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# Preparation of Ca α-SiAlON powders with rod-like crystals by combustion synthesis

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## Abstract

Ca α-SiAlON powders with rod-like crystals were prepared by combustion synthesis from different starting compositions. The growth mechanism of the rod-like Ca α-SiAlON crystals was investigated and two growth modes were observed. One is liquid phase precipitation, and the other is nucleation and growth on smooth surfaces of the as-developed large crystals. During the development of the rod-like Ca α-SiAlON crystals, anisotropic growth occurred with the [0 0 1] direction being the fast growth direction.

*Keywords:* A. Powders: solid-state reaction; B. Whiskers; D. Sialon

## 1. Introduction

SiAlON ceramics were discovered as solid solutions of silicon nitride more than 30 years ago, and since then they have been identified as one of the most promising structural materials owing to their high hardness, superior wear resistance and good anticorrosion performance, which are even more pronounced at elevated temperatures. Nowadays, SiAlON ceramics are used widely in high temperature industrial, automotive and aerospace applications, such as cutting tools, wire drawing, dies and blast nozzles [1–3].

There are two well-known variables of SiAlON called α and β, corresponding to α- and β-$Si_3N_4$ in crystal structure, respectively. It is generally accepted that α-SiAlON usually occurs in equiaxed grains while β-SiAlON in elongated grains, which results in the fact that the fracture toughness of α-SiAlON is lower than β-SiAlON. However, some recent studies have shown that α-SiAlON can also develop into elongated morphology by carefully controlling the nucleation and growth process, which represents a great breakthrough suggesting that hard and tough α-SiAlON ceramics can be developed [4–8].

Compared with the case in β-SiAlON, the microstructure of α-SiAlON is more sensitive to the composition, the processing conditions, as well as the starting compositions. In view of the complexity of microstructure control, seeding with elongated crystals seems to offer an attractive solution because it can affect templating growth of elongated grains. Several reports on seed addition in β-$Si_3N_4$ based ceramics have demonstrated the great potential of this method for microstructure tailoring in silicon nitride ceramics [9,10]. More recently, some studies on seed addition in α-SiAlON were also been reported and the additive seed crystals were proved to have important effects on the microstructure, resistant (R-curve) behavior, and Weibull modulus of the hot-pressed α-SiAlON ceramics [11]. Fabrication of seed crystals is a preliminary foundation for producing the in situ reinforced α-SiAlON ceramics with elongated grains. Until now, there are two main methods reported to prepare single-phase α-SiAlON seed crystals: growing from an appropriate liquid and combustion synthesis [12,13].

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As a facile and economically viable technique for the preparation of advanced ceramics, catalysts and nanomaterials, combustion synthesis has been widely applied in fabricating a variety of ceramic powders [14]. The α-SiAlON crystalline powders with a rod-like morphology prepared by combustion synthesis have a low contamination level and a high degree of conversion, and furthermore they are easy to be pulverized and dispersed because of little residual glassy phase and lower density than sintered ceramics. These characteristics make the combustion-synthesized rod-like α-SiAlON particles more attractive and confer them a higher potential for industry applications [13]. In this case, it will provide a productive and low-cost way for the fabrication of in situ reinforced α-SiAlON ceramics by using the combustion-synthesized rod-like crystals as seeds.

In this paper, Ca α-SiAlON powders with rod-like crystals were prepared by combustion synthesis. Additionally, further investigation on the growth mechanism of the rod-like Ca α-SiAlON crystals was performed. By the TEM results, the fast growth direction of the rod-like crystals in the anisotropic growth was also determined.

## 2. Experimental procedure

In the single-phase area of Ca α-SiAlON represented by the general formula of $Ca_{m/2}Si_{12-(m+n)}Al_{m+n}O_nN_{16-n}$, three composition points were investigated: $m = 1.6$, $n = 1.0$; $m = n = 1.6$; $m = 2.4$, $n = 1.6$.

Starting reactants were prepared by using $CaCO_3$ or CaO (A.R., Beijing Chemical Co., China), Si (99.0%, Fushun Al Factory, China), Al (99.5%, Gaizhou Al Co., China), α-$Si_3N_4$ (1.8 wt.% O, Fangda High-Technology Ceramics Co., China) and $SiO_2$ (A.R., Beijing Chemical Co., China) according to the proportions listed in Table 1. The surface oxygen content of α-$Si_3N_4$ was considered when calculating the compositions. To be brief, all the samples were labeled as CS1610, CS1616, CS1616-2 and CS2416, respectively.

