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The Synthesis of Calcium or Strontium Hexaluminate Added ZTA Composite Ceramics

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Abstract

This paper proposes new preparation methods for alumina–tetragonal zirconia–Ca or Sr hexaluminate composites. Two powder preparation routes were explored. In the first, aluminium and calcium or strontium nitrate hydrates were added to alumina zirconia powders and in the second only calcium or strontium nitrate hydrates were used. Powders produced by the second route are to be preferred since reinforcements do not inhibit the composite sintering process. © 1999 Elsevier Science Limited. All rights reserved

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1 Introduction

Alumina–zirconia composites have been widely studied as structural materials since it was understood that the transformation toughening mechanism of zirconia could improve toughness as well as the strength of alumina.[1–8] The properties of this class of particulate composites are now the subject of an extensive literature. The various mechanisms that lead to the improvement of alumina mechanical properties have been exhaustively explained.[9–13] On the other hand, the shortcomings of these composites are also well known. Their mechanical properties depend partly on the stability of the ZrO_2 tetragonal phase, which in turn depends on environmental conditions. It is known, for instance, that a moist environment may permit tetragonal-monoclinic transformation in yttria-zirconia grains at temperatures around 100°C.[14,15]

The literature also deals with the behaviour of zirconia-containing materials above the martensitic temperature.[16–20] In this case the presence of the stable tetragonal phase is not sufficient to improve mechanical properties because zirconia grains are inert toward the propagating cracks when the tetragonal-monoclinic transformation cannot occur.

It is therefore of great interest to compensate the loss in mechanical properties of zirconia-containing materials through the incorporation of other dispersoids which can interact with the fracture and therefore maintain good toughness and, if possible, strength also at high temperatures.[21] Unfortunately the processing of such materials is often complicated and high temperatures or expensive hot pressing or hot isostatic pressing are required to reach good density. Moreover whiskers, for example, constitute a health risk.

These problems may be partially avoided if dispersoids are able to grow during the sintering process and their shape is achieved by ‘in-situ’ reactions during the normal pressureless sintering in air. In that case, traditional procedures for the preparation of ceramics can be followed and the cost of this type of product will be moderate.

Several hexaluminates exhibit hexagonal symmetry and, if special preparation routes are followed, they can develop a plate-like shape during the sintering process. Cutler *et al.*[22] demonstrated that strontium hexaluminate can be crystallised in plate-like particles by ‘in-situ’ reaction in Ce–TZP–Al_2O_3 matrices by the addition of $SrZrO_3$ in small quantities. Chen *et al.*[23] have seen similar structures in an alumina matrix.

An *et al.*[24,25] demonstrated that calcium hexaluminate can be prepared as a reinforcing phase in alumina matrices. These authors say that the addition of sintering aids is a promising way of producing composites containing Ca and Sr hexaluminates up to 30% vol but the high-temperature mechanical properties of such materials are expected to be poor owing to the presence of glass phase at the grain boundaries.

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Belmonte *et al.*[26] and Maity *et al.*[27] demonstrated that the mechanical properties of zirconia-toughened aluminas can be improved by the in-situ formation of calcium and strontium hexaluminates, respectively.

This paper reports the production of ceramic composites containing 15% vol (3% mol Y_2O_3) zirconia–alumina as matrix and calcium or strontium hexaluminates as a second dispersed phase. Sintering aids were not added. Composites were obtained by following two different procedures: in the first, both components of the reactions leading to hexaluminates were added as nitrates, whereas in the second only one nitrate was added and reactions were expected between the alkaline earth oxide and α-alumina coming from the matrix powder. Nitrates were chosen for their high solubility in water and the low melting points of calcium and aluminium nitrate hydrates. These characteristics should have facilitated preparation processes and the chemical homogeneity of the starting slurries.

2 Experimental

Powders of alumina (Sumitomo AKP 15) and zirconia (Tosoh TZ3Y) were mixed in advance by wet-ball milling for 2 h in a plastic jar with alumina balls in isopropanol. The slurry was dried and powders divided into several batches.

Two batches were attritor-milled for 3 and 6 h at 300 rpm in isopropanol using alumina spheres. Slurries were dried and powders pressed into samples which were fired for 4 h at 1580°C and used as benchmarks.

The other batches were used for the first preparation route to obtain composites containing calcium or strontium hexaluminates.

Aluminium (Aldrich Chem. 98%) and the other (Ca, Sr, Aldrich Chem. 99%) nitrates were mixed as liquids to form clear solutions. Calcium nitrate tetrahydrate melts at 45°C, aluminium nitrate nonahydrate melts at 73°C and strontium nitrate does not melt but decomposes at higher temperatures.

