

# Sol–Gel Synthesis and Characterization of Alumina–Calcium Hexaaluminate Composites

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Boehmite sol was prepared by hot water hydrolysis of aluminum iso-propoxide using nitric acid as the catalyst. Calcium nitrate to yield 0–20 vol% calcia was added to the boehmite sol. The boehmite with additives was calcined at 600°C for 3 h. The calcined powder was milled at 230 rpm for 6 h and particle size was measured using Laser particle size analyzer. The powder samples were calcined at 1600°C for 3 h and the formation of calcium hexaaluminate was discussed using phase diagram, transmission electron microscope, energy dispersive spectra, and X-ray diffraction spectra. The powder samples calcined at 600°C for 3 h were compacted into cylindrical pellets and sintered at temperatures ranging from 1400° to 1600°C for 6 h and the formation of hexaaluminate (platelike) grains were confirmed using Scanning electron microscope and optical microscopy.

## I. Introduction

CERAMICS with heterogeneous microstructures exhibit improved toughness, principally via crack stabilization from grain bridging.<sup>1</sup> These composites are oxidation resistant, possess low fracture energy, and have high temperature stability, hence used for high temperature applications.

Calcium aluminates in particular are important constituents in high alumina cement, refractories, refractory castables, flame detectors, radiation shields, filling stainless steel honey comb, rocket nozzles, missiles, constructing flame detectors, radiation shields of nuclear reactors, catalyst supports, etc.<sup>2</sup> The super fine composite powders of alumina with SiC, TiC, etc. in the form of fibers, particles, or whiskers were successfully prepared by hightemperature mixing, exothermic decomposition method, or selfpropagating synthesis reaction.<sup>3,4</sup> The common methods of incorporating fibers, whiskers, or platelets into the ceramic matrix are hot forging, tape casting, extrusion, and slip casting. It is possible to synthesize ceramic composites by an "*in situ*" reaction of homogeneous powder which during densification leads to the development of randomly dispersed phases with platelike elongated structure.<sup>5,6</sup>

The incorporation of *in situ* platelets and/or needlelike grains during processing has proved to be a viable method for enhancing the mechanical properties of ceramic materials.<sup>7</sup> Compared with the whisker-reinforced materials, the *in situ* toughened approach has the advantages of high densities and better mechanical properties.<sup>8</sup> The health hazards because of handling of whiskers are also avoided. The mechanical properties of alumina ceramics depend closely on the microstructural properties such as grain size, shape, and grain size distribution. Particulate

reinforcement holds promise for achieving fully dense sintered bodies as well as microstructural control.

The sol–gel process is one of the effective methods to synthesize highly reactive, chemically homogeneous powders of uniform sizes. The recent interest in the processing of ceramics whose microstructure exhibits platelike morphologies has increased immensely because of the fact that elongated grains act as bridging sites in the wake of the crack, hence resulting in improved mechanical behavior.<sup>9,10</sup> The *in situ* formation of calcium hexaaluminate by the addition of calcia during sintering leads to novel creation of microstructure and improved mechanical properties. Hence this paper deals with the sol–gel synthesis and characterization of *in situ* alumina–calcium hexaaluminate composites.

## (1) $CaO-Al_2O_3$ system

The phase diagram of the CaO–Al<sub>2</sub>O<sub>3</sub> system (Fig. 1) reveals that there are many stable phases such as C<sub>3</sub>A, C<sub>12</sub>A<sub>7</sub>, CA, CA<sub>2</sub>, and CA<sub>6</sub>. Among these phases, calcium hexaaluminate has the highest melting point (1860°C). It is close to the melting point of alumina (2050°C).<sup>11</sup> This phase is the most alumina-rich intermediate compound of the CaO–Al<sub>2</sub>O<sub>3</sub> system.<sup>12</sup> It exhibits the most excellent thermal properties.<sup>13</sup> The thermal expansion behavior of hexaaluminate phase is highly anisotropic ( $\alpha_a = 7.3 \times 10^{-6} \text{ K}^{-1}$ ,  $\alpha = 11.8 \times 10^{-6} \text{ K}^{-1}$ ). Singh and Sharma<sup>14</sup> prepared CA<sub>6</sub> by the decomposition reaction using CaO and Al<sub>2</sub>O<sub>3</sub>. The morphology of the CA<sub>6</sub> grains could be changed from equiaxed to platelet by modifying the processing conditions.<sup>15</sup>

