

Lime–Alumina–Silica Processing Incorporating Minerals

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Abstract

The use of naturally occurring minerals to enhance the physical and mechanical properties of industrial ceramics such as alumina is an attractive alternative to synthetic materials due to cost, chemical stability and availability. Two systems, have been chosen for investigation, alumina–kyanite to produce an alumina–mullite composite and alumina–wollastonite to produce a lime aluminosilicate. Wet processing conditions were optimised using pH/rheology and microelectrophoresis techniques followed by slip casting. The resulting green compacts were subjected to a variety of sintering regimes to produce the desired composites. Sintered products were characterised by techniques such as electron probe microanalysis, hardness tests and toughness determinations. Results are discussed, both in terms of enhanced properties realised (toughness, wear resistance, dielectric), and with respect to the viability of using natural minerals in this application. © 1999 Published by Elsevier Science Limited. All rights reserved

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1 Introduction

Ceramic matrix composites, particularly mixed oxide systems, are of interest in a variety of technical ceramic applications including the auto-

motive, aircraft and electronics industries. These composites are traditionally expensive; thus, by selecting more economical reactants such as minerals, mixed oxide ceramic systems may be produced using processes such as reaction sintering. Naturally occurring minerals have not traditionally been considered for use in advanced ceramics presumably because of their chemical variability. In this work, two minerals of consistent chemical composition, kyanite and wollastonite, have been used to enhance selected properties of alumina in a fashion similar to more costly alternatives.

Traditional ceramics often utilise naturally occurring materials and minerals such as clays. This division, of ceramics is for the most part considered to be the domain of the silicate industries. The common denominator in these materials is the presence of aluminum, silicon and oxygen, generally in the form of hydrous clays. Advanced or technical ceramics may also contain aluminosilicates but also may encompass a range of other oxide as well as non-oxide species. This branch of ceramics places a strict limit on impurity levels as the products must exhibit reproducible properties.

Although the use of minerals is usually associated with traditional applications a different approach is to use the mineral as a reactant source prior to a reaction sintering operation. Two examples of this are addressed in this work: the use of wollastonite (CaO.SiO₂) in alumina to create a technical ceramic based on the system CaO–Al₂O₃–SiO₂(CAS)¹ and the-use of minerals which would form a binary system with alumina such as andalusite, sillimanite and kyanite. These latter minerals bear the same chemical formulation (Al₂O₃–SiO₂) yet possess different crystal structures due to their geological origin.² With respect to this system, andalusite could conceivably form at standard temperature and pressure; however, mullite (3Al₂O₃·2SiO₂) is the only truly stable unhydrated compound at standard pressure.³

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Mullite can be formed from processes such as sol-gel processing but is often rather costly to produce relative to alumina. However, it has a low density (3.16 g cm^{-3}) and an attractive coefficient of thermal expansion and dielectric constant when compared to alumina. Fortunately, when aluminosilicate minerals are heated above 1400°C they react to form mullite and silica. Thus, a reaction-sintering process as applied to a system such as alumina-kyanite should result in an alumina-mullite product.

With respect to the reaction-sintering of alumina-wollastonite mixtures, previous investigations have suggested that the resulting material will ideally be composed of alumina-gehlenite-anorthite-hibonite.¹ This should provide enhanced toughness and wear resistance at elevated temperatures as long as there is little or no glass in the final product.

As a process, reaction-sintering has shown promise in producing near net shape products at both high and low quality levels of ceramic production.⁴ The main advantage of this process is in-situ formation of a homogeneous secondary phase and the potential to reduce firing shrinkage. As well, there is usually a reduction in the firing temperature needed to obtain final density.³ Thus, the experimental approach taken in this work involved optimising aqueous processing conditions and densification procedures to produce alumina-based composite materials via reaction-sintering of alumina-mineral mixtures. Final products were characterised using chemical, microstructural and mechanical techniques.