The raw materials were milled by agate balls in a Teflon jar for 24 h with absolute ethanol used as medium, and the obtained slurry was dried in an oven at 70 °C for 8 h. Then the powder was poured into a porous crucible, which was later placed into a reaction chamber especially for combustion synthesis.

The reaction chamber was evacuated to a vacuum of $10^{-4}$ MPa and then inflated with high-purity $N_2$ at a pressure value of 2 MPa. The reactant powder was ignited by passing an electric current through a tungsten coil. The reaction temperature was recorded by a W-Re3/W-Re25 thermocouple, which was inserted into the sample and connected with a computer system for data acquisition.

Table 1
Starting compositions of the samples

| Samples | Compositions (wt.%) | | | | | |
|---|---|---|---|---|---|---|
| | CaO | $CaCO_3$ | Si | α-$Si_3N_4$ | Al | $SiO_2$ |
| CS1610 | 0 | 15.82 | 26.02 | 44.03 | 13.88 | 0.26 |
| CS1616 | 0 | 16.06 | 23.61 | 39.36 | 17.35 | 3.61 |
| CS1616-2 | 9.68 | 0 | 25.41 | 42.35 | 18.67 | 3.89 |
| CS2416 | 0 | 22.49 | 20.99 | 35.04 | 20.24 | 1.24 |

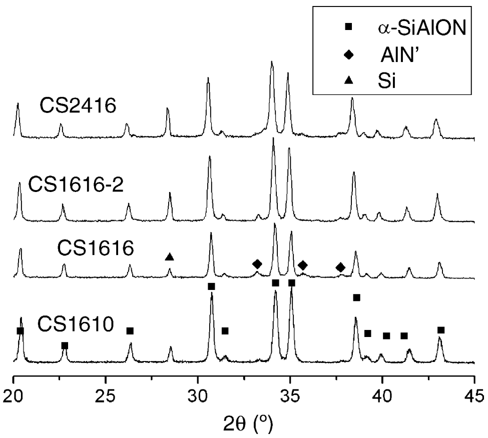

Fig. 1. XRD results of the final combustion products.

The phase composition was determined by X-ray diffraction (XRD; Cu Kα, Rigaku, Japan) and the lattice parameters were acquired using Si as internal standard. The microstructure was examined by scanning electron microscopy (SEM; JSM-6460LV, JEOL, Japan) equipped with energy dispersive spectroscopy detector (EDS; INCA, Oxford Instrument). Transmission electron microscope (TEM; JEM-2010F, JEOL, Japan) was also used to determine the fast growth direction of the rod-like Ca α-SiAlON crystals.

## 3. Results and discussion

### 3.1. Phase compositions of the final combustion products

The XRD results of the final combustion products are shown in Fig. 1. It can be seen that except for a little residual Si and slight AlN-polytypoid, almost single-phase α-SiAlON was obtained in all products, though they had different starting compositions. Based on the XRD results, the lattice parameters of as-synthesized Ca α-SiAlON are acquired and listed in Table 2. The experimental results are basically consistent with the calculated results according to the experiential equations reported in literature [15].

Table 2
Lattice parameters of the as-synthesized Ca α-SiAlON

| Samples | Experimental results | | Calculated values[a] | |
|---|---|---|---|---|
| | a (Å) | c (Å) | a (Å) | c (Å) |
| CS1610 | 7.852 | 5.708 | 7.859 | 5.715 |
| CS1616 | 7.855 | 5.706 | 7.860 | 5.711 |
| CS1616-2 | 7.851 | 5.703 | 7.860 | 5.711 |
| CS2416 | 7.905 | 5.749 | 7.914 | 5.755 |

[a] According to Ref. [15].

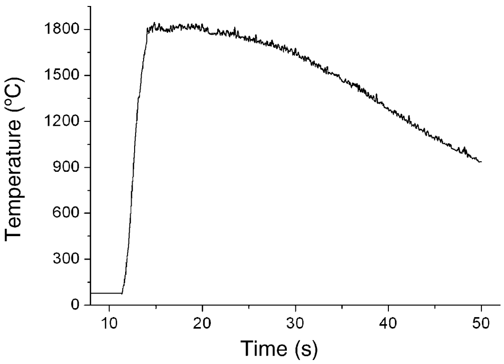

Fig. 2. Typical temperature history in the combustion synthesis of Ca α-SiAlON.

