Fracture behaviour of alumina–calcium hexaluminate composites obtained by colloidal processing

A.J. Sánchez-Herencia, R. Moreno, C. Baudín *
Instituto de Cerámica y Vidrio, Ctra de Valencia Km 24,300, Arganda del Rey, 28500 Madrid, Spain

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Abstract

Three different alumina (90 vol.%)–calcium hexaluminate (10 vol.%) composites have been prepared by colloidal processing of high purity starting powders in aqueous media and conventional sintering at 1500, 1550 and 1600 °C. Calcium hexaluminate has been synthesised by high temperature reaction of alumina and calcium carbonate powders. The optimum dispersion conditions for the mixture have been selected from data for alumina and calcium hexaluminate slips studied independently. The microstructure of the obtained materials has been characterised by scanning electron microscopy. All of them showed a highly dispersed distribution of small CA₆ grains inside the alumina matrix. Grain size and shape of the alumina grains was highly dependent on the sintering temperature whereas the grain size of calcium hexaluminate remained almost constant. The fracture behaviour of the composites was analysed using Vickers indentation and optical and scanning microscopies. Higher loads could be applied to the composites without additional lateral cracking than to a monophase alumina material of the same average grain size. The fracture toughness values of the composites were highly dependent on the microstructure and for two of them values were larger than for the alumina material. Results have been discussed in terms of residual thermal stresses between the grains due to thermal expansion anisotropy. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The critical fracture energy and, therefore, toughness of alumina materials is highly dependent on grain size. This trend has been related to local stresses developed between grains due to thermal expansion anisotropy (TEA), as in other non-cubic and non-transforming ceramics.

Thermal expansion anisotropy stresses which develop upon cooling may assist in microcracking generation around the loaded crack tip. These microcracks constitute a mechanism of energy absorption and, for materials with grain size up to approximately half the value corresponding to spontaneous fracture, may increase the fracture toughness. Early theories proposed this toughening mechanism for alumina materials.¹⁻³ Careful observations of the indentation crack paths in alumina materials representing a wide range of grain sizes showed that in fine-grained materials (d < 5 μm), the predominant fracture mode was intergranular and that the extent of transgranular fracture increased with increasing grain size. These variations of fracture morphology with grain size are opposite to those expected where microcracking is the dominant mechanism and suggest that crack branching plays an important role in the toughness increase with grain size.⁴ Grain boundary microcracking due to TEA may act as initiation sites for crack branching. Later in situ observations of cracks with well defined shapes during loading showed that crack interface bridging by interlocked grains behind the crack tip was responsible for crack stabilisation in all alumina materials with grain size larger than 5 μm.⁵,⁶ Crack bridging phenomena and, consequently, flaw tolerance in monophase ceramics may be enhanced only by scaling up the grain size. This way of toughness enhancement is limited by the amount of spontaneous microcracking that the material may stand without generalised failure.

Second phases with lower thermal expansion than that of the alumina matrix may enhance the effective-
ness and density of the bridges as observed in alumina–aluminium titanate composites. Increasing the volume fraction and particle size of the second phase enhances flaw tolerance of the material, but this increase is also limited by spontaneous microcracking of the matrix due to the opening stresses that the second phase particles exert on the matrix walls.

Calcium hexaluminate, CaAl_{12}O_{19} (CA\textsubscript{6}), is an interesting compound as a second phase in alumina based composites because it is thermodynamically compatible with alumina and it has the same average thermal expansion coefficient ($\approx 8.5 \times 10^{-6} \, ^\circ\text{C}^{-1}$). But its thermal expansion behaviour is highly anisotropic ($\alpha_a = 7.3 \times 10^{-6} \, ^\circ\text{C}^{-1}$, $\alpha_c = 11.8 \times 10^{-6} \, ^\circ\text{C}^{-1}$). Hence, thermal expansion mismatch between alumina and CA\textsubscript{6} particles may be expected.

Extensive work has been devoted to the study of CA\textsubscript{6} as a component of refractory materials but few papers deal with the fabrication or characterisation of alumina–CA\textsubscript{6} dense composites for structural applications.

