density. Unlike conventional sintering of ceramic powder compacts, higher sintering temperatures do not increase the density but result in severe bloating of the samples (Fig. 3).

Bloating has already been described for conventionally sintered RBAO bodies which is due to water physically adsorbed or chemically bonded to the powder surface in the form of Al_2O_3–xH_2O or $Al(OH)_x$ [13]. Especially during fast firing, the outer part of the samples sinter first according to the temperature gradient forming a dense outer shell and a porous inner core [7]. The evaporation of trapped water or other fugitive species is hindered and, on further heating, the increasing gas pressure leads to superplastic deformation of the fine-grained samples known as "bloating" [13]. The results of fast fired RBAO indicate that transport processes out of the reaction-bonded ceramic body and early pore closure at the surface can be directly related to end density. This is confirmed by the Vickers hardness which gradually decreases from the surface (15.9 GPa) to the inner region (12.3 GPa). A schematic model is shown in Fig. 4.

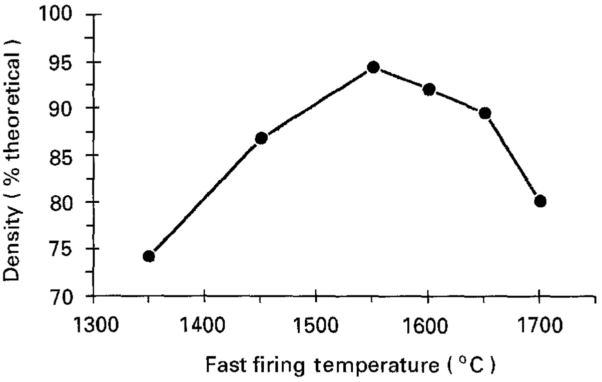

Figure 2 Density versus fast firing temperature for a hold time of 20 min.

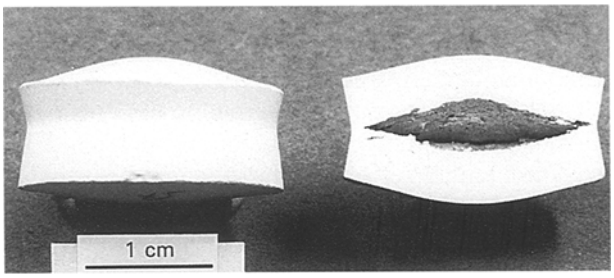

Figure 3 Bloated RBAO body after fast firing at > 1550 °C showing a large cavity in the centre.

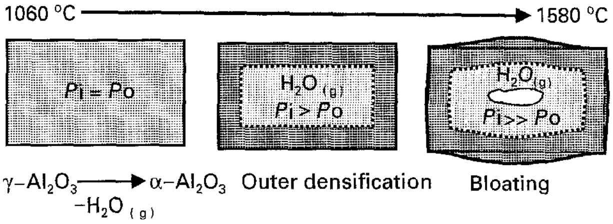

Figure 4 Schematic diagram of "bloating" of RBAO bodies due to moisture.

Thermogravimetric (TG) and differential thermogravimetric (DTG) measurements of oxidized samples ($T_{max} = 1000\,°C$) at temperatures from 20–1600 °C (Fig. 5) show that physically adsorbed water is removed at temperatures up to ≈350 °C, but chemically bonded water remains up to ≈1200 °C. The loss of chemically bonded water can be associated with phase transition(s) from δ- or θ-Al_2O_3 to α-Al_2O_3, as described by various authors [14–16]. In accordance with these phase transitions, the TG curve shows a considerable weight change of 0.24%, beginning at 1100 °C with a maximum at 1250 °C (DTG curve).

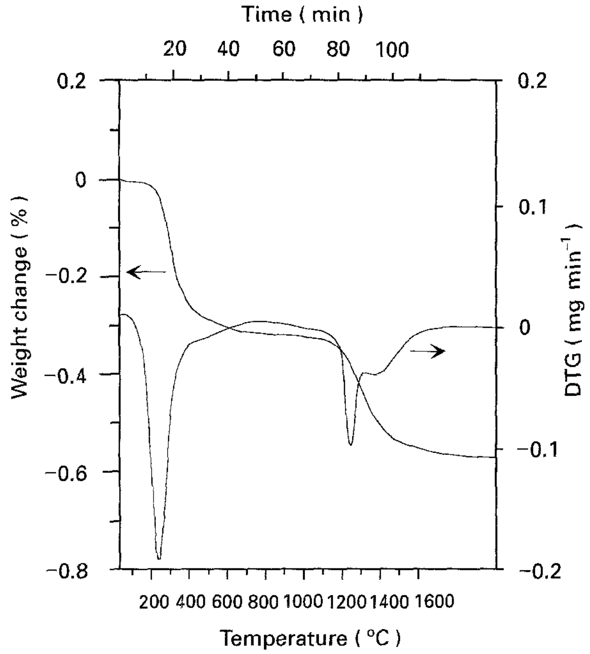

Figure 5 TG and DTG diagram for RBAO sample oxidized at $T_{max} = 1000\,°C$.

