

Low-shrinkage Reaction-bonded Alumina

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Abstract

A novel method of manufacturing strong Al_2O_3 bodies with low (<1%) shrinkage is presented. Compacts of attrition-milled Al/ Al_2O_3 powder mixtures are heat treated at temperatures between 1200 and 1550°C such that the expansion due to the Al → Al_2O_3 reaction and the shrinkage on sintering of Al_2O_3 is nearly balanced. Depending on processing parameters such as Al/ Al_2O_3 ratio, compaction pressure and heating cycle, a variety of different microstructures can be developed. In spite of some residual porosity, strengths of ~300 MPa are attained.

Es wird ein neuartiges Verfahren zur Herstellung von Al_2O_3 -Keramiken beschrieben, bei dem sehr geringe (<1%) Schrumpfungen auftreten. Pulverpreßkörper aus attritierten Al/ Al_2O_3 -Mischungen werden bei Temperaturen zwischen 1200 und 1550°C reaktionsgebunden. Dabei wird die Sinterschrumpfung des Al_2O_3 durch die mit der Al → Al_2O_3 -Reaktion verbundene Volumenausdehnung kompensiert. Durch Variation des Al/ Al_2O_3 -Verhältnisses, des Preßdrucks und des Temperaturzyklus lassen sich unterschiedliche Gefüge einstellen. Trotz einer gewissen Restporosität werden Biegefestigkeiten von ~300 MPa erreicht.

On présente une nouvelle méthode de fabrication de pièces résistantes en alumine caractérisées par un faible retrait (<1%). Des compacts préparés à partir de mélanges de poudres Al/ Al_2O_3 ont subi un traitement thermique entre 1200 et 1550°C de telle sorte que l'expansion provoquée par la transformation Al → Al_2O_3 compense le retrait dû au frittage de l'alumine. Des microstructures différentes peuvent être obtenues en variant les paramètres d'élaboration tels que le rapport Al/ Al_2O_3 , la pression de com-

paction et le traitement thermique. Malgré la porosité résiduelle, des résistances mécaniques de l'ordre de 300 MPa ont été atteintes.

1 Introduction

The sintering of ceramic powder compacts usually involves linear shrinkage of 10–20% causing such well-known problems as shape distortion or cracking and, in the case where non-yielding second-phase constituents are to be incorporated, limited densification and harmful residual stresses. These problems do not exist, however, with melt-oxidation derived composites^{1,2} or with some reaction-formed non-oxide ceramics,³ e.g. reaction-bonded Si_3N_4 (RBSN). It appears obvious to apply RBSN-type technology to metal powder compacts for manufacturing oxide ceramic bodies if small dimensional changes are required. However, due to the large exothermic heats associated with the oxidation reaction of some fine metal powders or to the rapid surface passivation of larger metal particles, the respective processes are difficult to control. Exploratory experiments, however, have indicated that, when attrition-milled Al/ Al_2O_3 powder mixtures are used with small additions of wetting elements, strong fully-reacted Al_2O_3 bodies can be readily fabricated with virtually no dimensional changes between the green compact and the reaction-bonded product.

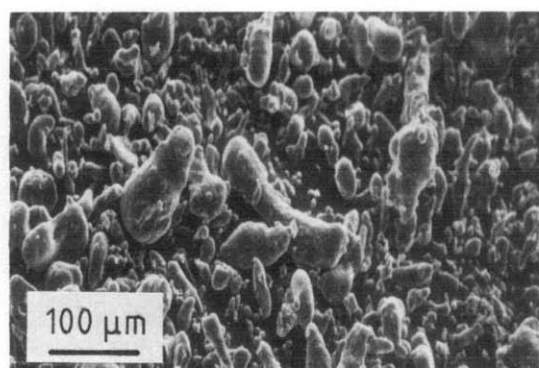
The present paper reports on a method for preparing low-shrinkage Al_2O_3 bodies emphasizing processing aspects. It will be shown that the heating cycle, the Al_2O_3 particle size, the Al/ Al_2O_3 ratio and the compaction pressure are important parameters controlling the microstructure development. Even though strengths comparable to those of conventionally sintered Al_2O_3 have been obtained, the

process conditions chosen for most of the experiments are far from being optimized. The bonding mechanism, which, in the temperature range employed, results from a combination of the $\text{Al} \rightarrow \text{Al}_2\text{O}_3$ reaction and of sintering, is also still unclear. Depending on the type of heating cycle, the stages of sintering and reaction can either be superimposed or separated.