2 Methods and materials

2.1 Wet processing

To produce green compacts of alumina-kyanite or alumina-wollastonite techniques such as mineral beneficiation, sedimentation, microelectrophoresis and rheological manipulation were employed. Details of the methodology for each system have been described elsewhere;¹⁻⁵ a synopsis for each system is given below.

2.1.1 Alumina-kyanite

The kyanite was beneficiated from its ore using a grinding/magnetic separation step to remove iron-bearing minerals such as garnet; the kyanite was subsequently subjected to a heavy-media separation step to liberate quartz. A final calcination treatment at 850°C for 12 h followed by shatterbox grinding and sedimentation to $<5 \mu\text{m}$ yielded a 99.0 wt% kyanite product. Minor impurities were, in wt%, 0.29 CaO; 0.25 K_2O ; 0.30 FeO and 0.16 TiO_2 .

To obtain optimum casting conditions, the alumina (Reynolds RHCP-DBM, $0.5 \mu\text{m}$) and kyanite were independently sedimented to $<5 \mu\text{m}$, and various mixtures of alumina and kyanite were equilibrated at a variety of pH levels (2-11) while being agitated on a high speed Tubula mixer for 12 h. Rheological properties of these suspensions were obtained using a Brookfield LVTDV-II digital viscometer attached to a computer for data acquisition.

2.1.2 Alumina-wollastonite

The as-received wollastonite had been previously liberated from calcite, the major impurity, using a flotation process. Composition was, in wt%, 50.6 SiO_2 , 49.0 CaO; 0.14 FCO; 0.1 Cr_2O_3 ; 0.02 TiO_2 , 0.06 MnO; 0.05 Na_2O and 0.03 Al_2O_3 .⁶ Mineral grains were acicular (aspect ratio approximately 10:1) and the particle size ($30 \mu\text{m}$) was large relative to the Reynolds alumina. Thus the mineral was reduced in size ($<4.5 \mu\text{m}$) and aspect ratio ($<3:1$) using a shatterbox (10 min) and a few drops of a 50:50 ethanol:acetic acid mixture as dispersant to prevent particles from adhering to the mill. Sedimentation to $<5 \mu\text{m}$ and rheological examination followed as for the alumina-kyanite system. The optimum alumina:wollastonite ratio was 80:20 by weight.

2.2 Reaction sintering

The sintering regime used was chosen to effect full conversion/dissociation of the starting mineral. This was assisted by the use of thermodynamic calculations using the Facility for the Analysis of Chemical Thermodynamics (FACT)⁷ and Differential Thermal Analysis (DTA). The DTA system was developed previously⁸ and was calibrated using K_2SO_4 as a reference. Briefly, the process involved measuring a ΔT voltage output between an alumina standard and the composite mixture (wollastonite or kyanite/alumina; 1.6 g); both standard and unknown were held in 6 mm diameter alumina crucibles. Because a CAS glass was predicted to form at the dissociation temperature of wollastonite (1365°C)⁹ the final sintering procedure for alumina-wollastonite necessarily contained a nucleation step to avoid enhanced levels of CAS glass in the final product.

2.3 Characterisation

X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to assess the sintered products, both for chemical composition and morphology. For microscopy, samples were either thermally etched (alumina-kyanite) or chemically etched (alumina-wollastonite), the latter being required to remove CAS glass to expose the alumina

microstructure. Standard metallographic techniques were used to polish/prepare samples for mechanical testing as well as for thermal expansion and dielectric constant (alumina–kyanite) determinations.

3 Results

3.1 Wet processing

3.1.1 Alumina–kyanite

Sedimentation profiles for kyanite and alumina as a function of pH were separately obtained and using these results a pH of 4 was identified as optimum when considering both minerals. This was confirmed from microelectrophoresis measurements⁵ and was used in all future work. In order to optimise both solids content and alumina:kyanite ratio the plot given in Fig. 1 was determined whereby the apparent viscosity (shear rate 79 s^{-1}) was used as an indicator. A kyanite:alumina ratio of 20:80 at 20 vol% solids was the maximum loading possible in the absence of a dispersant thus all green compacts were cast from such suspensions at a pH of 4.

