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# Fabrication of yttrium-stabilized α-SiAlON powders with rod-like crystals by combustion synthesis

**Guanghua Liu · Kexin Chen · Heping Zhou · Xiaoshan Ning · C. Pereira · J. M. F. Ferreira**

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**Abstract** Yttrium-stabilized α-SiAlON powders with rod-like crystals were fabricated by combustion synthesis. Effects of starting compositions including relative content of diluents on final phase assemblage and grain morphology of combustion products were discussed. With appropriate proportions of α-SiAlON seeds and $NH_4F$ additive, α-SiAlON powders with rod-like crystals could be fabricated. It was found that the addition of α-SiAlON and $NH_4F$ could improve the anisotropic growth of rod-like crystals. However, if too much $NH_4F$ was added, the phase purity of combustion products would be decreased obviously and more β-SiAlON was produced. Additionally, the as-synthesized α-SiAlON powders were heat treated at 1800 °C for 1 h to examine their stability at the elevated temperature. The experimental results showed that after the heat treatment, single-phase α-SiAlON was obtained, revealing the high stability of combustion synthesized α-SiAlON powders.

## Introduction

Owing to the superior mechanical properties and good thermal shock resistance, SiAlON ceramics have been identified as one of the most promising structural materials at both room and elevated temperatures. SiAlON ceramics are used widely for high temperature industrial, automotive and aerospace applications. There are two well-known SiAlON variables called α and β, as solid solutions of α- and β-$Si_3N_4$, respectively. With a high hardness and good wear resistance, α-SiAlON is a good candidate for fabricating cutting tools. However, compared with β-SiAlON, α-SiAlON has a poor toughness associated with the usually observed isotropic grain morphology, which has strongly limited its further applications [1–6].

In recent years, a large amount of efforts have been made to fabricate new tough α-SiAlON ceramics. These studies have revealed that, by controlling the nucleation and grain growth processes carefully, α-SiAlON grains can also develop into rod-like morphology and the fracture toughness can be remarkably improved [7–10]. In this way, new α-SiAlON ceramics exhibiting both high hardness and improved toughness can be fabricated and the potential of α-SiAlON for industrial applications can be enhanced.

For silicon nitride-based ceramics, seeding has been proved to be an effective method to produce coarse rod-like grains [11–15]. Synthesis of small α-SiAlON seed crystals by liquid-phase growth has been reported [16, 17]. At the same time, combustion synthesis can also be used to prepare α-SiAlON powders. In this technique, because of high reaction temperature and fast heating rate, α-SiAlON grains can develop into rod-like morphology very quickly [18, 19]. Due to the cheaper raw materials and low energy consumption, combustion synthesis appears to be a low-cost method to prepare α-SiAlON seed crystals. In addition, the combustion products are not as dense and hard as general sintered α-SiAlON ceramics, and thus they can be pulverized more easily. These advantages make the

G. Liu · K. Chen (✉) · H. Zhou · X. Ning
Department of Materials Science and Engineering, State Key Laboratory of New Ceramics and Fine Processing, Tsinghua University, 100084 Beijing, People's Republic of China
e-mail: kxchen@mail.tsinghua.edu.cn

C. Pereira · J. M. F. Ferreira · G. Liu
Department of Ceramics and Glass Engineering, University of Aveiro, CICECO, 3810-193 Aveiro, Portugal

combustion-synthesized α-SiAlON seed crystals more attractive for industrial applications.

More recently, novel functional characteristics of α-SiAlON such as transparency and photoluminescence have been noticed. Highly transparent α-SiAlON ceramics have been prepared and the photoluminescence of α-SiAlON doped with different cations have been well studied [20–24]. These reports have shown that, besides usual applications as a structural material, α-SiAlON can also be used as a functional material. As a facile and economic technique, combustion synthesis can probably provide a low-cost way for fabricating α-SiAlON phosphor powders in a large quantity, although no complete results about this topic have been reported.

Among a variety of α-SiAlON systems, α-SiAlONs stabilized by rare-earth metals have received great attentions, because of higher temperature for the appearance of ternary oxide eutectic melt, which is helpful to improve the mechanical properties of α-SiAlON ceramics at elevated temperatures. Yttrium (Y) is one of well-know rare-earth metals exhibiting a high ability to stabilize α-SiAlON structure, and the phase relationships involved in Y–Si–Al–O–N system have been well studied. In this way, Y is selected as stabilizing element in this work to prepare α-SiAlON powders with rod-like crystals.