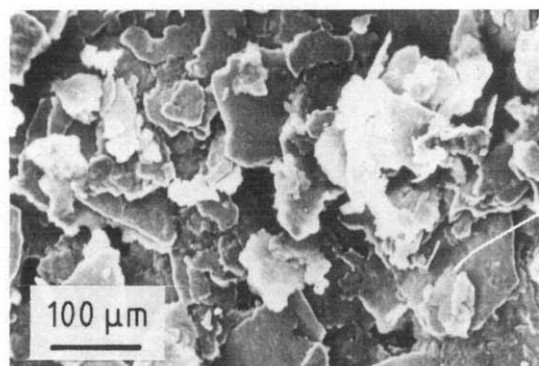
2 Experimental Procedure

Two aluminium powders were used in this study: globular particles (>99% Al, Aldrich-Chemie GmbH, FRG) with diameters between 20 and 200 μm , and flakes (Al, 'fein gepulvert', E. Merck AG, Darmstadt, FRG) with diameters in the range from 30 to 300 μm and thicknesses in the range 3 to 5 μm (Fig. 1). In order to improve the wetting and reaction behavior,¹ 5% wt Si, 2.5% wt Mg and 1% wt Zn powder (E. Merck AG, Darmstadt, FRG) were added to the Al powder. The metal powders were admixed to either a fine Al_2O_3 powder (Alcoa CT-1000, The Aluminum Co. of America, USA) (1 μm) or a coarse Al_2O_3 abrasive (F500/13, H. C. Starck, Berlin, FRG) (13 μm) in amounts between 25 and 40% vol. The majority of the experiments were carried out using a composition of 35% vol. Al flakes with the coarse Al_2O_3 powder (labelled 35C). In two cases, 10% vol. ZrO_2 powder alloyed with 3% mole Y_2O_3 (TZ-3Y, Tosoh, Tokyo, Japan) or 15% vol. Al_2O_3 platelets (Al-13pl, Showa Aluminum Industries KK, Tokyo, Japan) were respectively added to the 35C composition. The powder mixtures were attrition milled in either distilled water, acetone or isopropanol in UHMW polyethylene containers using 3 mm TZP balls. After milling for 1 to 12 h (the platelets being added for the last 30 min of the milling time), the powder mixtures were dried in a rotary vaporizer. The mixtures were isostatically pressed at 200–900 MPa to form square section bars of 24 mm \times 4 mm \times 4 mm. The samples were machined in the green state, and the exact dimensions were measured with a micrometer before heat treatment.

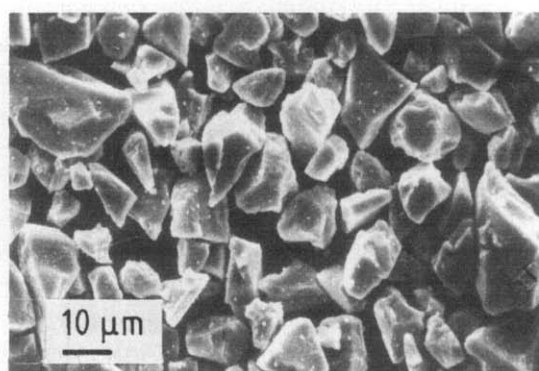
Shrinkage–heating cycle studies were carried out in a vertical dilatometer (Bähr Gerätebau GmbH, Hüllhorst, FRG) in air at temperatures between 1000 and 1500°C with different heating rates. The microstructural development was studied by optical microscopy using resin infiltrated partially or fully reacted samples. Specimens for physical property measurements were reaction-bonded in a box furnace by applying a heating cycle consisting of a



(a)



(b)



(c)

Fig. 1. SEM micrographs of the powders used in this work. (a) Globular Al particles; (b) Al flakes; (c) Al_2O_3 abrasive grains (13 μm).