3.1.2 Alumina–wollastonite

Because of the chemically basic nature of the wollastonite surface and the optimum stability of alumina suspensions being pH 4–5 a cationic polyelectrolyte dispersant, BETZ 1190, was necessary to stabilise these suspensions.¹ Optimum conditions for stability were 1500 ppm dispersant at a pH of 2.3. All green compacts were cast from these suspensions.

3.2 Reaction sintering

3.2.1 Alumina–kyanite

DTA results for this system are given in Fig. 2(a) and 2(b). Although rather inconclusive, a kyanite-

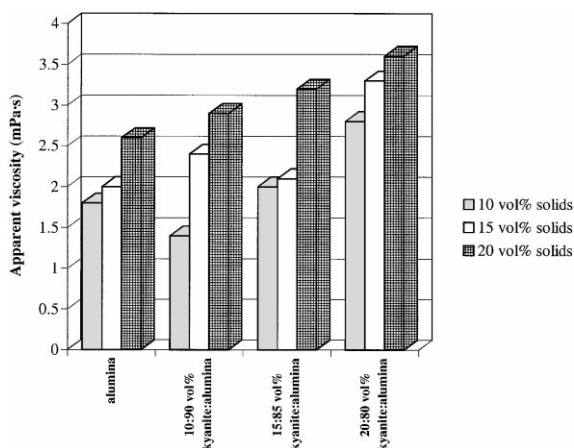


Fig. 1. Effect of solids content on apparent viscosity (shear rate 79 s^{-1}) of suspensions at pH 4.

mullite reaction temperature of about 1490°C could be estimated from the data. This temperature is about 70°C higher than reported for the thermal transformation of kyanite to mullite in the absence of excess alumina¹⁰ and may be due to kinetics involved with the reaction of silica and alumina to form additional mullite. Thermodynamically both the dissociation of kyanite to form mullite and silica and the subsequent reaction of this silica with matrix alumina to form additional mullite are favourable in the temperature range $1470\text{--}1560^\circ\text{C}$. Thus, sintering regimes in this temperature range using heat soak times of 1–12 h and ramp rates of $3\text{--}130^\circ\text{C min}^{-1}$ were examined. Figure 3 is a summary of this study, optimum sintering conditions were found to be $6.4^\circ\text{C min}^{-1}$ ramp to 1560°C (about 4 h) with a 5 h soak at temperature followed by furnace cooling to room temperature. The $6.4^\circ\text{C min}^{-1}$ rate was chosen as it represented the most rapid approach to the holding temperature without sacrificing density.

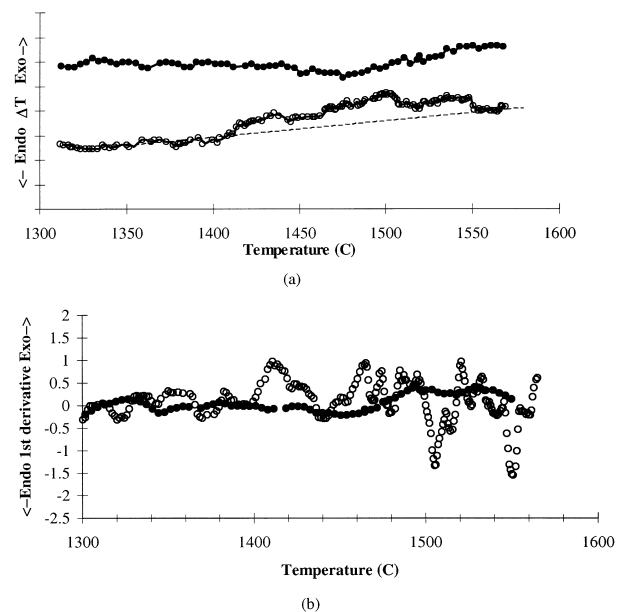


Fig. 2. (a) DTA plot and (b) first derivative for kyanite (O) and 80:20 alumina:kyanite (●) at a heating rate of $8.5^\circ\text{C min}^{-1}$.