This paper presents Y-stabilized α-SiAlON powders with rod-like crystals prepared by combustion synthesis. Effects of starting compositions on the phase assemblage and grain morphology of combustion products are discussed in detail. Additionally, a heat treatment experiment is also performed to examine the stability of as-synthesized α-SiAlON powders.

## Experimental procedure

The overall compositions investigated here are located in the single-phase area of Y α-SiAlON, which can be represented by the general formula of $Y_{m/3}Si_{12-(m+n)}Al_{m+n}O_nN_{16-n}$. In this study, five compositions of ($m$ = 1.2, $n$ = 0.9), ($m$ = 1.2, $n$ = 1.2), ($m$ = 1.2, $n$ = 1.5), ($m$ = 1.5, $n$ = 1.2), and ($m$ = 1.8, $n$ = 1.2) were studied. Specially, the composition of ($m$ = 1.5, $n$ = 1.2) was selected to investigate the effects of various diluents and additives.

Starting powder mixtures were prepared by using $Y_2O_3$ (99.9%, General Research Institute for Nonferrous Metals, China), Si (99.0%, Fushun Al Factory, China), Al (99.5%, Gaizhou Al Co., China), α-$Si_3N_4$ (94% α, 1.7 wt.% O, Fangda High-Technology Ceramics Co., China), β-$Si_3N_4$ (1.5 wt.% O, self-fabricated by combustion synthesis), AlN (2.0 wt.% O, Fujian Sinocera advanced materials Co., China), $SiO_2$ (A.R., Beijing Chemical Co., China), α-SiAlON (self-fabricated by combustion synthesis), and $NH_4F$ (A.R., Beijing Chemical Co., China). The surface oxygen of nitride powders was considered when calculating the composition. The starting compositions of all the samples are reported in Table 1, in which each sample composition is given a simple code.

The raw materials were mixed by agate balls in a plastic jar for 24 h with absolute ethanol used as medium. The obtained slurry was dried in an oven at 70 °C for 8 h and then passed through an 80-mesh sieve with the pore size of ~180 μm. The as-prepared reactant powder mixture was contained in a porous graphite crucible and subsequently placed in a special reaction chamber 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 about 30 A through a tungsten coil. The reaction temperature was recorded by a W-Re3/W-Re25 thermocouple, which was directly inserted into the sample and connected with a computer system for data acquisition.

The phase assemblage was identified by X-ray diffraction (XRD; Cu$K_\alpha$, Rigaku, Japan). The microstructure was examined by scanning electron microscopy (SEM; JSM-6460LV, JEOL, Japan) equipped with an energy dispersive spectroscopy detector (EDS; INCA, Oxford Instrument).

## Results and discussion

During the combustion synthesis process, once the combustion reaction is triggered, the nitridation reactions of Al and Si will process very quickly and produce a large amount of heat energy, leading to a dramatic increase in temperature. Figure 1 shows the temperature–time curve of the sample YS1512-C, representing the typical temperature history during the combustion synthesis. It can be seen that in only several seconds, the temperature increases to the apex of about 1840 °C, and the average heating rate is higher than 250 °C/s. The cooling stage lasts about 40 s from the apex to 1360 °C, which is close to the eutectic formation temperature in Y–Si–Al–O–N system [25]. Since the phase transformation and grain growth of α-SiAlON generally take place via the dissolution-reprecipitation mechanism with the aid of a co-existing liquid phase, it can be simply assumed that below the eutectic formation temperature the α-SiAlON crystals undergo no further change.

Although compared with common reaction sintering process, the whole reaction period of combustion synthesis is very short and the total reaction time is no more than