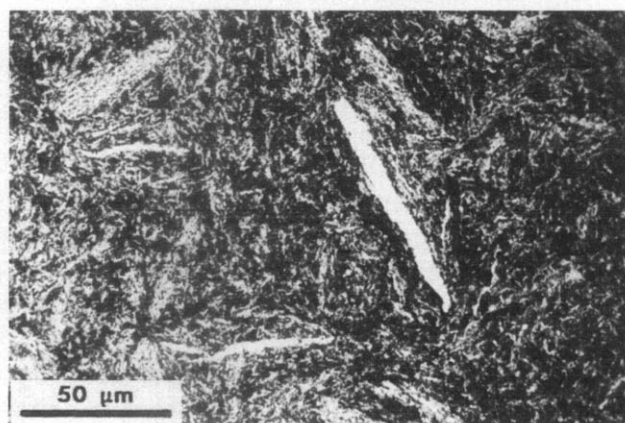
heating rate of 5°C/min, with a first hold at 1200°C for 8 h, a second hold at 1550°C for 3 h, and a cooling rate of 15°C/min. After complete reaction, the sample dimensions were again measured. Phase content and microstructure were characterized by XRD, SEM and TEM.

The fracture strength and chevron-notch toughness (K_{Ic}) of samples ground and polished to dimensions of 22 mm \times 3.5 mm \times 3.5 mm were determined in four-point bending using an inner and outer span of 18 and 6 mm, respectively. The thermal shock behavior was examined by quenching samples from different temperatures into room-temperature water and then measuring the retained strength.

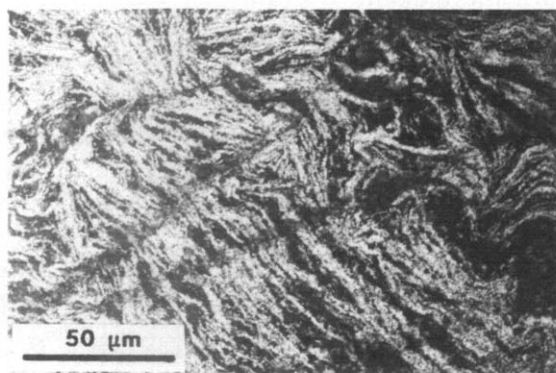
3 Results and Discussion

3.1 Powder mixture processing

The main purpose of this study was to find milling conditions which would strongly reduce the Al particle size without converting too much into either Al_2O_3 or $\text{Al}(\text{OH})_3$. When flaky Al was attrition milled with fine Al_2O_3 powder in isopropanol or acetone, flake-like shapes were always retained in the green compacts as shown in Fig. 2(a), even after milling for 12 h. A similar microstructure was developed when globular Al powder was used (Fig. 2(b)). Hence combined milling with fine Al_2O_3 resulted in repeated plastic deformation of the Al particles without effective comminution; this may be due to a buffer effect of the submicron Al_2O_3 powder and to continued cold welding of fractured Al flakes. When water was used as milling fluid, the Al particles were successfully broken; however, the conversion to Al_2O_3 and $\text{Al}(\text{OH})_3$ was rapid, i.e. after 1 h, all flakes and, after 3 h, all globular Al particles were reacted to essentially $\text{Al}(\text{OH})_3$. Owing to the low density of $\text{Al}(\text{OH})_3$ (2.42 g/cm^3) the amount of shrinkage would increase on sintering



(a)



(b)

Fig. 2. Green compact of 35% vol. Al/65% vol. fine Al_2O_3 powder mixture milled for 8 h in isopropanol and isopressed at 700 MPa. (a) Using Al flakes; (b) globular particles.