A series of fine grained ($\approx 5 \, \mu m$) reaction sintered alumina–CA\textsubscript{6} composites containing different CA\textsubscript{6} amounts was studied but toughness values did not show any benefit from the CA\textsubscript{6} particles in spite of their plate-like shape, a result attributed to the larger porosity present in the composite materials. The lower density was due to the fact that in situ formation of CA\textsubscript{6} during sintering involves a volume expansion during the formation of the different intermediate calcium–alumina compounds. Even though the critical temperature interval for fracture initiation during thermal shock tests of these composites was of the same order as that of monophasic alumina materials, the resistance to thermal shock damage of the composites was found to be of the same order as that of CA\textsubscript{6} dense composites. Even though the critical temperature interval for fracture initiation during thermal shock tests of these composites was of the same order as that of monophasic alumina materials, the resistance to thermal shock damage of the composites was found to be of the same order as that of CA\textsubscript{6} dense composites. Hence, thermal expansion mismatch between alumina and CA\textsubscript{6} particles may be expected.

In this work a colloidal processing route for manufacturing homogeneous alumina–CA\textsubscript{6} composites is described. High purity commercial alumina and already reacted micrometer sized CA\textsubscript{6} powders have been dispersed in water and rheologically characterised. The compacts have been obtained by a colloidal filtration route and further conventional sintering. Special attention has been paid to the microstructural characterisation of the composite and to the effect of the microstructure on the fracture behaviour.

2. Experimental

2.1. Starting materials and slurries preparation

A commercial high purity (99.99%) alumina (Condea HPA 0.5, USA) and a calcium hexaluminate (CA\textsubscript{6}) synthesised in the laboratory were used as starting powders for the composite materials.

Calcium hexaluminate was obtained by high temperature reaction of alumina and calcium carbonate (Merck, Germany, 99.0% purity). Stoichiometric concentrations were attrition milled for 4 h in isopropanol using alumina balls for a complete homogenisation. After mixing the powders were dried and sieved below 60 µm. The dried mixture was isostatically pressed at 200 MPa and calcined at 1600°C for 3 h and at 1650°C for 4 h. The reaction of CA\textsubscript{6} formation was followed by X-ray diffraction (XRD) using a Siemens D5000 diffractometer (Germany) to establish the best
and then sintered in the range of temperatures 1500–

bodies. Samples were left to dry in air for at least 48 h to cast on plaster of Paris moulds to obtain the green bodies.

2.2. Samples preparation and characterisation

N2 adsorption method (Monosorb, Quantachrome, USA). Specific surface areas were determined by the one point Brunauer-Emmett-Teller (BET) method with the Multipycnometer, Quantachrome, USA. Particle size distributions were determined with a light scattering system (Mastersizer S, Malvern, UK) using a liquid dispersion unit with distilled water.

A12O3 slips and CA6 slips were prepared to a solid loading of 70 wt.% (38 and 39 vol.%, respectively) in deionised water with different concentrations of a barbotic acid based polyelectrolyte as deflocculant (Dolapix CE64, Zschimmer-Schwarz, Germany), and the dispersion conditions for the slips were determined. For the A12O3–10 vol.% CA6 composites, 70 wt.% slips were prepared using the optimum dispersing conditions for each component in the mixture following a two step procedure. Firstly, the CA6 was energetically stirred in deionised water in the presence of the total amount of dispersant required for homogenising the mixture using a high shear mixer (Silverson, L2R, UK). Secondly, after complete coverage of the dispersant onto the CA6 particles, the A12O3 powder was then added. This mixture was homogenised by ball milling overnight using alumina jar and balls.

For rheological measurements a rheometer (Haake, RS50, Germany) with a double cone/plate geometry was used. Measurements were performed by changing shear rate from 0 to 1000 s⁻¹ for 2 min, for both the up and down ramps with 1 min at the maximum rate. Temperature was maintained constant at 25°C.