**Table 1** Starting compositions and final phase assemblages of all the samples

| Sample code | Starting composition | | | | | | Phase assemblage | | |
|---|---|---|---|---|---|---|---|---|---|
| | *m* | *n* | $Si_3N_4$/Si (molar ratio) | AlN/Al (molar ratio) | α-SiAlON (wt.%) | $NH_4F$ (wt.%) | α-SiAlON | β-SiAlON | Si |
| YS1209 | 1.2 | 0.9 | 1/5 | 1/4 | | | s | | w |
| YS1212 | 1.2 | 1.2 | 1/5 | 1/4 | | | s | | |
| YS1215 | 1.2 | 1.5 | 1/5 | 1/4 | | | s | w | |
| YS1812 | 1.8 | 1.2 | 1/5 | 1/4 | | | s | | w |
| YS1512-A | 1.5 | 1.2 | 1/5 | 1/4 | | | s | | w |
| YS1512-B | 1.5 | 1.2 | 1/5 | 1/4 | | | s | w | |
| YS1512-C | 1.5 | 1.2 | 1/7 | 1/4 | | | s | | w |
| YS1512-D | 1.5 | 1.2 | 1/9 | 1/4 | | | s | | m |
| A10F0 | 1.5 | 1.2 | 0 | 0 | 10 | 0 | s | w | m |
| A10F2 | 1.5 | 1.2 | 0 | 0 | 10 | 2 | s | w | w |
| A10F5 | 1.5 | 1.2 | 0 | 0 | 10 | 5 | s | m | w |
| A10F10 | 1.5 | 1.2 | 0 | 0 | 10 | 10 | m | s | |
| A20F0 | 1.5 | 1.2 | 0 | 0 | 20 | 0 | s | | w |
| A20F2 | 1.5 | 1.2 | 0 | 0 | 20 | 2 | s | | w |
| A20F5 | 1.5 | 1.2 | 0 | 0 | 20 | 5 | s | m | |
| A20F10 | 1.5 | 1.2 | 0 | 0 | 20 | 10 | s | s | |
| YS1209-HT | | | | | | | s | | |
| YS1512-A-HT | | | | | | | s | | |

*Note*: (1) α-$Si_3N_4$ was used as diluents in the samples from YS1209 to YS1512-D, except for YS1512-B, in which β-$Si_3N_4$ was used

(2) For describing the phase assemblage briefly, s = strong, m = medium, w = weak

(3) For the samples YS1209-HT and YS1512-A-HT, ''-HT'' means after heat treatment

50 s, the phase evolution has been basically completed. In most samples, α-SiAlON is produced as the predominant crystalline phase, occasionally accompanied with a small amount of residual Si or β-SiAlON. Single-phase α-SiAlON is obtained in the samples YS1212 and A20F2. As common intermediate phases usually associated with the formation of α-SiAlON, AlN polytypoids are not found in the combustion products for a variety of starting compositions. This result has not been well understood and perhaps it should be attributed to the fast heating rate and short reaction period in combustion synthesis.

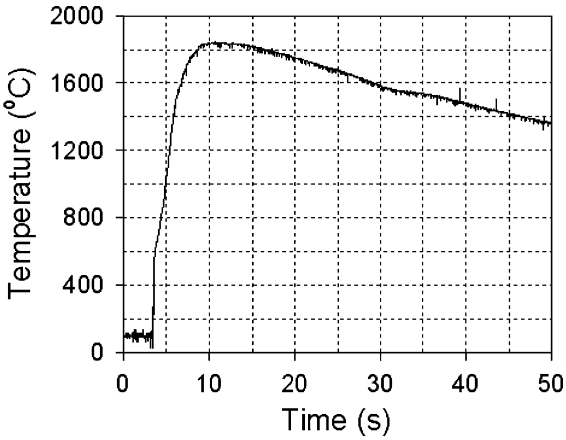


**Fig. 1** Typical temperature history during the combustion synthesis (from the sample YS1512-C)

Figure 2 shows several typical XRD patterns of combustion products, and the phase assemblages for all samples are reported in Table 1 in detail. It is noticed that, in the XRD pattern of A10F5 shown in Fig. 2e, the diffraction peaks corresponding to α-SiAlON shift slightly toward high degree, in comparison with those in the other samples. This shift may be attributed to the formation of

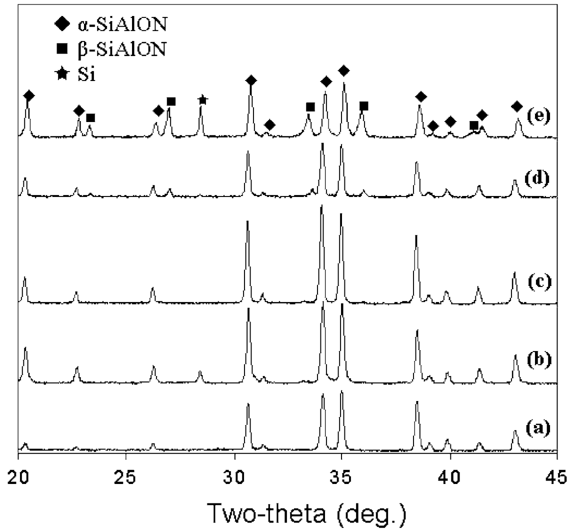


**Fig. 2** XRD patterns of the combustion products: (**a**) YS1212; (**b**) YS1512-A; (**c**) YS1512-A-HT, after being heat treated at 1800 °C for 1 h; (**d**) YS1512-B, with β-$Si_3N_4$ as raw material; (**e**) A10F5, with the addition of 10 wt.% α-SiAlON and 5 wt.% $NH_4F$