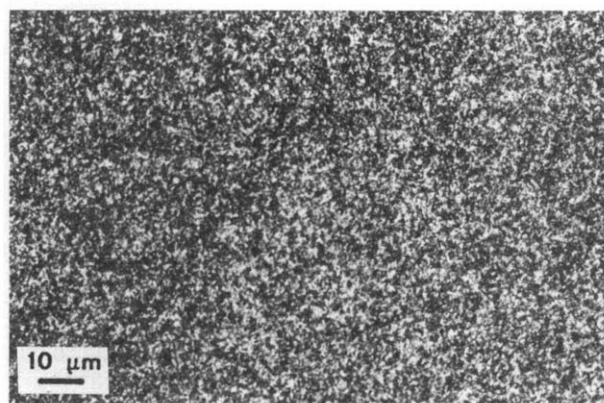


Fig. 3. Green compact 35C composition milled for 8 h in acetone and isopressed at 700 MPa.

this material which would be counter to the general idea of this work.

Comminution and homogenization of Al was much more successful when flakes were milled with the coarser Al_2O_3 powder in either acetone or isopropanol. The $13 \mu\text{m}$ abrasive Al_2O_3 grains obviously acted as additional milling media cutting the Al particles into smaller pieces and, at the same time, preventing any rewelding. The size of the Al flakes was rapidly reduced, i.e. after 2 h to $<10 \mu\text{m}$. After 8 h, all Al particles were $\leq 5 \mu\text{m}$ and homogeneously dispersed (Fig. 3) without development of the flaky microstructure that had been observed with the fine Al_2O_3 compositions. At the same time, the Al_2O_3 particles attained a size of $\sim 1 \mu\text{m}$. Prolonged milling, e.g. for 12 h, did not result in noticeable changes in the green microstructure. The amount of Al converted to either Al_2O_3 or $\text{Al}(\text{OH})_3$ was $<1\%$ after milling for 8 h in acetone.

3.2 Heat treatment

The dilatometer results indicate that different mechanisms are active in the dimensional change and reaction bonding process of the Al/ Al_2O_3 composites (Fig. 4). Between room temperature and 550°C , the sample expands slightly due to the larger coefficient of expansion of Al when compared to the Al_2O_3 reference sample. At 550 to 950°C , some rearrangement on melting of the metal phase takes place associated with a small shrinkage. At temperatures $>950^\circ\text{C}$ and, more rapidly, $>1100^\circ\text{C}$, the molten Al is oxidized, probably forming a Laxide-type¹ reaction product, leading to an expansion of the sample. This reaction stage stretches over a long period of time when the temperature is held at $\leq 1250^\circ\text{C}$, e.g. at 1200°C for 8 h as shown in Fig. 4(a). It is expected that the expansion will continue (c.f. dashed curve in Fig. 4(a)) until the melt-oxidation

