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# Preparation of (Ca, Mg) $\alpha$-SiAlON powders by combustion synthesis

GUANGHUA LIU*, KEXIN CHEN, HEPING ZHOU
*Department of Materials Science and Engineering, State Laboratory of New Ceramics and Fine Processing, Tsinghua University, Beijing 100084, People's Republic of China*
*E-mail: liugh02@mails.tsinghua.edu.cn*

C. PEREIRA, J. M. F. FERREIRA
*Department of Ceramics and Glass Engineering, UIMC, University of Aveiro, 3810–193 Aveiro, Portugal*

SiAlON ceramics were discovered more than 30 years ago, and nowadays they have been identified as one of the most promising structure materials owing to the outstanding properties. There are two well-known SiAlON crystalline phases called $\alpha$ and $\beta$ with similar crystal structure to $\alpha$- and $\beta$-$Si_3N_4$ respectively. Compared with $\beta$-SiAlON, $\alpha$-SiAlON has a much higher hardness, but its fracture toughness is relatively low because of the equiaxed grains. This poor toughness has ever been a troublesome barrier limiting the further application of $\alpha$-SiAlON ceramics [1–5].

However, some recent reports show that $\alpha$-SiAlON can also develop into elongated grains with appropriate condition [6–10]. The novel *in-situ* toughened $\alpha$-SiAlON ceramics have been fabricated by carefully controlling the nucleation and grain growth process. Having high hardness and high toughness simultaneously, these new tough $\alpha$-SiAlON ceramics are more attractive for industrial applications, especially when wear resistance is much concerned.

In view of complexity of microstructure control, seeding seems to offer an attractive solution because it can effect templated growth of elongated grains. More recently, seeding method was applied in $\alpha$-SiAlON ceramics and increased fracture toughness was observed [11–12].

Preparation of single-phase crystalline seeds is the prerequisite for the fabrication of *in-situ* toughened $\alpha$-SiAlON ceramics by seeding method. In previous work [9, 13, 14], we have successfully prepared single-phase Ca, Y, and Yb $\alpha$-SiAlON powders with rod-like crystals by combustion synthesis. As an energy and time-saving technique, combustion synthesis has been attracting the interest of many researchers. Seeding with combustion-synthesized $\alpha$-SiAlON crystalline powders will provide a convenient and low-cost method to fabricate the *in-situ* toughened $\alpha$-SiAlON ceramics with elongated grains.

In this paper, (Ca, Mg) $\alpha$-SiAlON crystalline powders were prepared by combustion synthesis. The effects of multiple cation addition on the phase composition and grain morphology of the final products were discussed.

In the general formula of $M_{m/2}Si_{12-(m+n)}Al_{m+n}O_nN_{16-n}$, the composition of $m = n = 1.6$ was investigated in this work. Starting powder mixtures were prepared by using $CaCO_3$ (A. R., Beijing Chemical Co., China), $MgCO_3$ (A. R., Beijing Chemical Co., China), Si (99.0%, Fushun Al Factory, China), Al (99.5%, Gaizhou Al Co., China), $\alpha$-$Si_3N_4$ (2.0 wt.% O, Fangda High Technology Ceramics Co., China), and $SiO_2$ (A. R., Beijing Chemical Co., China) according to the proportions shown in Table I. The surface oxygen content of silicon nitride was taken into account.

The raw materials were mixed by agate balls in absolute ethanol (Beijing Chemical Co., China) for 24 hr. The obtained slurry was dried in an oven for 8 hr. Then the powder mixture was kept in a porous crucible, which was subsequently placed into the CS chamber. Evacuation was performed up to a vacuum of $10^{-4}$ MPa. The powder mixture was ignited by passing an electric current through a tungsten coil in $N_2$ with a pressure value of 2 MPa.

In order to demonstrate the stability of the as-synthesized (Ca, Mg) $\alpha$-SiAlON, the combustion product was pulverized and sieved. Then the powder was cold-pressed into a cylindrical green body by a mechanical pressure of 10 MPa and sintered at 2073 K for 2 hr. in a nitrogen atmosphere. The heating rate of 20 K/min was applied from room temperature to 1473 K and 5 K/min from 1473 K up to the apex.