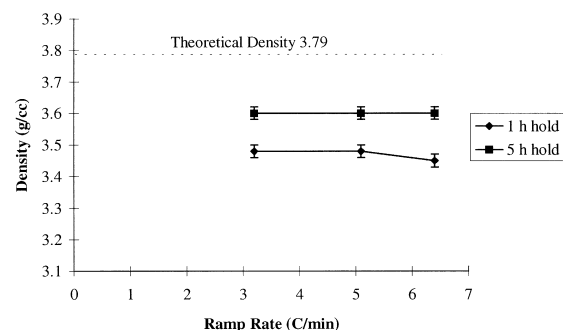


Fig. 3. Density variation of 80:20 alumina:kyanite with respect to the time taken to reach 1560°C followed by a sintering hold time of 1 and 5 h.

3.2.2 Alumina–wollastonite

In order to achieve wollastonite dissociation concurrent with a dense final product sintering temperatures were such that a CAS glass formed as one of the reaction products. This necessitated a devitrification step. From the DTA scan an exothermic crystallisation peak occurred at 1200–1300°C, followed by a large endothermic peak. The latter commenced at 1365°C, indicating formation of a liquid phase. Examination of peak area versus sample temperature gave 1032°C as the nucleation temperature whereas a crystallisation temperature of 1180°C was noted after 2 h nucleation at 1032°C. Thus, the optimum sintering regime was determined from the DTA experiments⁸ to be: (a) reaction liquid phase sinter to 1500°C and quench to room temperature followed by (b) a nucleation period at 1032°C (4 h) and final crystallisation step at 1180–1200°C (4 h).

3.3 Characterisation

3.3.1 Alumina–kyanite

XRD results for reaction-sintered compacts indicated complete conversion of kyanite to mullite, as a result, the final product contained only alumina and mullite. Thus, the silica released from the thermal transformation of kyanite to mullite did indeed react with the alumina matrix to form additional mullite rather than possibly forming a glass, as would be expected in the absence of alumina.¹⁰ A SEM image for the final alumina–mullite composite is given in Fig. 4 after sintering 5 h at 1560°C. The relatively equiaxed grain size of the final product is worthy of note.

With respect to mechanical behaviour, observed hardness using an applied force of 5 kg and fracture toughness as calculated using the Evans and Charles relationship¹¹ decreased relative to alumina (13.4 GPa; 1.86 MPa m^{1/2} versus 16.9 GPa:

2.92 MPa m^{1/2}). However when the indentation load was increased to 10 kg the hardness and fracture toughness increased to 16.8 GPa and 3.64 MPa m^{1/2}, respectively.

The permanent shrinkage experienced by the composite was 11.5%, approximately 2% less than the 13.4% exhibited by the cast alumina reference samples, this was not reversible. The decrease was anticipated due to the 18% volume expansion upon conversion of kyanite to mullite.¹² An additional expansion of about 13% occurs from the reaction of silica with matrix alumina to form additional mullite.¹³

Dielectric properties at room temperature were also examined. The dielectric constants in the frequency range 1–500 MHz were approximately 11.2 and 17.0 for the composite and alumina, respectively.

3.3.2 Alumina–wollastonite

XRD was again used to provide a qualitative determination of the final mineralogical composition of the reaction-sintered compacts. The only crystallisation product found on quenching was alumina (although minor CAS glass is also present), whereas gehlenite and anorthite were detected in the spectrum after devitrification. The absence of hibonite was noteworthy.

An SEM micrograph of a CAS glass–alumina sample following a chemical etch treatment (boiling phosphoric acid, 30 s) is given in Fig. 5. The glass in the microstructure has readily dissolved which enabled clear examination of the platelike alumina grains. Prior to applying the etch the glass was analysed using EPMA and found to have the composition 40 alumina, 29 lime, 31 silica, all in wt%. Alumina grains were confirmed to be 100% alumina.