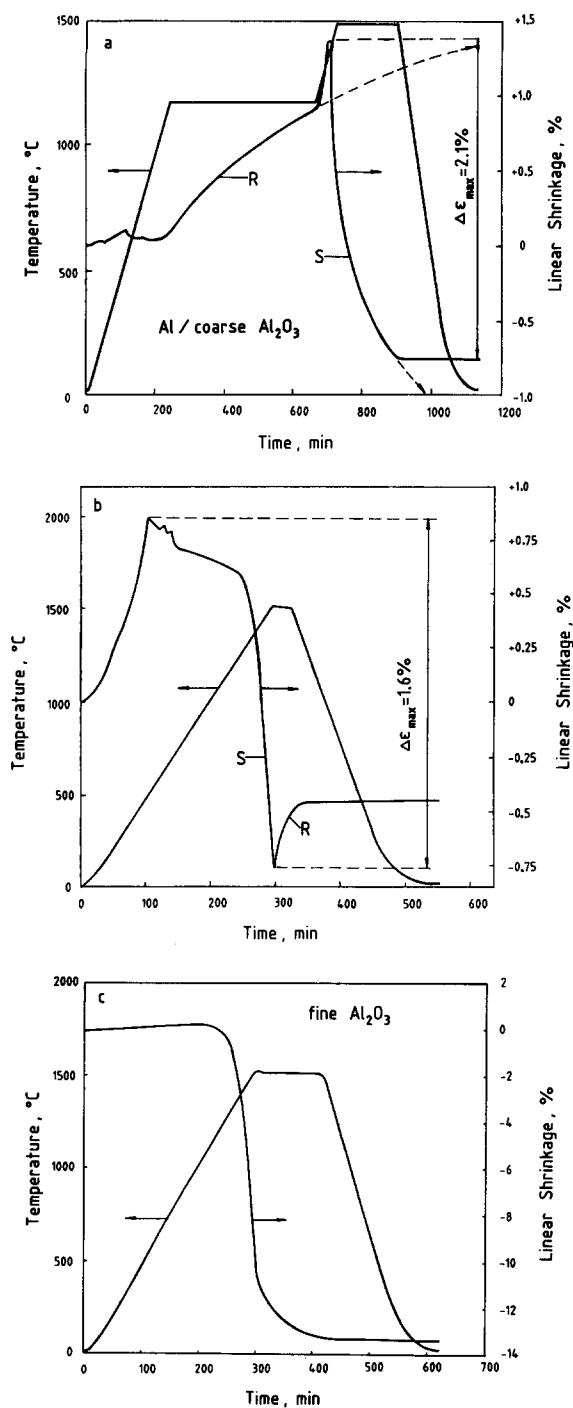


Fig. 4. Dilatometer diagrams of two different Al/Al₂O₃ compositions and of Al₂O₃ alone, milled for 8 h in acetone and isopressed at 700 MPa. (a) Composition 35 C (35% vol. Al flakes and 65% vol. coarse Al₂O₃) heat treated in two steps, i.e. first reacted (R) at 1200°C and then sintered (S) at 1500°C. (b) Composition of 35% vol. Al flakes with 65% vol. fine Al₂O₃ heat treated in one step, i.e. 30 min at 1500°C, resulting in rapid sintering (S) before reaction (R) of the molten Al. (c) Sintering of fine Al₂O₃ powder.

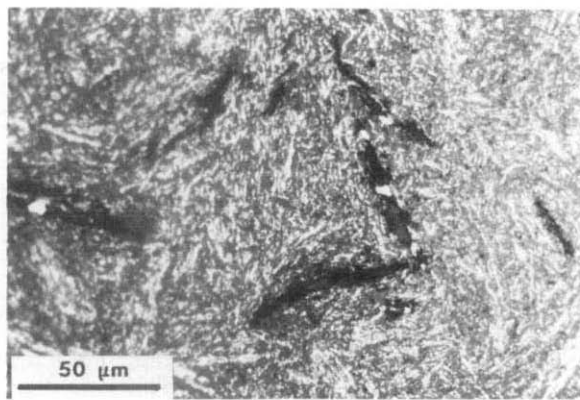
reaction is complete, reaching a total of $\sim 1.4\%$ for the 35 C composite isopressed at 700 MPa. When the temperature is taken to $>1250^\circ\text{C}$, e.g. to 1500°C as shown in the diagram of Fig. 4(b), without the low-temperature hold, the reaction step is overrun by the much faster shrinkage resulting from sintering of the

Al₂O₃ in Fig. 4(c). In this case, the reaction process occurs essentially after sintering and is completed at a much slower rate than when the reaction occurs before sintering. Since most pores are closed during sintering, the Al \rightarrow Al₂O₃ reaction must proceed mainly by oxygen diffusion along the Al₂O₃ grain boundaries.

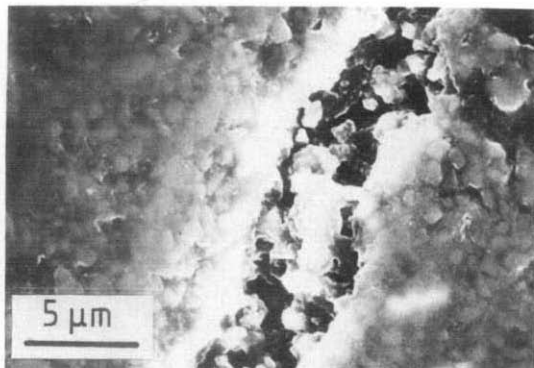
The macroscopic appearance of the cross-section at different stages during the heating cycle demonstrates that the reactions start from the surface of the sample and proceed inward with relatively well defined boundaries. For instance, at the beginning of the 1200°C hold (c.f. Fig. 4(a)), the cross-section exhibits a thin white skin with a dark metallic interior typical for melt-oxidation derived composites. After 8 h at 1200°C , the dark inner core has shrunk to about 1/4 of the area, and, after the complete cycle, the sample is thoroughly white, i.e. the Al has been completely reacted to Al₂O₃. For the case where the sample is taken rapidly to 1500°C (c.f. Fig. 4(b)), the black inner core still covers about half of the area after 8 h and only disappears after annealing at 1500°C for times >24 h. Thus rapid sintering results in premature pore closure preventing the direct access of oxygen to the aluminium.