The phase composition was determined by X-ray diffraction (XRD; Cu K$\alpha$, Rigaku, Japan) and the microstructure was observed by scanning electron microscopy (SEM; JSM-6460LV, JEOL, Japan) equipped with energy dispersive spectroscopy detector (EDS; INCA, Oxford Instrument).

Fig. 1 shows the XRD results of the combustion-synthesized and pressureless-sintered samples. It can be seen that $\alpha$-SiAlON was the predominant crystalline phase in the combustion products for both MS and CMS. Besides $\alpha$-SiAlON, a small amount of intermediate phases such as $\beta$-SiAlON and AlN polytypoids and remnant Si were also found. It is noticeable that no $\beta$-SiAlON was detected in the final product of CMS, indicating that the addition of $Ca^{2+}$ is helpful to prevent the formation of $\beta$-SiAlON. It is also found that using the combustion product as precursor powder, single-phase $\alpha$-SiAlON could be prepared by pressureless sintering. This confirms the high thermal stability and

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*Author to whom all correspondence should be addressed.

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TABLE I Starting compositions of the designated samples

| Sample | Composition (wt.%) | | | | | |
|---|---|---|---|---|---|---|
| | $MgCO_3$ | $CaCO_3$ | Si | $Si_3N_4$ | Al | $SiO_2$ |
| MS | 13.85 | | 24.24 | 40.40 | 17.81 | 3.71 |
| CMS | 6.83 | 8.14 | 23.92 | 39.88 | 17.58 | 3.66 |

The molar ratio of Ca/Mg in CMS was designed to be 1.

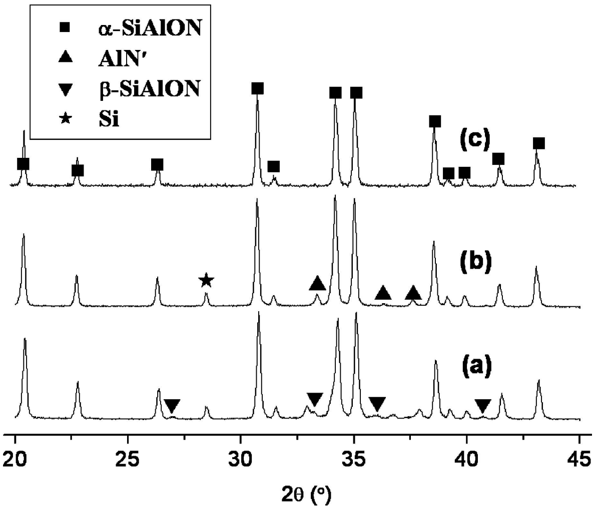

*Figure 1* XRD results for the combustion synthesized and pressureless sintered samples: (a) MS; (b) CMS; (c) sintered CMS.

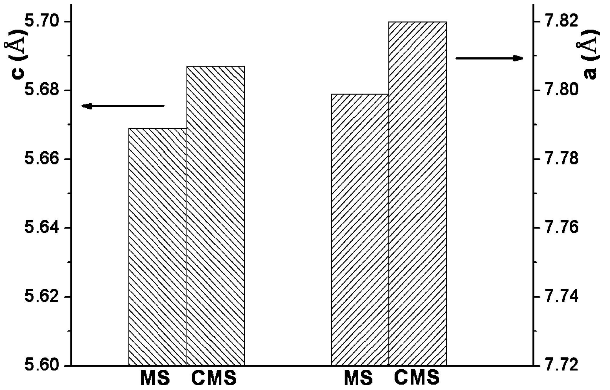

*Figure 2* Experimental results of lattice parameters for MS and CMS.

the potential for seeding of the combustion-synthesized (Ca, Mg) $\alpha$-SiAlON crystalline powders.

The experimental results of lattice parameters for the samples MS and CMS are presented in Fig. 2. It is clear that the lattice parameters of CMS are larger than those of MS, which may be caused by the following two factors. One is the increase of solid solution degree, and the other is the excess of ionic radius of $Ca^{2+}$ over $Mg^{2+}$.