For the addition of calcium and aluminium nitrate, in the first case calcium nitrate was melted at 50°C and aluminium nitrate was dissolved in the liquid. In the second, aluminium nitrate was melted at 75°C and then strontium nitrate was dissolved into the liquid. Ten percent wt of tartaric acid was added to the solutions and then the matrix powder was added to form slurries which were tempered in an oven at 200°C and aged 12 h.

The cakes were cooled down to room temperature, crushed, sieved through a 200 μm sieve, calcined for 2 h at 900°C, quenched in air at room temperature, crushed again, sieved through a 160 μm sieve and stored under vacuum.

In the second route, a concentrated (10% mol) solution of the metal nitrate was prepared first, 10% wt of tartaric acid was added and then the alumina zirconia mixture was poured into the solution. The resulting paste was treated as described above. In this case a quantity of alumina greater than the stoichiometric quantity was introduced in the ZTA powders so that the stoichiometric excess could react with the added metal oxide to form the desired hexaluminate, giving materials with the same final composition as for the first preparation. Pure calcium and strontium hexaluminates were also prepared using nitrate blends as starting materials.

All these thermal treatments must be performed under the fume hood to avoid dispersion of N-containing gases into the working environment. Powders were first ball-milled for 2 h in plastic jar with alumina spheres then attritor-milled for 3 and 6 h at 300 rpm in all cases using isopropanol, alumina spheres and plastic containers. Slurries were added with 2% wt of polyethylene glycol as binder ten min before the end of the milling process and then dried.

Powders were sieved through a 160 μm sieve, isostatically cold pressed into bars or cylindrical specimens at 200 MPa and then fired for 4 h at 1580°C.

STA analysis was performed using a Netzsch apparatus. Average thermal expansion coefficients were calculated after dilatometric tests carried out with a Netzsch dilatometer from room temperature to 1400°C. Densities were measured, when possible, by a Hg pycnometer. If sample density was too low, the value was determined by the ratio between weight and volume. X-ray diffractions were made with a Philips instrument using CuKα_1 radiation. Microstructures were examined by an Assing Stereoscan Scanning Electron Microscope (SEM) coupled with an EDAX microprobe.

3 Results and Discussion

Precursor thermal treatment is a delicate step in the preparation of high-density sintered bodies. Low-temperature calcination can lead to the incomplete decomposition of nitrates used and so to high-porosity materials after final sintering. In contrast, prolonged calcinations at high temperature lead to powders containing large, strong agglomerates that result in poor sinterability. In order to identify the optimal thermal treatment for hexaluminate precursors, mixed calcium or strontium and aluminium nitrate mixtures and calcium or strontium nitrate–alumina mixtures were submitted to STA analysis after ageing at 200°C. X-ray diffractions were also performed on powders calcined at 900°C for 2 h and on those resulting from the STA tests. STA diagrams of the precursors are quite different.

In the case of mixed nitrates leading to $CaO{\cdot}6Al_2O_3$ the powder weight loss (50% wt) is coupled with two endothermic peaks and ends around 540°C [Fig. 1(a)]. Gases evolved during precursor decomposition contain nitrogen oxides and water. They are brown in colour, which is characteristic of N–O compounds.

Two exothermic peaks, without weight changes, appeared at 890 and 1145°C, respectively. X-ray patterns of the powders calcined at 900°C did not show the presence of crystallographic phases whereas patterns after STA analysis showed the presence of calcium hexaluminate and α-alumina. The first exothermic peak could be attributed to the onset of reaction between two amorphous oxides or to the onset of crystallisation. The higher temperature sharp peak is probably due to the reaction formation of $CaO{\cdot}6Al_2O_3$.

The STA diagram of calcium nitrate–alumina mixture appears more complicated [Fig. 1(b)]. Four steps of weight losses (21 % wt) and relative endothermic peaks were observed. The last such peak, at 830°C, can be attributed to calcium carbonate decomposition. The formation of this compound is reasonable as a result of contact between CaO and atmospheric CO_2 during storage after the first thermal treatment.

The X-ray analysis performed on the calcined material at 900°C indicated α-alumina, calcium oxide and also calcium carbonate. In this case CaO, after nitrate thermal decomposition, quickly reacts with CO_2 and transforms to carbonate.