much more $\beta$-SiAlON phase, which probably modifies the chemical composition of $\alpha$-SiAlON.

Figure 3 shows SEM micrographs of the combustion products. No remarkable difference has been found in the grain morphology of the samples YS1512-A, YS1209, and YS1812, as shown in Fig. 3a, e, and f. The micrographs of the samples YS1212 and YS1215 (not shown here) are also similar with those of the above three samples. This indicates that the chemical composition ($m$ and $n$ values) does not considerably affect the grain morphology of as-synthesized $\alpha$-SiAlON products. It seems that there is some difference between the combustion synthesis and common reaction sintering. For reaction sintering process, the final grain morphology of $\alpha$-SiAlON is usually sensitive to its chemical composition. This is not difficult to understand, since on one hand different chemical compositions will lead to different driving force for phase transformation and grain growth, and on the other hand different chemical compositions indicate different oxygen contents in the co-existing liquid phase, and the amount, distribution, and viscosity of this liquid phase usually have important effects on the formation and grain growth of new $\alpha$-SiAlON phase. The fact that no obvious effect of chemical composition on the final grain morphology of $\alpha$-SiAlON has been noticed in this study should be attributed to the very fast reaction rate and short reaction period in combustion synthesis. Under this condition, the reaction system has no adequate time to arrive at an equilibrium or near-equilibrium state and the difference in driving force resulted from different chemical compositions makes no great sense. In other words, the combustion synthesis seems to be not a thermodynamically determined but a kinetically determined process, which is different with the case of reaction sintering.

Due to the fast heating rate, in the combustion reaction the Al and Si particles in raw materials will melt and agglomerate when the temperature is elevated in a short time, which is not beneficial to subsequent infiltration of $N_2$ or further progress of nitridation reactions. In this case, some diluents with relative high melting points are required to be added into starting powders in order to reduce the agglomeration and improve $N_2$ infiltration, thus ensuring the continuous progress of combustion reactions. In this study, two types of diluents are used. One is silicon nitride