Figs 3 and 4 show the SEM images of the combustion products for MS and CMS. Most grains in the final products of MS have an isotropic morphology, but a large number of rod-like grains are found in the products of CMS. This indicates that the addition of $Ca^{2+}$ enhances the anisotropic grain growth and facilitates the development of rod-like crystals.

According to the reports by Wang *et al.* [15] on the shape evolutions of $\beta$-$Si_3N_4$ and $\beta$-SiAlON crystals, the anisotropic grain growth is caused by the interfacial segregation mechanism based on acid–base theory. On the basis of this viewpoint, the aspect ratio of crystals strongly depends on the difference in acidity between the crystals and liquid phase, and more basic cations will lead to remarkable interfacial segregation and result in higher aspect ratios. Carre *et al.* [16] have determined the surface acidity of dozen of solid oxides considering the ionization potential (IP) of the corresponding metallic elements. The calculated $pH_0$ values of the oxides involved here are listed in Table II, from which it can be seen that CaO is more basic than MgO. In this way, in sample CMS with $Mg^{2+}$ partially substituted by $Ca^{2+}$, the anisotropic growth is easier to take place and rod-like grains are more likely to be formed.

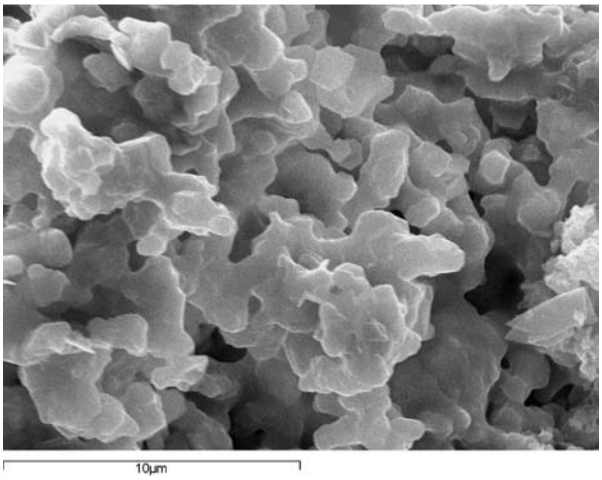

*Figure 3* Microstructure of the combustion product of MS.

The difference in basicity between CaO and MgO also results in the heterogeneous distribution of $Ca^{2+}$ and $Mg^{2+}$ in final products for sample CMS. By acid-base theory, weak acid will preferentially react with weak base and strong acid with strong base. The acidity of nitride particles can be considered by $pH_0$ values of the corresponding oxides formed on surface. From Table II, it can be deduced that CaO will preferentially react with $Si_3N_4$ and MgO with AlN. As a result, more $Ca^{2+}$ entered the interstitial sites in $Si_3N_4$ crystal lattice and $Mg^{2+}$ mainly existed in the AlN polytypoids. From the EDS results in Figs 4c and d, it can be found that roughly more calcium than magnesium is existing in the rod-like $\alpha$-SiAlON crystals and vice versa in the AlN polytypoids. In other words, the molar ratio of Ca/Mg appears to be higher in the $\alpha$-SiAlON

TABLE II Acidity/basicity of the involved oxides

| Oxide | IP of M (MJ/mol) | $pH_0$ |
|---|---|---|
| CaO | 1.74 | 10.7 |
| MgO | 2.19 | 10.3 |
| $Al_2O_3$ | 5.14 | 7.7 |
| $SiO_2$ | 9.95 | 3.4 |

Data listed in this table come from reference [16]. IP represents the ionization potential of the metallic element (M) and $pH_0$ is the point of zero charge of a solid surface, which corresponds to the pH at which the immersed solid has a zero net surface charge.