The results discussed so far indicate that a number of different microstructures can be obtained depending on the specific heating cycle. However, for the present purpose of fabricating a low-shrinkage pure α -Al₂O₃ body, a cycle favoring a reaction before sintering appears to be preferable. Hence only this type of heat treatment has been applied in preparing property measurements of samples. It is important to recognize, however, that multi-step or rate-controlled type heat treatments may be superior in conferring densification and strength. It is also probable that an annealing cycle which can lead to simultaneous reaction and sintering, i.e. a combination of the two strain curves in Fig. 4(a) and (b), can reduce the maximum strain difference, $\Delta\epsilon_{\text{max}}$. The relevance of $\Delta\epsilon_{\text{max}}$ is for the incorporation of large second-phase components; for the sample shown in Fig. 4(a), $\Delta\epsilon_{\text{max}} = 2.1\%$, and for that in Fig. 4(b), $\Delta\epsilon_{\text{max}} = 1.6\%$. These values are, however, far below those typical for conventionally sintered Al₂O₃ ($\sim 14\%$ in Fig. 4(c)). As indicated by the dashed extension of the sintering part of the curve in Fig. 4(a), the sample (density 93% theoretical density) is expected to continue to shrink during non-prolonged holding at 1500°C , e.g. to $\sim 1.5\%$.

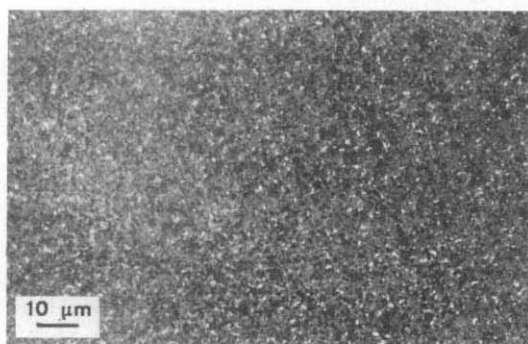
Microstructures of samples heated to 700°C are given in Fig. 5. In composites with fine Al₂O₃ powder where large aluminium flakes remain after the milling process (c.f. Fig. 2(a)), the aluminium



(a)



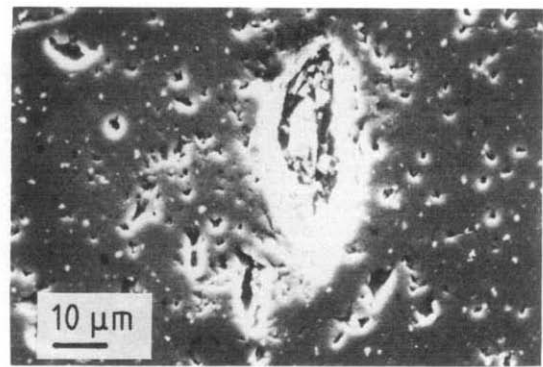
(b)



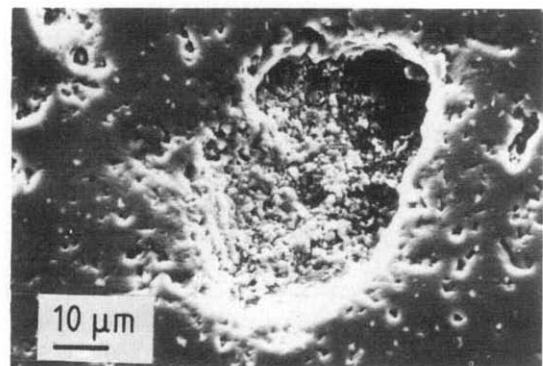
(c)

Fig. 5. Samples heated to 700°C. (a) Optical micrograph of composite as given in Fig. 2(a); (b) SEM micrograph of same; (c) optical micrograph of composite as shown in Fig. 3.