Powders coming from nitrate decomposition may be assumed to be extremely reactive so calcium oxide will immediately react with alumina to form aluminates. In contrast, powders deriving from calcium nitrate–alumina mixtures have lower reaction rates since Ca ions must diffuse throughout the well packed α-alumina crystallographic network. This hypothesis is also supported by the shift of the high temperature exothermic peak, which appeared in the mixed nitrates mixture at 890°C, to higher temperature (930°C). X-ray diffraction of powders after the STA test indicated the presence of α-alumina and $3CaO{\cdot}5Al_2O_3$.[28] Only after prolonged heating (4 h) at 1580°C was the starting mixture transformed into hexaluminate.

In the case of mixed nitrates leading to $SrO{\cdot}6Al_2O_3$, weight is lost in two steps (47 % wt) and ends at 700°C [Fig. 2(a)]. One exothermic peak was observed at 870°C and another broad peak at 1220°C. The X-ray patterns of the powders calcined at 900°C showed the presence of $SrO{\cdot}Al_2O_3$[29] and $3SrO{\cdot}Al_2O_3$[30] but no free α-alumina was observed. The former compound was also detected

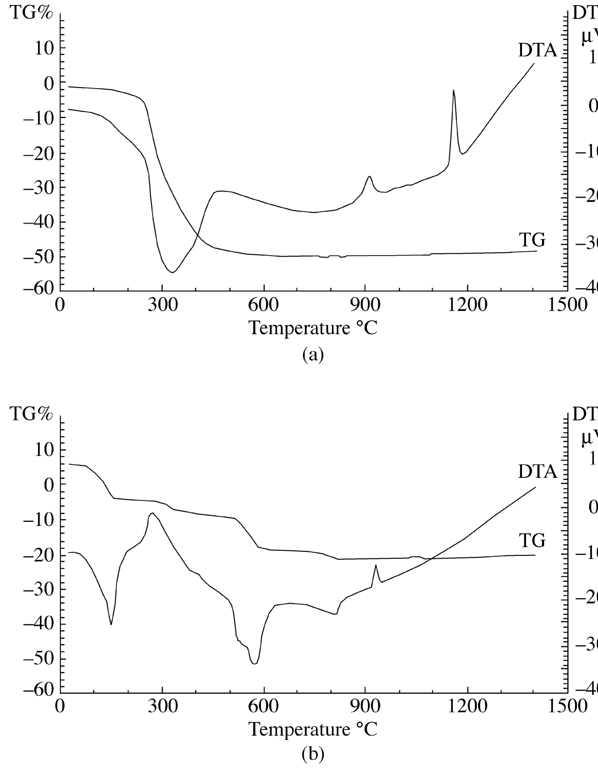


Fig. 1. STA diagrams for the precursors leading to $CaO{\cdot}6Al_2O_3$: (a) mixed nitrates and (b) calcium nitrate–alumina mixture.

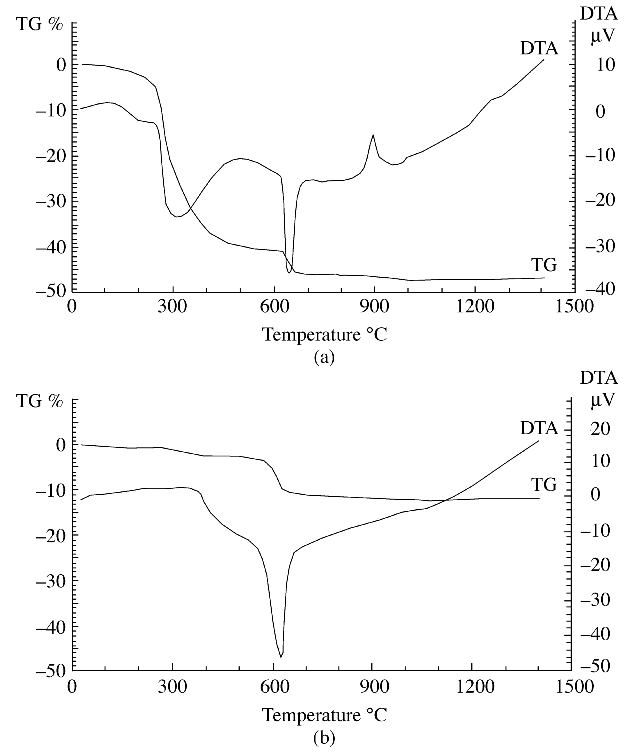


Fig. 2. STA diagrams for the precursors leading to $SrO{\cdot}6Al_2O_3$: (a) mixed nitrates and (b) calcium nitrate–alumina mixture.

in powders submitted to STA analysis which contain also the $3SrO{\cdot}16Al_2O_3$[31] and α-alumina phases. Only prolonged heating at 1580°C transformed the starting powders into strontium hexaluminate.