2.2. Samples preparation and characterisation

The well-dispersed A12O3–10 vol.% CA6 slips were cast on plaster of Paris moulds to obtain the green bodies. Samples were left to dry in air for at least 48 h and then sintered in the range of temperatures 1500–1600°C for 2 h (heating and cooling rates 5°C/min).

Archimedes’ method, using mercury and water, respectively, was used to determine green and sintered densities.

Sintered samples were polished using diamond paste down to 1 μm for microscopic and indentation experiments. Scanning electron microscopy (DSM 950, Zeiss, Germany) was performed on thermally etched (1450°C–1 h, heating and cooling rates 10°C/min) surfaces. To differentiate alumina from calcium hexaluminate, EDX was performed to obtain Ca X-ray maps and single particles or groups of particles of sufficient size (>2 μm) were also analysed. With the same purpose back-scattered images were used. The average particle size of alumina was determined quantitatively using the linear intercept method on SEM micrographs and the aspect ratio of these particles was calculated as the ratio of the length to the width directly measured on the micrographs. The approximate size of the CA6 particles was directly measured on the micrographs. These measurements were performed on two different random areas of 86×97 μm for each sample, which included at least 200 grains.

Dynamic Young’s modulus was calculated from the resonance frequency of bars tested in flexure using the impact method (Grindosonic, Belgium).

Indentations were performed on polished samples using a Vicker’s indenter and maintaining the fixed load for 15 s (LECO, USA). Loads between 10 and 500 N were applied and the indentation cracks were observed using optical (Zeiss, Germany) and scanning microscopes. Crack lengths corresponding to well defined indentations (no chipping, only two perpendicular lateral cracks) were measured by optical microscopy and values were used to calculate toughness using the equation of Ref. 14.

3. Results and discussion

3.1. Calcium hexaluminate synthesis

The X-ray diffraction spectra of powders milled from the alumina–calcium carbonate compacts thermally treated at 1600 and 1650°C were analysed. The composites treated at 1600°C showed some residual alumina, as an indication that the reaction was not complete. The peaks corresponding to the alumina disappeared in the XRD diagram of the sample treated at 1650°C and only CA6 was detected. The diagrams of the samples treated at 1650°C for 3 and 4 h were identical. Therefore, the temperature of the heat treatment used to synthesise the CA6 was 1650°C.

The evolution of the particle size distribution of ground CA6 powders versus attrition milling time was followed. After 6 h (Fig. 1a), the particle size distribution was bimodal, centered at 0.3 and 1.1 μm, and no further decrease of the particle size with longer milling times (8 h) was obtained. The size bimodality of the powders, plotted in Fig. 1a, can be observed in the SEM micrograph of the powder shown in Fig. 1b. The alumina powders presented a unique particle size distribution with average particle size of 0.3 μm (Fig. 1a). Apart
from size distribution, the alumina and CA6 powders differ in density values (3.69 and 3.88 g/cm³ for CA6 and alumina, respectively) and specific surface area (3.1 and 9.5 m²/g for CA6 and alumina, respectively).

3.2. Rheological behaviour and fabrication of the green compacts

For the preparation of the mixtures the rheological behaviour of slips of each material was previously characterised. Aqueous slips with a solid loading of 70 wt.% were prepared by adding concentrations of deflocculant between 0.2 and 1.0 wt.% referred to solids. Fig. 2a shows the flow curves corresponding to the CA6 slips. They behave as dilatant at high shear rates. In addition, for deflocculant contents up to 0.6 wt.%, there is a noticeable time dependency. The dilatancy significantly decreases for dispersant additions of 0.7 wt.%. The viscosity is reduced for 0.8 wt.%, and no significant reduction is achieved for larger deflocculant contents.