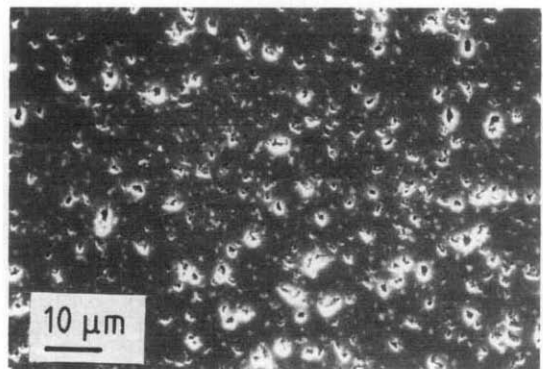
infiltrates the surrounding area leaving cavities with the shape of the original flakes (Fig. 5(a) and (b)). These cavities persist even after the complete heating cycle (Fig. 6(a) and (b)). As indicated in Fig. 5(c), this type of infiltration is not observed in composites with coarse Al_2O_3 where the Al particles are homogeneously dispersed (c.f. Fig. 3). These samples also exhibit an even distribution of fine ($<5\ \mu\text{m}$) pores (Fig. 6(c)) when heated according to the schedule given in Fig. 4(a). Small aluminium droplets are apparently not drawn into the surrounding porous powder matrix by capillary forces, i.e. the



(a)



(b)



(c)

Fig. 6. SEM micrographs of composites treated according to the complete heating cycle as given in Fig. 4(a). (a) and (b) Samples as shown in Fig. 2(a); (c) is a sample as shown in Fig. 3.

molten aluminium particles remain at their original sites. During the reaction step, the aluminium droplets form reaction product towards all sides leaving fine pores at the original site (Fig. 6(c)).

The shrinkage of Al/ Al_2O_3 composites, milled for 8 h and heat treated according to the schedule shown in Fig. 4(a), is presented in Fig. 7 as a function of the isostatic compaction pressure. The densities of the 35C samples pressed at 400 and 700 MPa were 92 and 93%, respectively. The densities of the composites with the fine Al_2O_3 powder were 90 and 91%, 88 and 89%, and 86 and 87% TD for compositions with 25, 35 and 40% vol. Al, respectively, where the

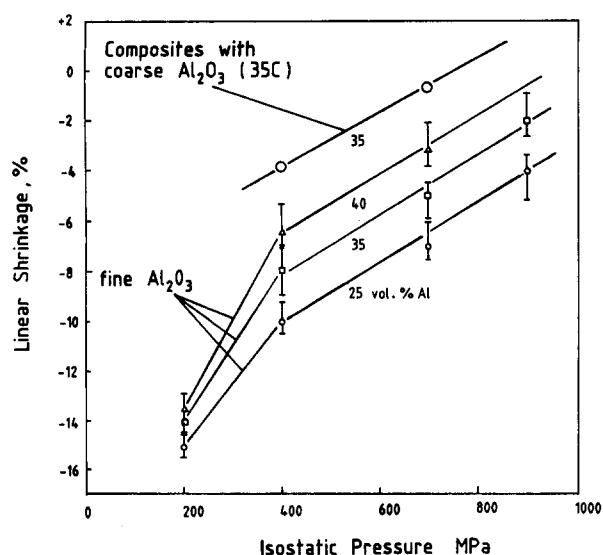


Fig. 7. Shrinkage versus isostatic compaction pressure of Al/Al₂O₃ composites attrition milled for 8 h in isopropanol and heat treated according to the schedule given in Fig. 4(a), i.e. 8 h at 1200°C and 3 h at 1550°C.

higher density corresponds to the higher isopressure. It is obvious that the coarse Al/Al₂O₃ exhibit lower shrinkage at higher densities than the respective composites with the submicron powder. Further reduction in shrinkage may be expected with compositions of ~40% Al and coarse Al₂O₃.