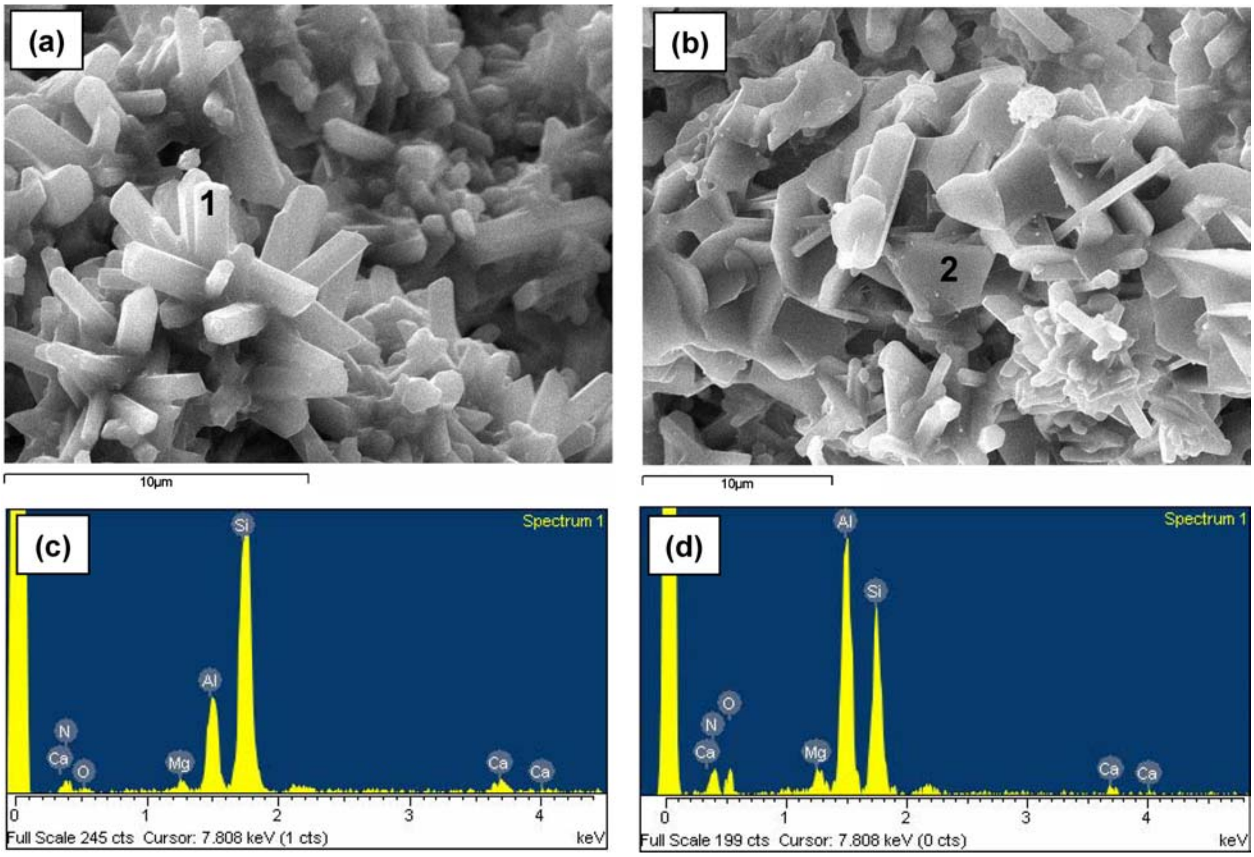

*Figure 4* Micrographs and EDS results of the combustion product of CMS: (a) rod-like $\alpha$-SiAlON crystals; (b) tabular AlN polytypoids; (c) EDS for spectrum 1; (d) EDS for spectrum 2.

crystals than in the AlN polytypoids, despite the designated overall composition of Ca/Mg = 1.

In summary, by combustion synthesis (Ca, Mg) $\alpha$-SiAlON crystalline powders were successfully prepared. It was found that the addition of $Ca^{2+}$ was beneficial for the development of rod-like $\alpha$-SiAlON crystals. The distribution of $Ca^{2+}$ and $Mg^{2+}$ in final products was found not to be homogeneous, and the molar ratio of Ca/Mg is obviously higher in the rod-like $\alpha$-SiAlON crystals than in those tabular AlN polytypoids.

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