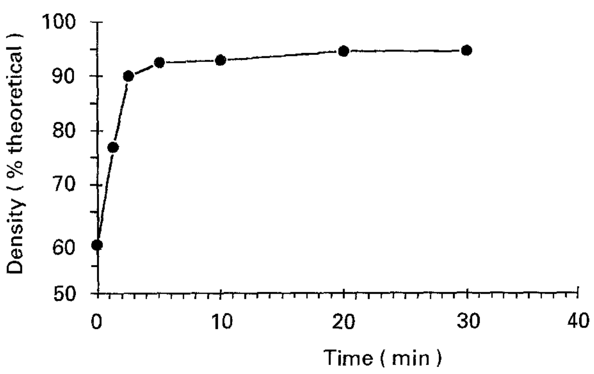

Figure 6 Density of fast fired samples as a function of sintering time ($T_{max} = 1550\,°C$).

Experiments with samples stored at 300 °C for several hours to remove the moisture were not successful.

Using the ideal gas equation and assuming that only 10% of the 0.24% water remains in the sample after pore closure as vapour, a simple calculation leads to an inner gas pressure of about 16 MPa. This calculation confirms that tiny portions of remaining water trapped in the sample are sufficient to cause bloating leading to a residual porosity, hence limiting the density to about 95% theoretical. As shown in Fig. 6, 90% theoretical density was reached after only 2 min sintering at 1550 °C and a sintering time of 20 min at this temperature was sufficient to attain the final density of 95% theoretical. Owing to the dense outer shell of the samples, extension of the sintering time cannot further increase the density.

Even though 95% theoretical density could not be exceeded, the strength of the fast fired samples reached values of 608 ± 79 MPa and is therefore similar to that of conventionally sintered RBAO [11]. The good mechanical strength is due to the very fine-grained microstructure with an average grain size of < 0.5 μm (see Fig. 7). Furthermore, the pores have small diameters and are homogeneously distributed. XRD investigations of fracture surfaces show no significant change in the amount of t- or m- ZrO_2 compared to polished samples Therefore, strengthening by transformation toughening does not occur in these samples.

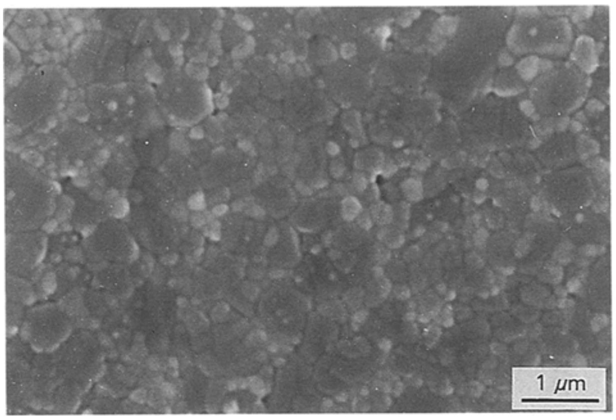

Figure 7 Microstructure of a fast fired RBAO body (1550 °C/ 20 min) showing an average grain size of 0.5 μm.

4. Conclusion

Al_2O_3/ZrO_3 composites have been prepared by fast firing of oxidized $Al/Al_2O_3/ZrO_2$ precursors produced by the RBAO technique. The samples were placed directly into the furnace which was already at the sintering temperature (up to 1700 °C) and after sintering for a certain period of time (1–30 min), were taken out and air cooled. Fast firing at 1550 °C for 20 min results in samples with 95% theoretical density. In spite of the remaining porosity, the bending strength of fast fired samples is > 600 MPa, similar to that of conventionally sintered RBAO bodies. Unlike conventional sintering of ceramic powder compacts, higher sintering temperatures do not increase the density but result in severe bloating of the samples during densification. The results indicate that transport processes out of the reaction-bonded ceramic body and early pore closure at the surface can be directly related to end density. Thermogravimetric measurements and calculations show that only tiny portions of the remaining water lead to bloating and incomplete densification.

5. Acknowledgement

Financial support by German Research Foundation (DFG) under contract Ja 655/4 is gratefully acknowledged.

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Received 22 December 1994
and accepted 28 April 1995