For alumina, well-dispersed slips were obtained for deflocculant contents of 0.6 wt.% and very small differences were found depending on the concentration. The slips presented a nearly Newtonian behaviour with very low viscosities (< 10 mPa s). In principle, the rheological behaviour of a mixture depends mainly on that of the major constituent, in this case alumina. Moreover, the optimum amount of dispersant for the alumina slip is in the same range as that for the CA6 one. But, the differences in the powder characteristics mentioned above (shape, specific surface area) might be responsible for preferential adsorption of the dispersant on the major constituent. In order to assure a complete coverage of dispersant (0.6 wt.%) to the surface of CA6 particles, the slips were prepared using a two step method. Firstly, the CA6 powder was added to the water containing the total deflocculant amount. In a second step, the major phase was added and homogenised in the ball mill. Fig. 2b shows the flow curve of the alumina + 10 vol.% CA6 with the 0.6% of dispersant. It is clearly observed that a Newtonian behaviour is obtained with a viscosity value as low as 10 mPa s.

3.3. Microstructure

The green density of the slip-cast samples was 2.61 g/cm³, which represents 66% of the theoretical density of the mixture (3.69 g/cm³). This high density is possible because of the bimodal particle size distribution and the good dispersion of the mixture.

The homogeneity of the sintered composite material can be observed in Fig. 3. In this micrograph, taken...
from the backscattered electron image, the CA₆ grains can be distinguished because they are brighter than the alumina ones; the Ca X-ray map confirmed this observation. CA₆ grains are very small and are homogeneously dispersed inside the alumina matrix.

The sintering temperature did not affect density values of the obtained materials and all values were in the range 99–99.5%. Fig. 4 shows micrographs of the samples sintered at the three different temperatures. The quantitative microstructural analysis of these samples is summarised in Table 1.

The three materials present the same kind of microstructure (Fig. 4, Table 1), constituted of equidimensional and small (<2 μm) CA₆ grains embedded in a bimodal alumina matrix in which the smaller grains (<3 μm) are equidimensional and the larger ones are tabular. The sintering temperature has a major role in the development of the microstructure, mainly regarding to the size and shape of the alumina grains, as deduced from quantitative values in Table 1. For the materials treated at the lower temperatures (1500 and 1550°C, Fig. 4a and b, respectively) there are not large differences in average alumina grain size ($D_{50} = 3.3–3.4$ μm) and the size of the smallest grains ($D = 0.8–2$ μm). But a clear increase of both parameters ($D_{50} = 5$ μm, $D = 1–3$ μm) is observed for the material treated at 1600°C (Fig. 4c). The tabular growth of the alumina grains is favoured at 1500 and 1550°C (shape factors = 2–3) whereas in the compacts treated at 1600°C the aspect ratio is lower (shape factor = 1.2) and pore trapping occurs, revealing exaggerated grain growth (Fig. 4c). In order to evaluate the influence of CA₆ as a second phase in the Al₂O₃ based material, a monolithic Al₂O₃ material was prepared controlling the sintering conditions to obtain a similar grain size. This was achieved for the same Al₂O₃ powder after sintering at 1600°C/1 h. The grains of the monolithic alumina material are mostly equidimensional (Fig. 4d) and the average size determined for this material was 5 μm. Some of the largest grains in this material are tabular, with lengths >5 μm.

The development of faceted grains in ceramics is often associated with the presence of a wetting boundary phase, which leads to slow growth rates which are responsible for anisotropic growth, but no liquid phase formation is expected at the sintering temperatures in the high purity compacts studied here, as liquid phase in biphasic alumina–CA₆ composites does not form up to temperatures over 1800°C.

Dynamic Young’s modulus values for the three composites were in the range 363±9 GPa, which agrees well with the Voight limit for the Young’s modulus of composite materials considering the values of 380 GPa for alumina and 260 GPa for dense monophase calcium hexaluminate (260±10 GPa). Therefore, no extensive spontaneous cracking takes place in these materials during cooling from the sintering temperature.
The four studied materials had different behaviour under Vickers' indentation. The maximum load that could be applied to the pure alumina material without extensive chipping was 200 N and no variation of toughness as a function of load (50, 100 and 200 N) was found. Conversely, loads up to 500 N could be applied to the alumina–CA6 compacts sintered at 1500 and 1550°C, and up to 300 N to the one sintered at 1600°C without chipping (Fig. 5a and b), indicating that no additional cracking occurred under the indentation.