After heat-treating using the devitrification schedule (1032°C, 4 h; 1200°C, 4 h) the structure was as

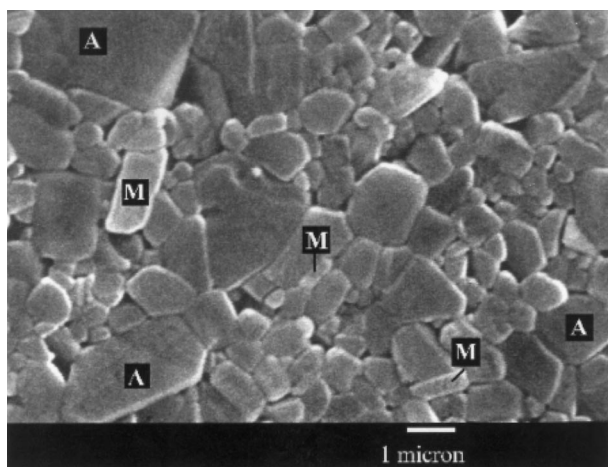


Fig. 4. Alumina–mullite composite microstructure showing fine-grained matrix. Higher aspect ratio grains are mullite.

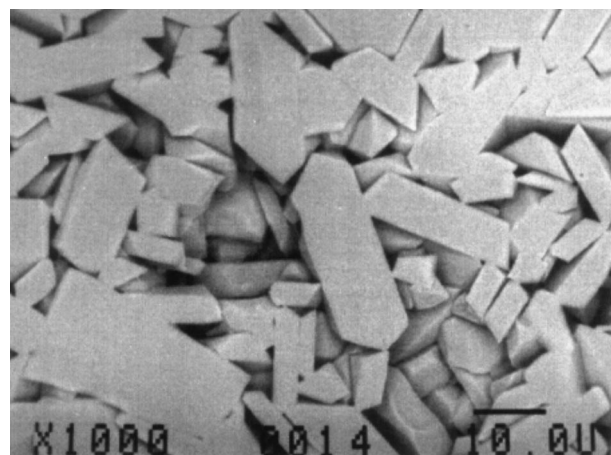


Fig. 5. SEM backscatter micrograph of quenched CAS ceramic chemically etched in boiling phosphoric acid.

shown in Fig. 6. The matrix glass has been removed but, unfortunately, the new crystalline phases were too fine to resolve using EPMA. However, since XRD confirmed the presence of gehlenite and anorthite it can be assumed that these minerals make up the newly formed species. Alumina grains within the material were approximately $2\ \mu\text{m}$ in length with an aspect ratio of 2–2.5:1. The composite also exhibited a lower CTE over a relatively broad temperature range compared to alumina.^{1,14} Although other crystalline and glass phases are present, this finding suggests that the new material has a thermal shock resistance superior to alumina.

Vickers hardness tests using 5 and 50 kg loads were applied to both alumina and the new CAS material. Values obtained were 17.4; 14.6 GPa (alumina) and 8.3, 9.4 GPa (CAS). These results are within reported ranges for 99% alumina and C-780 Class,¹⁵ respectively. Toughness values were determined using five Kc models;¹ mean values were 3.1, 4.2 and 4.8 MPa $\text{m}^{1/2}$ for the alumina standard, CAS quenched and CAS quenched/devitrified, respectively. The latter value is in the lower range for a high toughness ceramic.

4 Discussion

The wet-processing/reaction sintering procedure, developed for both the alumina–kyanite (final product alumina–mullite) and alumina–wollastonite (final product alumina–anorthite–gehlenite) systems has shown that natural minerals, if properly beneficiated, can be used to produce advanced technical ceramic components useful in select applications.