The STA pattern [Fig. 2(b)] of the powders coming from the mixture strontium nitrate-alumina was very simple with two weight loss steps between 300 and 620°C (10 % wt). No exothermic peaks were observed. X-ray analysis of powders calcined at 900°C showed the presence of α-alumina, $3SrO{\cdot}Al_2O_3$ and $SrO{\cdot}Al_2O_3$.

After the STA test, powders contained α-Al_2O_3 and $SrO{\cdot}Al_2O_3$. Strontium hexaluminate was obtained only after 4 h at 1580°C. The results of these investigations can be summarised as follows:

- the introduction of tartaric acid avoids the 'explosive' decomposition of nitrates;
- the mixtures of nitrates and α-alumina lead to powders which react more slowly than those obtained from mixed nitrate solutions;
- the calcination temperature of 900°C seems to be sufficiently high to promote precursor decomposition but low enough to limit particle agglomeration.

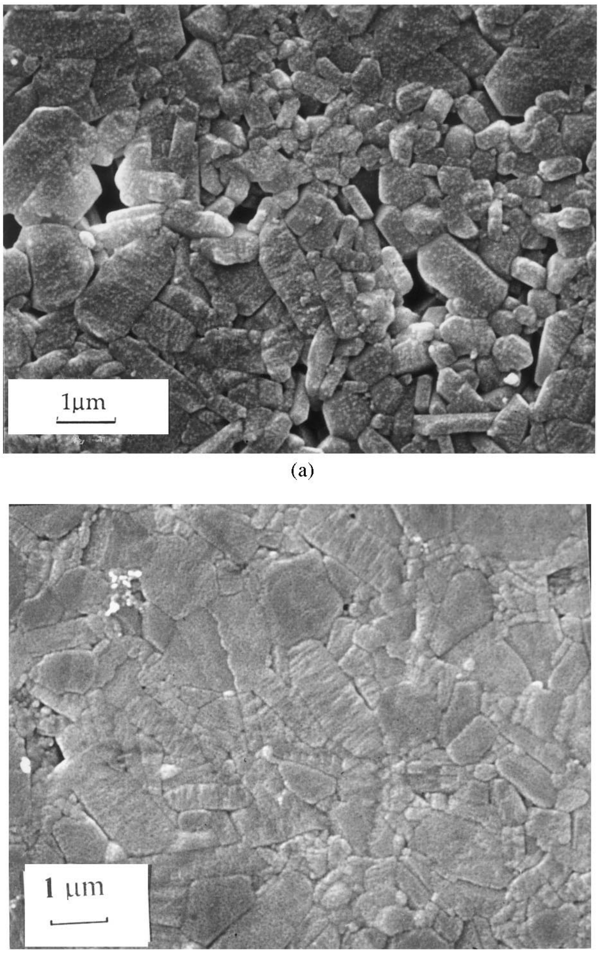
Some attempts were made to obtain high-density compacts of pure calcium and strontium hexaluminates. For this purpose the powders from calcination were attritor-milled for 6 h in order to break up the agglomerates formed during calcination, which are detrimental for the densification process.

Despite the high temperature (up to 1620°C) and the long soaking time (up 24 h), it was not possible reach high relative density by either of the preparation methods. X-ray analysis confirmed formation and the SEM showed grains with plate-like shape.

Full density sintered bodies of calcium and strontium hexaluminates were obtained by Masaoka *et al.*[32] only by using the hot pressing technique. The relative densities of our samples ranged from 88% (calcium hexaluminates) to 80% (strontium hexaluminate). The resulting microstructures consisted of tabular crystals are reported in Fig. 3(a) and (b). This kind of microstructure was also obtained by Criado *et al.*[33]

The pure hexaluminate compacts were examined to measure their thermal expansion coefficients and to extrapolate their Young moduli. Elastic modulus is a function of density so the experimental results were corrected following the Mackenzie approach.[34]

Table 1 reports the thermal expansion coefficients and Young moduli of the two hexaluminates and those of the Al_2O_3–ZrO_2 matrix.



(a)

(b)

Fig. 3. SEM microstructures of (a) pure calcium hexaluminate and (b) pure strontium hexaluminate.

Composites were prepared by the procedure described in the experimental section. On the basis of theoretical considerations,[21] the minimum content of the dispersoid in the matrix was set at 15 % vol. Lower quantities are not sufficient to assure an appreciable increase in toughness.