Combustion synthesis is a technique in which the reaction is maintained by the heat energy produced during the combustion reaction itself. Once the reaction starts with an ignition process, a large amount of heat is produced in a very short time period, resulting in a dramatic increase in temperature. Hence, high reaction temperature and rapid heating rate are two main characteristics of combustion synthesis [14]. Fig. 2 exhibits the temperature–time curve of CS1610, representing typical temperature history in the combustion synthesis of Ca α-SiAlON. It can be seen that as soon as the combustion reaction started, the temperature increased very quickly from about room temperature up to the apex above 1800 °C in no more than 10 s. During the reaction process, the maximum heating rate was higher than 300 °C/s. Owing to this fast heating rate, the reactants were kept in intermediate temperature range for considerably short time and thus the formation of various intermediate phases was weakened or avoided. Consequently, almost single-phase Ca α-SiAlON was prepared as the final product.

From the XRD results shown in Fig. 1, it is noticed that some residual Si existed in the final products, but no Al was found. This is probably attributed to their different melting points and energy barrier for nitridation reactions. In the combustion synthesis, the reaction temperature was clearly higher than the melting points of Al (660 °C) and Si (1412 °C), so the metallic particles would melt and

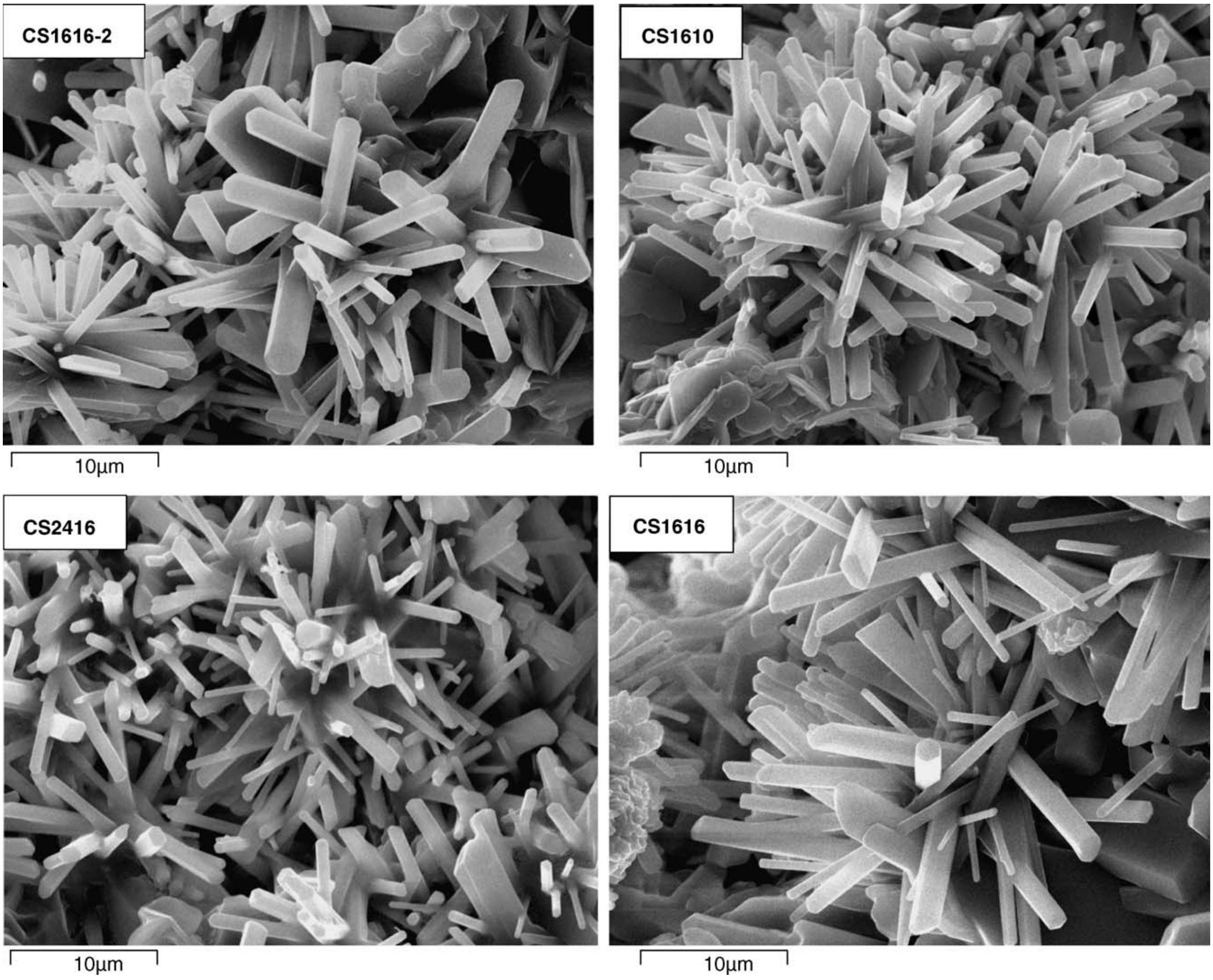

Fig. 3. Microstructures of the final combustion products.

vaporize after being heated. Because of lower melting point, Al will be nitridated at first after melting and vaporizing. Therefore, there is more adequate time for Al to complete the nitridation reaction compared with that for Si. On the other hand, the energy barrier for the nitridation of Al is lower than that for Si [7], thus the nitridation reaction of