CA<sub>6</sub> is chosen as a reinforcing material in alumina composites, because of chemical compatibility and mechanical and thermal expansion properties.<sup>16</sup> The elongated morphology of CA<sub>6</sub>, when combined with its mechanical and thermal expansion properties, suggests being a promising *in situ* toughening agent.<sup>17</sup>

 $CA_6$  may be formed by

(i) the reaction between CaO(C) and Al<sub>2</sub>O<sub>3</sub>(A) obtained in the reaction mix by the low temperature dissolution of calcia and  $\gamma$  alumina

(ii) the reaction between C and A

(iii) the reaction between CA<sub>2</sub> and A

(iv) the reaction among CA, CA<sub>2</sub> and A.

The equations representing probable reactions as reported by  $Singh^{18}$  are

$$C + 6A \longrightarrow CA_{6}$$

$$CA + 5A \longrightarrow CA_{6}$$

$$CA_{2} + 4A \longrightarrow CA_{6}$$

$$CA + CA_{2} + 9A \longrightarrow 2 CA_{6}$$

$$2CA + CA_{2} + 14A \longrightarrow 3 CA_{6}$$

 $C + CA_2 + 10A \rightarrow 2CA_6$ 

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CA and CA<sub>2</sub> are both reaction intermediates and are minimized with the formation of CA<sub>6</sub>. The lime-rich phases  $C_3A$  or  $C_{12}A_7$ formed as a transient phase are also converted to CA<sub>6</sub>, as the lime-rich calcium aluminates are very reactive.



Fig. 2. X-ray diffraction pattern of alumina-calcium hexaluminate composites: (a) 5 vol% calcia, (b) 10 vol% calcia, (c) 15 vol% calcia, and (d) 20 vol% calcia.



Fig. 3. (a) Transmission electron microscope observations of alumina– 5 vol% calcia composite powders; (b) the Energy dispersive spectra of the alumina–5 vol% calcia composite powders calcined at  $1600^{\circ}$ C/3 h.

## **II. Experimental Procedure**

Boehmite sol was prepared by hot water hydrolysis of aluminum iso-propoxide using nitric acid as the catalyst. Hydrolysis was carried out using double distilled water by stirring for 1.0 h at 80°C. Then 0.3 mol of nitric acid/mol of alkoxide was added as the peptizing agent. The peptization was carried out with vigorous stirring for 1 h at 80°C. Calcium nitrate to yield 0-20 vol% calcia was added. Both hydrolysis and peptization were performed under reflux conditions resulting in no loss of material. Boehmite sol with additives was precipitated in ammonia, aged overnight, vaccum filtered, oven dried at 120°C for 2 days, and calcined at 600°C for 3.0 h. The calcined powder was ground in a planetary mill at 230 rpm for 6.0 h in propanol medium using alumina balls. The powder sample calcined at 1600°C/3 h was used for transmission electron microscope (TEM), X-ray diffraction (XRD), and particle size analysis. TEM studies were conducted using JEOL 3000 FX high-resolution TEM (HRTEM, Tokyo, Japan). X-ray powder diffraction spectrum was observed on Philips analytical diffractometer PW 3710 model (Eindhoven, Netherlands) using CuKa radiation. The samples were scanned from  $10^{\circ}$  to  $80^{\circ}$  (2 $\theta$ ) (high angle XRD). The particle size analysis was performed using Laser particle size analyzer Shimadzu SALD 1100 model (Kyoto, Japan). The powder calcined at 600°C was compacted into cylindrical pellets using uni-axial press at 180 MPa and sintered at temperatures ranging from 1400° to 1600°C for 6.0 h. The pellets were mirror polished using different grades of silicon carbide May 2005



(a)

Fig. 4. (a) Transmission electron microscope observations of alumina– 15 vol% calcia composite powders; (b) the Energy dispersive spectra of the alumina–15 vol% calcia composite powders calcined at  $1600^{\circ}$ C/3 h.

sheets. The samples were thermally etched, coated with gold using POLORON 500 sputter coating unit, and then analyzed using Leica LEO Stereoscan 440 (Wetzlar, Germany) scanning electron microscope (SEM) under secondary electron (SE) mode.