Attempts to obtain composites with a density near to the theoretical value by following the first preparation method failed. Prolonged firings (8 h) or higher temperatures (1620°C) did not lead to materials with final density any higher than 94%. In the case of calcium hexaluminate-containing materials, it was observed that if the soaking time at 1580°C exceeds 4 h, CaO dissolves into the ZrO_2 network and $CaO{\cdot}6Al_2O_3$ decomposes. X-ray analysis performed on samples submitted to prolonged firing processes showed only the presence of α-alumina and tetragonal zirconia. Better results were

Table 1. Average thermal expansion coefficients and corrected Young modula of ZTA, CA_6 and SA_6

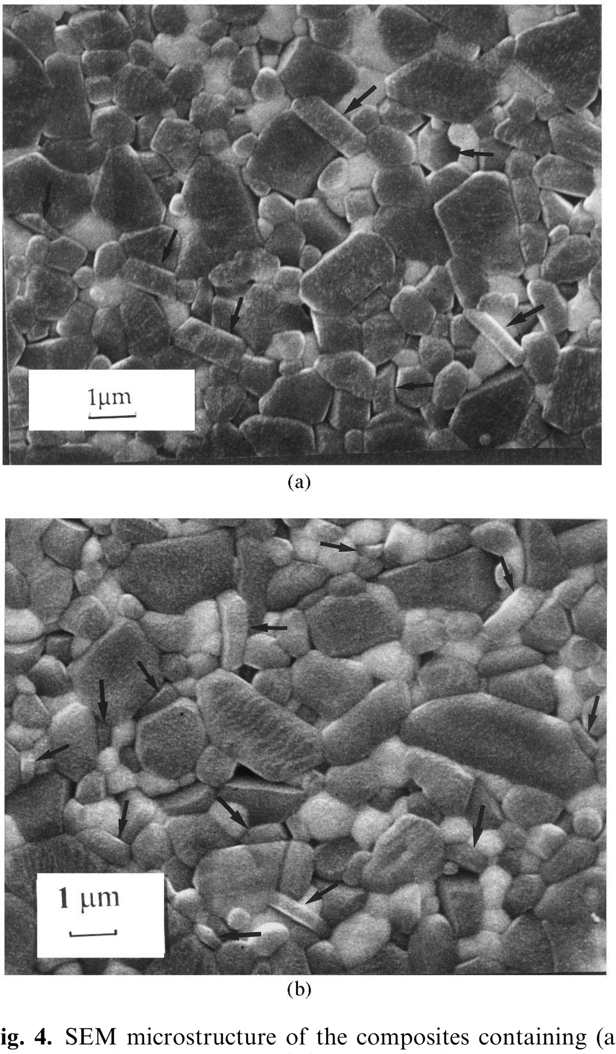
	ZTA	*CA_6*	*SA_6*
$\alpha(10^{-6}\,°C^{-1})$ 200–1200°C	11·95	11·53	10·75
E (GPa)	320	295	290

obtained using the second preparation procedure. In Fig. 4(a) and (b), the resulting microstructures are shown. The plate-like hexaluminate grains are indicated by arrows.

The relative density of the matrix is close to the theoretical (>99%), whereas that of the composites containing hexaluminates are lower. In particular the composite with Calcium hexaluminate reaches a relative density of 98%, while that with Strontium hexaluminate reaches 97%, both after sintering at 1580°C for 4 h. Therefore it is possible to affirm that hexaluminate crystals act as 'rigid inclusions' during the densification process and retard sintering.

It has been reported above that powders from two nitrate precursors react quickly and hexaluminate crystals grow promptly at low temperatures, retarding the sintering process of the surrounding α-alumina and zirconia particles.

In contrast, using powders from nitrate–alumina mixtures delays the formation of $CaO{\cdot}6Al_2O_3$ and $SrO{\cdot}6Al_2O_3$ and the composites can reach a higher density than those prepared by the first procedure. The mechanical behaviour of these composites will be discussed in detail in a future paper.



(a)

(b)

Fig. 4. SEM microstructure of the composites containing (a) calcium hexaluminate and (b) strontium hexaluminate.

4 Conclusions

Nitrates can be used as precursors for the synthesis of alumina–zirconia–Ca or Sr hexaluminate composites. In order to avoid problems related to the energetic decomposition reactions of nitrates during the thermal treatments, tartaric acid may be used. The resulting green compacts can be pressureless-sintered into materials with a density close to the theoretical one. Powders produced by the second route, i.e. addition of one nitrate only to the ZTA matrix, are to be preferred since the growth rate of the reinforcing particles is delayed. If growth rate exceeds the sintering rate of the matrix, reinforcements act as rigid inclusions and inhibit the composite sintering process.

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