3.3 Mechanical properties

The room-temperature flexural strength of the 35C sample isopressed at 400 MPa (c.f. Fig. 7) is 281 ± 15 MPa and the respective K_{Ic} is 2.35 ± 0.2 MPa m^{1/2}. Addition of either 10% vol. 3Y-ZrO₂ powder or 15% vol. Al₂O₃ platelets to the 35C composition causes the K_{Ic} to increase to 2.6 and 2.75 MPa m^{1/2} respectively. As revealed by the fracture surface (Fig. 8) of an Al₂O₃-platelet reinforced 35C sample pressed at 400 MPa (c.f. Fig. 7), the fracture is mixed-

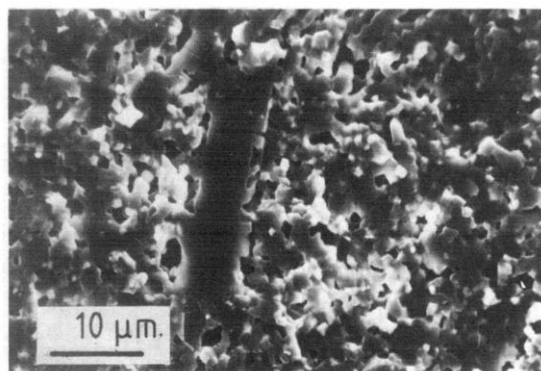


Fig. 8. Fracture surface of an Al₂O₃-platelet reinforced 35C sample pressed at 400 MPa (c.f. Fig. 7) showing a mixed-mode fracture and strong bond bridges when compared to the originally smooth platelets.

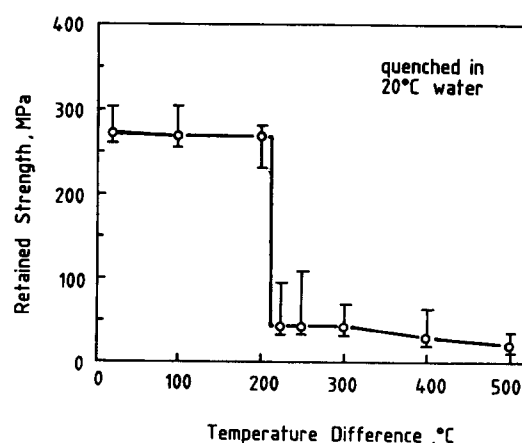


Fig. 9. Retained strength of samples 35C pressed at 400 MPa (c.f. Fig. 7) as a function of quenching temperature difference.

mode. It is also evident that the bonding to the originally smooth Al₂O₃-platelet is strong due to solid grain bridges to the matrix. The lack of any pull-out of the platelets explains the rather small effect on K_{Ic} . The K_{Ic} data presented are comparable to those found for material B in Ref. 2, where the Lanxide process has been run to completion. In the present work, partially reacted samples with retained Al-channels comparable to material A in ref. 2 have not been tested. The strength of the reaction-bonded 35C sample is considerably higher than that of material B. The thermal shock behavior represented in Fig. 9 resembles that of conventionally sintered Al₂O₃.

4 Conclusions

- (1) A simple powder metallurgical technique has been developed to fabricate strong low-shrinkage reaction-bonded alumina (RBAO) bodies. Low total shrinkage is achieved by combining the expansion due to the oxidation of an aluminium melt and the shrinking due to the sintering of an alumina powder.
- (2) The experimental results indicate that further optimization towards lower shrinkage (zero shrinkage) and increased strength seems feasible, e.g. via alteration of aluminium content or of heat-treatment schedule.
- (3) Some porosity is unavoidable in RBAO; however, the strength is comparable to that of conventionally sintered dense Al₂O₃.
- (4) Although the mechanisms of microstructural change associated with RBAO remain to be clarified, control of the heat-treatment schedule allows some separation of the contributing processes.

Acknowledgements

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