Al is easy to take place. Finally, there are more Si than Al in the starting reactants. Because of the above reasons, the nitridation reaction of Al was fully completed and no residual Al was found in the final products, while the nitridation reaction of Si was not finished and some unreacted Si was remnant.

By comparing the phase composition of CS1616-2 with that of CS1616, it can be found that it had no remarkable effect other than a slight change in the amount of residual Si to replace $CaCO_3$ by CaO as Ca source. Since $CaCO_3$ will decompose above 825 °C and release $CO_2$ gas, which is helpful to weaken the agglomeration of melting Si and enhance the infiltration of $N_2$, it is better to use $CaCO_3$ instead of CaO so as to improve the nitridation reaction and reduce residual Si.

### 3.2. Microstructures of the final combustion products

Fig. 3 shows the micrographs of the final combustion products. In all samples, rod-like crystals are visible as the predominant grain morphology. These rod-like crystals precipitate and grow towards various directions from the co-existing liquid phase and exhibit a radiate shape. Most crystals have a width from 0.5 to 2 μm and a length about 10 μm. Some rod-like crystals have an aspect ratio beyond 10. Compared with the equiaxed α-SiAlON grains, these rod-like crystals are more attractive in fabricating tough α-SiAlON ceramics.

Generally speaking, the final morphology of crystalline grains relates to the following two processes: nucleation and growth. By choosing appropriate techniques to manipulate these two processes, one can control the final grain morphology. The fast heating rate and short reaction time period of combustion synthesis are beneficial to the development of rod-like α-SiAlON crystals.

On one hand, in the combustion synthesis the fast heating rate favors the dissolution of nitride particles and is helpful to limit the nucleation. In this way, a small number of nuclei