An increase of toughness values with the applied load was found for the three composites in all cases with well developed cracks ($C > 2.5$, $c = 0.5$ radial crack size, $a = 0.5$ diagonal of the plastic zone); this feature was not observed in the alumina material. The fact that this dependence does not take place in the alumina material, which microstructure is similar to that of the composite sintered at 1600°C (Fig. 4c and d) implies that it should be related to the presence of CA6. For the two composites sintered at the highest temperatures the toughness values in the constant region (loads larger than 200 and 300 N, 1550 and 1600°C, respectively) are larger than the obtained constant value for the alumina material (Fig. 6). The larger toughness values of the composite sintered at the highest temperature when compared to those corresponding to the alumina material with similar microstructure reveal that an energy absorbing mechanism is taking place in the composites during fracture. Characteristic crack patterns for the indented samples are shown in Fig. 7. The crack paths in the pure alumina material were straight and showed a mixture of intergranular and transgranular modes (Fig. 7a), being very similar to that reported by other authors for fine-grained materials. In the composite materials (Fig. 7b-d),
the fracture mode of the alumina matrix was also mixed inter-transgranular but, the crack changed its direction of propagation, even traversing the alumina grains, to link areas where intergranular fracture around the small grains (mostly CA₆) occurred, as seen in detail in Fig. 7d. This feature is similar to that observed in alumina based composites in which crack bridging takes place. In these materials, crack propagation occurs in two steps: (a) opening of a microcrack ahead of the crack tip, (b) joining of the microcrack to the primary crack.¹⁹

The same fracture processes might be the energy absorbing mechanisms in the composites as the observed dependence of toughness on microstructure is in agreement with the crack bridging hypothesis: the coarse grained composite material sintered at 1600°C presents the largest toughness values (Figs. 4 and 6, Table 1) and for the two composites sintered at the lower temperatures, which present similar average grain size, an increase of toughness with shape factor occurs (Figs. 4 and 6, Table 1).

Due to differences between the average expansion coefficient of the alumina matrix and the c-axis expansion
coefficient of CA₆, thermal mismatch stresses perpendicular to the Al₂O₃/CA₆ interfaces are expected. Such stress system does not add to the indentation load to develop additional lateral cracking across the matrix, and, in fact, the composite materials support larger loads than the monophase alumina material without chipping (Fig. 5). This stress system leads to microcracking around the CA₆ particles when loading, and these microcracks constitute the initiation sites for crack branching. The alumina grains located between two areas of intergranular fracture would act as elastic bridges before being traversed by the primary crack and crack bridging will be responsible for the observed change in crack direction in the surface of the indented samples (Fig. 7b–d).

Fig. 6. Toughness values as a function of the applied load for the studied materials.

Fig. 7. Indentation crack path in the studied materials, SEM micrographs of thermally etched polished and indented surfaces: (a) alumina; (b) alumina–CA₆ composite sintered at 1500°C; (c) alumina–CA₆ composite sintered at 1550°C; (d) alumina–CA₆ composite sintered at 1600°C.
4. Conclusions

Alumina-based composites with a homogeneous dispersion of small (≈5 μm) and equidimensional calcium hexaluminate particles can be obtained by colloidal processing and conventional sintering. The dispersion of CA₆ inside the alumina matrix can be controlled using rheological parameters when the complete adsorption of the dispersant on the minor phase (CA₆) is assured. In the range of sintering temperatures 1500–1600°C, CA₆ grains are equidimensional and small sized and the size and shape of the grains of the Al₂O₃ matrix is controlled by the sintering process.

The presence of CA₆ as a second phase affects the fracture behaviour of the alumina matrix. First, larger indentation loads can be applied to the composites, compared to a monophasic alumina material with similar grain size, without multiple cracking and, second, larger toughness values are obtained for the composites than for the alumina material.

The dependence of the toughness values of the composites on their microstructural differences (grain size and shape) as well as the crack path features agree with a hypothesis of crack bridging phenomena occurring in the composites originated from microcracking around the CA₆ particles.

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