#### III. Results and Discussion

#### (1) XRD Analysis Studies

The XRD pattern of samples heat-treated at  $1600^{\circ}C/6$  h are shown in Fig. 2. The XRD confirms the formation of CA<sub>6</sub>. It is also observed that alumina and CA<sub>6</sub> as major phases and CA<sub>2</sub> in traces are present. With the increase in the CaO concentration in alumina, the calcium hexaaluminate phase becomes prominent. Taking into consideration the phase diagram of the CaO–Al<sub>2</sub>O<sub>3</sub> system, the presence of CA<sub>6</sub>, Al<sub>2</sub>O<sub>3</sub>, and traces of CA<sub>2</sub> phases are observed in 20 vol% CaO. The presence of CA<sub>6</sub> and Al<sub>2</sub>O<sub>3</sub> phases are observed even below 10 vol% of calcia content.

# (2) TEM and Energy Dispersive Spectra (EDS) Studies

The size and location of calcia particles in the composite powder were analyzed using HRTEM. Figure 3(a)–(b) shows the results of the TEM observations and the EDS spectra of the alumina– 5 vol% calcia composite powders calcined at  $1600^{\circ}C/3$  h and Fig. 4(a)–(b) shows the results of the TEM observations and the EDS spectra of the alumina–15 vol% calcia composite powders calcined at  $1600^{\circ}C/3$  h. It can be seen that the particles are in the range of 500 nm. The alumina–calcia composite powders con-

 
 Table I.
 Particle Size Analysis for Various Concentrations of Calcia

Concentration of calcia (vol%)	Particle size (µm)		
	$d_{10}$	$d_{50}$	$d_{90}$
0	0.32	0.54	1.26
5	0.38	0.68	1.39
10	0.44	0.77	2.77
15	0.58	0.96	2.94
20	0.69	0.98	3.12

sisted of fine particles and large columnar particles with length > 500 nm. The EDS analysis and the selected-area electron diffraction (SAD) pattern with Debye–Scherrer rings showed that the fine particles with a uniform size around 100–500 nm were alumina. The X-ray analysis indicated that the particles consisted of CaO  $\cdot$  6Al<sub>2</sub>O<sub>3</sub>. This is consistent with the SAD patterns of these particles. The SAD pattern shows that the particles are crystalline in nature and the grain growth is accelerated by crystallization. The crystalline nature of alumina and hexaaluminate formed are confirmed through TEM. The spectra is taken on the composite powder, focused on the alumina particle and calcia particles at its surroundings.

# (3) Particle Size Analysis

The particle sizes of the powders containing 0, 5, 10, 15, and 20 vol% calcia were measured using laser diffraction particle size analyzer. Narrow particle size distribution was observed. The average particle size of the powders calcined at  $1600^{\circ}$ C/3 h and wet milled for 6 h was found to increase with the amount of calcia. The results of the particle size analysis for various concentrations of calcia are given in Table I. The samples with different concentrations of calcia calcined at  $1600^{\circ}$ C/3 h were ground and the phases formed were identified by XRD analysis. The formation of different calcium aluminate was confirmed by comparing the values of the observed peaks with the standard values as per JCPDS. The full-width at half-maximum was measured for each peak and the crystallite size *t* was calculated from the Scherrer equation (X-ray diffraction by Cullity<sup>19</sup>):

$$t = \frac{0.9 \,\lambda}{\beta \,\cos \,\theta}$$

where  $\lambda$  is the wavelength of CuK $\alpha$  radiation,  $\beta$  the full-width at half-maximum, and  $\theta$  the diffraction angle of the characteristic peak.