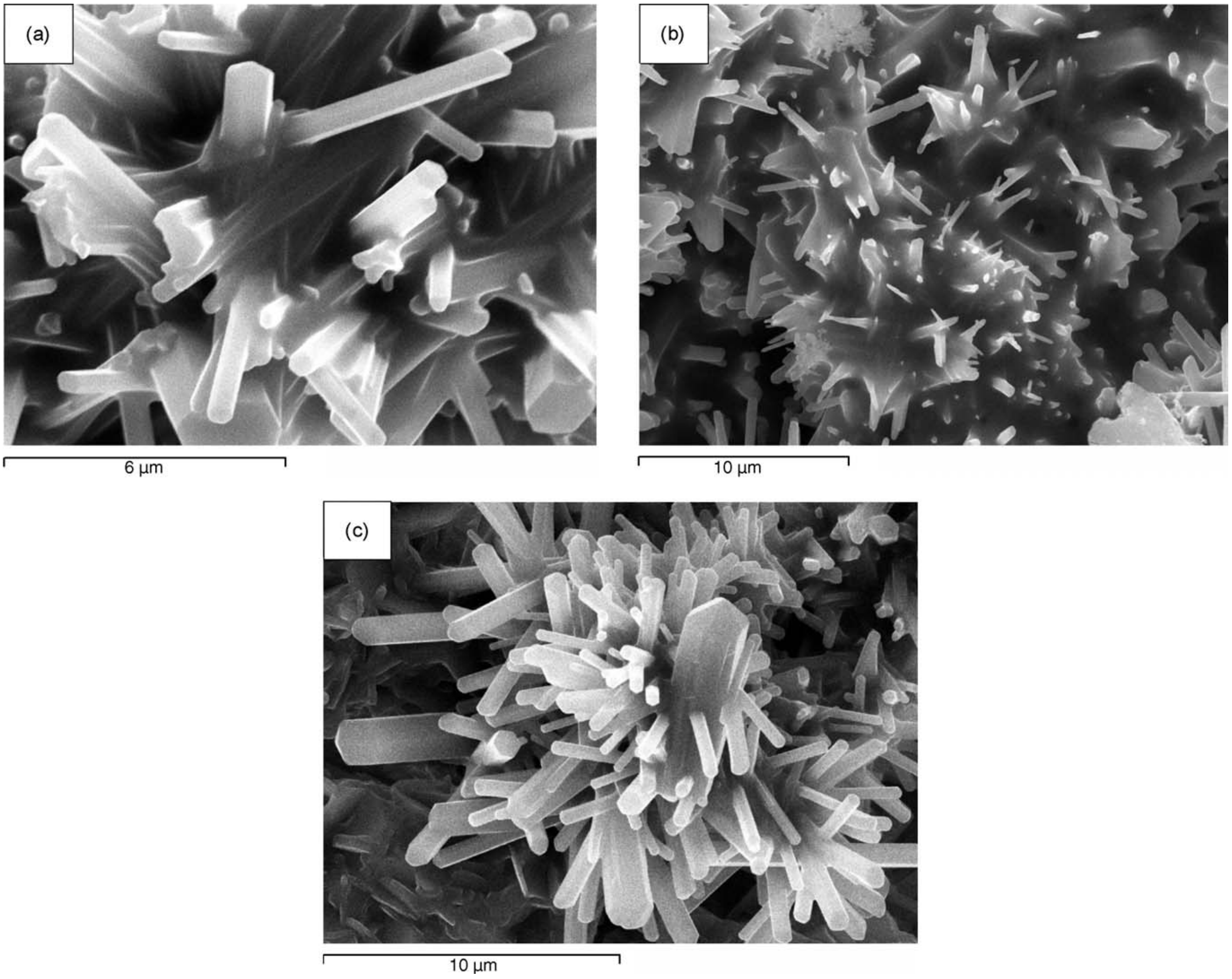

Fig. 4. Growth modes of rod-like Ca α-SiAlON crystals.

are formed at the initial nucleation stage, and at the later growth stage these nuclei have adequate space to develop into rod-like grains.

On the other hand, because of the fast heating rate and short reaction time, the reactant system has no enough time to reach equilibrium and thus exists in a non-equilibrium state. In this state, the composition of the liquid phase is dramatically out of equilibrium with that of the matrix crystalline grains, and thereby a strong chemical driving force for the liquid and matrix to equilibrate is created. This results in a dramatically enhancement of the kinetics of the dissolution and transport of appropriate species yielding a very fast anisotropic grain growth [16]. Owing to the drastic impact of such a non-equilibrium state on the grain growth, well-faceted rod-like Ca α-SiAlON crystalline grains were quickly developed in tens of seconds, as shown in Fig. 3.

### 3.3. Growth mechanism of the rod-like Ca α-SiAlON crystals

In general, the growth of α-SiAlON grains is performed via a dissolution-reprecipitation mechanism, assisted by a co-existing liquid phase. At high temperatures, a large number of fine silicon nitride particles will dissolve into liquid, and the materials are transported onto the surfaces of un-dissolved grains by diffusion in liquid. Thus, new α-SiAlON crystals precipitate from the liquid phase and grow into large grains.

Similarly, precipitating from liquid was also proved the predominant growth mode for the rod-like Ca α-SiAlON crystals prepared by combustion synthesis in this work. Fig. 4(a) and (b) exhibits the very scene of the rod-like crystals growing from liquid phase. At the same time, another growth mode for the rod-like α-SiAlON crystals was also observed. Based on the smooth surfaces of the as-existing larger grains, some new crystals could nucleate and grow up, as shown in Fig. 4(c).