With respect to the alumina–mullite product, the increase in toughness with an increase in load has been observed previously.¹⁶ The earlier work was for a graded material, and suggested that the increase was related to the presence of a residual

stress. In the present study, it is likely that some residual stress is also present following the conversion of kyanite and excess silica to mullite due to differences in the thermal expansion coefficients of mullite and alumina (4.5 and $8.0 \times 10^{-6}\ \text{K}^{-1}$, respectively). Thus the material should possess the mechanical characteristics typical of alumina–mullite. The dielectric constant determined for the alumina standard (17.0) was slightly higher than reported in literature (8.6 – 10.55).¹⁷ However, the formation of mullite in the alumina matrix reduced the dielectric constant by 34%, this was anticipated, due to the attractive dielectric constant of mullite (6.7).³ Finally, the attractive response to thermal treatment in the form of an 11% improvement in the coefficient of linear thermal expansion relative to alumina suggests that the material should be useful in applications where thermal cycling is inevitable.

For the new CAS ceramic XRD results the presence of alumina, gehlenite and anorthite after the devitrification treatment. Although hibonite ($\text{CaO} \cdot 6\text{Al}_2\text{O}_3$) should have formed as well according to the ternary CAS diagram, the mineral was not found. This may have been due to low reaction kinetics or perhaps the influence of minor impurities in the samples. As well, it appeared that more gehlenite was present than anorthite. This could be due to higher diffusivity of CaO inside the glass, which would favour production of gehlenite, the lime-rich compound. However, a higher proportion of gehlenite to anorthite would lead to the appearance of free silica in the product implying either a crystalline silica or residual glass. As the former was not found, some residual glass may still be present. The low hardness values appear to be due to the voids between grains of the devitrified CAS material. The removal of the glass appears to have had no impact on this property although anecdotal evidence tends to support the theory that impact toughness is greatly improved after the devitrification treatment. The platelike structure of the liquid phase sintered alumina seems to improve toughness by crack deflection. The fracture surface has a rough texture and the crack front follows the edge of the alumina grains. Thus, the material should be attractive for use in aggressive physical environments.

Finally, wear properties may be estimated by relating critical indentation or groove size and critical load to fracture toughness and hardness.¹⁸ Although the relationship can only be used as a preliminary calculation suggests that the devitrified material has up to 20 times the abrasion load resistance compared to fully dense alumina. Thus, it is expected that the new material would have properties which make it amenable to anti-abrasion

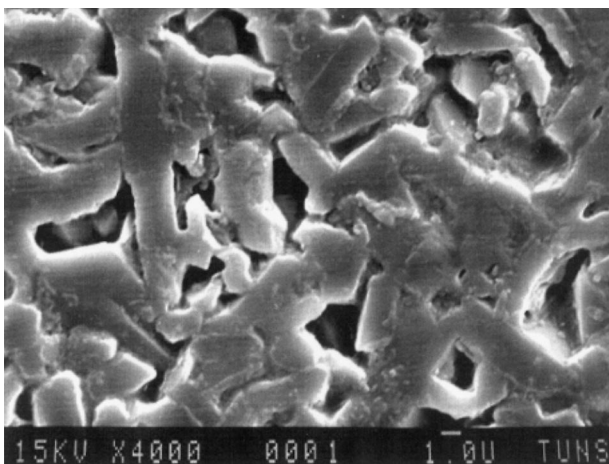


Fig. 6. Micrograph of polished CAS surface after devitrification.

applications such as wear parts and abrasion-resistant linings.

5 Conclusions

1. A wet processing/reaction sintering procedure by which two natural minerals, kyanite and wollastonite, are used to produce alumina-based technical ceramics has been described.
2. Two composite materials, alumina–mullite and alumina–gehlenite–anorthite were formed and characterised. Both materials displayed attractive properties relative to unmodified alumina: alumina–mullite had enhanced thermal expansion and dielectric properties whereas the CAS composite appeared to enjoy an increase in toughness and abrasion resistance.
3. It is postulated that reaction-sintering as applied to alumina–mineral mixtures is a viable alternative to more expensive approaches to forming technical ceramic composite products with enhanced physical and mechanical properties.

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