It is found that with the increase in the CaO content, the calcium hexaaluminate phase becomes prominent. The crystallite size of alumina and calcium hexaaluminate are given in Table II.

## (4) Density Studies

The final densities of pure alumina are often controlled by the onset of abnormal grain growth (AGG). Upon sintering, AGG abruptly occurs at certain microstructural conditions. The AGG

 
 Table II.
 Crystallite Size Using XRD for Different Concentrations of Calcia

Vol% of calcia	Crysta	Crystallite size (nm)		
	Al <sub>2</sub> O <sub>3</sub>	$CaO \cdot 6Al_2O_3$		
0	30.6	_		
5	52.7	196.9		
10	73.4	225.4		
15	96.5	315.3		
20	103.2	468.7		

XRD, X-ray diffraction.



Fig. 5. Dependence of density on concentration of calcia.



Fig. 6. (a)–(c) Optical micrographs of alumina–15 vol% Calcia sintered at  $1600^{\circ}C/6$  h. Composites under varying magnifications.



Fig. 7. (a)–(c) Fracture surface (scanning electron microscope) of alumina–15 vol% calcia composites sintered at  $1600^{\circ}C/6$  h.

and density depend on the purity, particle size, size distribution, and the type of additive added to the powder. The density also depends on the sintering conditions such as the heating rate, furnace environment, and cleanliness.<sup>20</sup> Handwerker *et al.*<sup>21</sup> have observed AGG in microstructural regions containing high calcium and Silicon concentrations. The formation of platelike abnormal grains has been observed in alumina containing a large amount of liquid forming dopants. In order to identify the optimum firing conditions, the sintering temperature was varied from 1400° to 1600°C (Fig. 5). The density is found to increase with the increase in the sintering temperature. However there is a slight decrease in density with increase in calcia content. Goswami and Roy<sup>22</sup> have reported that the slight decrease in the sintered density is because of the AGG occurring because of the May 2005

addition of calcia. During sintering, grain growth and densification occur simultaneously as intergranular pores are removed through grain-boundary diffusion until a few grains start to grow extremely fast and become excessively large by consuming small matrix grains. Then, further densification becomes difficult because the majority of the pores are trapped within or between the abnormally grown large grains. In the densification of alumina with the addition of calcia, the AGG occurs. Since the pores are trapped within or between the abnormally grown large grains, further densification becomes difficult.

## (5) Microstructure

Figure 6(a)–(c) shows the optical micrographs of alumina– 15 vol% Calcia composites under varying magnifications. Figure 7(a)-(c) shows the fracture surface of alumina-15 vol% calcia composites viewed under SEM. This shows the dispersed state of calcium hexaaluminate grains in the alumina matrix. The CA<sub>6</sub> grains are elongated platelike morphology while the alumina grains are small and equiaxed. A typical bimodal microstructure of AGG with large grains dispersed in a finegrained matrix appears.

AGG in alumina and the density is affected by the amount of liquid forming impurities. The higher the liquid content, a larger number of grains grow abnormally. As a result, a typical bimodal microstructure of AGG with large grains dispersed in a finegrained matrix appears. Song and Coble<sup>23</sup> have reported that the number of abnormal platelike grains increases with increasing doping concentration (CaO+SiO<sub>2</sub>) from 0.3 to 3 wt%. It is also because of the variation of abnormally grown grains  $(N_A)$ with liquid content. Materials containing calcium hexaaluminate develop some intermediate liquid phase during sintering and the matrix grains are therefore larger.<sup>24</sup>

## IV. Conclusions

(a) Alumina-calcium hexaaluminate composites were synthesized by the sol-gel technique.

(b) The powders were characterized using TEM and EDS and the presence of alumina and calcium hexaaluminate were confirmed.

(c) X-ray diffraction analysis confirmed the presence of the calcium hexaaluminate, calcium dialuminate, and alumina phases.

(d) The microstructural analysis shows the presence of bimodal microstructure with equiaxed alumina grains and elongated platelike calcium hexaaluminate grains.

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