During the development of rod-like Ca α-SiAlON crystals, the anisotropic grain growth took place. The rod-like morphology indicated that the growth rates of Ca α-SiAlON crystals in different directions were not equal. In the length direction, the rod-like crystals grew much faster. Fig. 5 shows the TEM results of a certain rod-like Ca α-SiAlON crystal. From the TEM, HREM images and SAD pattern, it can be found that the rod-like α-SiAlON crystals have the fastest growth rate in [0 0 1], viz. the *c*-axis direction of the hexagonal crystal lattice. The basal plane is the fast growth plane for the rod-like Ca α-SiAlON crystal.

Anisotropic growth is very common in β-$Si_3N_4$ based ceramics, and the growth mechanism of elongated β-$Si_3N_4$ or β-SiAlON crystals have been widely studied [17–19]. Krämer et al. [17] calculated the theoretical growth form of β-$Si_3N_4$ to be a rod-like prism bounded with the F-faces {1 0 0} and {1 0 1} by the periodic bond chain (PBC) theory. They also pointed out that in the case where larger amounts of oxygen are present, the {1 0 1} form was replaced by (0 0 1), which suggested that oxygen was specifically adsorbed on (0 0 1) surfaces causing a retardation of normal growth.

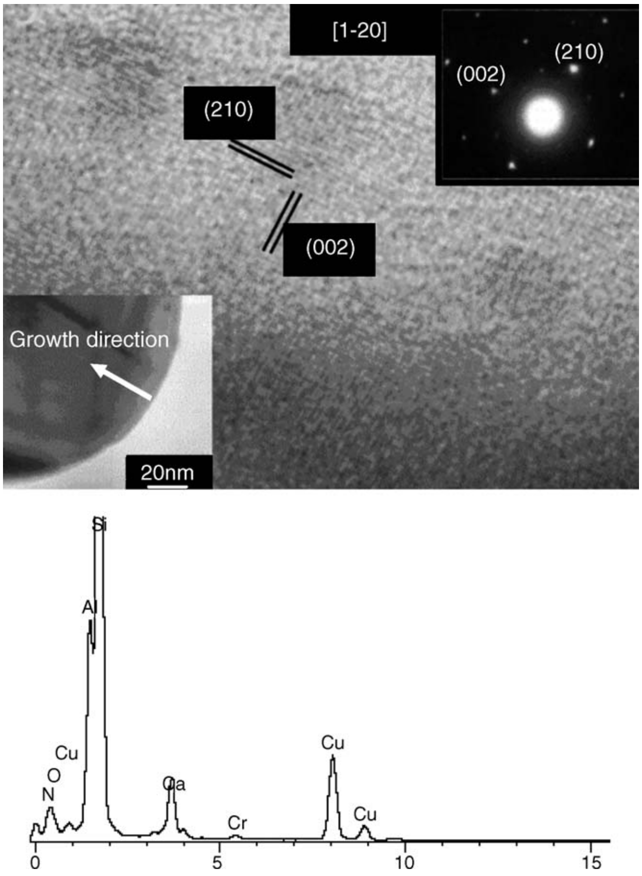

Fig. 5. TEM results of a certain rod-like Ca α-SiAlON crystal.

In this work, the anisotropic grain growth occurring in the microstructural development of rod-like Ca α-SiAlON crystals shows some similarity to the case in β-$Si_3N_4$ based ceramics. This similarity may be attributed to their analogical crystal lattices, i.e. both α-SiAlON and β-$Si_3N_4$ or β-SiAlON have a hexagonal lattice with the ratio $c/a < 1$ and the atom arrangement on the basal plane is alike.

## 4. Conclusions

Almost single-phase Ca α-SiAlON powders with rod-like crystals were prepared by combustion synthesis with different starting compositions. The phase compositions and the microstructures of the final combustion products were discussed in detail. The growth mechanism of the rod-like Ca α-SiAlON crystals was investigated and two growth modes were observed: precipitating from liquid phase; nucleating and growing based on the as-developed large crystals. During the development of the rod-like Ca α-SiAlON crystals, the anisotropic growth took place. It was proved by TEM results that [0 0 1] was the preferred growth direction and the basal plane was the fast growth plane.

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