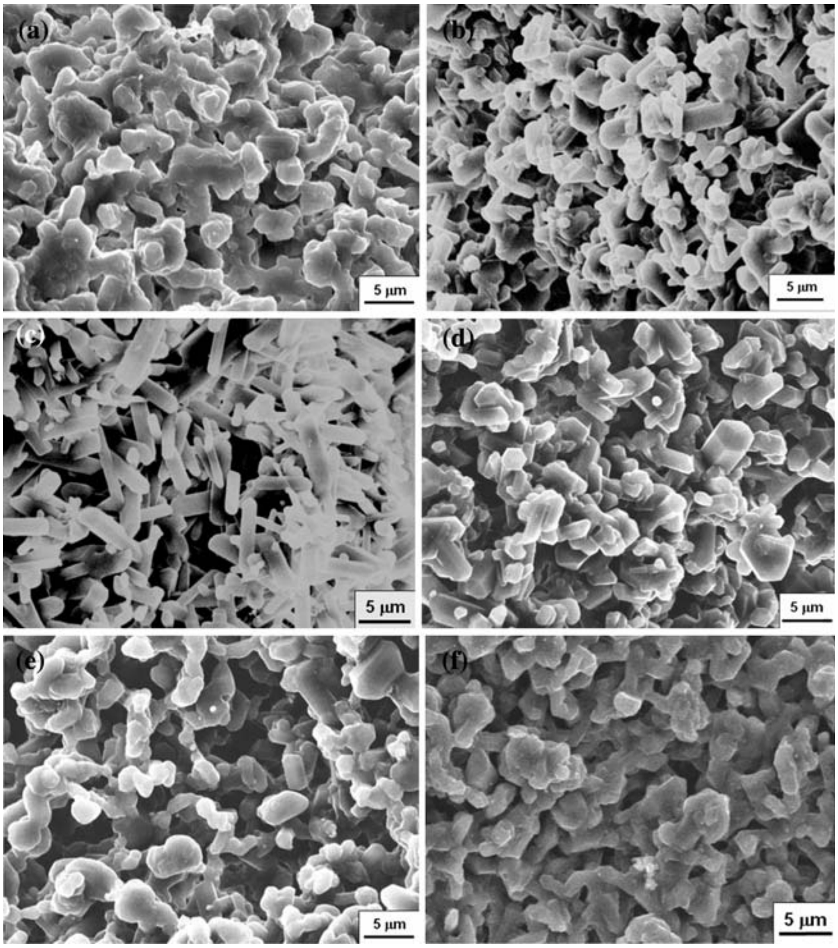


**Fig. 3** Microstructure of the combustion products: (**a**) YS1512-A, with $Si_3N_4/Si = 1/5$ and $AlN/Al = 1/4$; (**b**) YS1512-B, with $Si_3N_4/Si = 1/5$ and $AlN/Al = 1/4$, and with $\beta$-$Si_3N_4$ as raw material; (**c**) YS1512-C, with $Si_3N_4/Si = 1/7$ and $AlN/Al = 1/4$; (**d**) YS1512-D, with $Si_3N_4/Si = 1/9$ and $AlN/Al = 1/4$; (**e**) YS1209, with $Si_3N_4/Si = 1/5$ and $AlN/Al = 1/4$; (**f**) YS1812, with $Si_3N_4/Si = 1/5$ and $AlN/Al = 1/4$

($\alpha$-$Si_3N_4$ or $\beta$-$Si_3N_4$) together with AlN, and the other is $\alpha$-SiAlON together with $NH_4F$. In the first type, only the molar ratio of $Si_3N_4$/Si is changed, and the molar ratio of AlN/Al is fixed to be 4, which has been proved to be reasonable in our previous work. In the second type, both the content of $\alpha$-SiAlON and that of $NH_4F$ are changed, and the weight percentages of various diluents and additive are shown in Table 1 in detail.

From the experiment results, it is found that the character and relative amount of diluents has important influence on the phase assemblage and grain morphology of combustion products. For the sample YS1512-A with $\alpha$-$Si_3N_4$ as diluents, the combustion product is almost single-phase $\alpha$-SiAlON with very little residual Si. But in the product of YS1512-B with $\beta$-$Si_3N_4$ as diluents, some $\beta$-SiAlON is found. This is because that, during the phase transformation process new crystalline SiAlON phases will heterogeneously nucleate based on the undissolved silicon nitride particles and coherent nucleation usually take place [26]. Due to the similarity in crystal structure and thus lower energy barrier for nucleation, it is easy for $\alpha$-SiAlON to nucleate on $\alpha$-$Si_3N_4$ and for $\beta$-SiAlON to nucleate on $\beta$-$Si_3N_4$ particles. In this way, the $\beta$-$Si_3N_4$ diluents facilitate the formation of $\beta$-SiAlON, which will remain in final product if it cannot be completely consumed by the formation of $\alpha$-SiAlON during reaction period. Figure 3 a and b show the micrographs of YS1512-A and YS1512-B, from which it can be seen that using $\beta$-$Si_3N_4$ as diluents some rod-like crystals are formed, and the relevant EDS results (not shown here) confirm they are $\alpha$-SiAlON. The formation of these rod-like $\alpha$-SiAlON crystals probably arises from the reduced nucleation when $\beta$-$Si_3N_4$ is used as diluents.

Figure 3 also reveals that the addition content of $\alpha$-$Si_3N_4$ diluents has obvious influence on the grain morphology of $\alpha$-SiAlON products. When the molar ratio of $Si_3N_4$/Si is decreased from 1/5 to 1/7, the $\alpha$-SiAlON crystals develop better and the grain morphology varies from isotropic to rod-like shape. And at the same time, the phase assemblage does not change obviously. In the combustion synthesis, the nitridation reactions of Al and Si are the source generating heat energy, while the nitride powders as diluents will absorb heat and limit the increase of temperature. With the decrease of $Si_3N_4$/Si ratio, the relative amount of Si is raised and the amount of diluents is reduced, and in this case more heat energy can be provided to sustain the combustion reaction. Accordingly, the reaction system can stay longer at high temperature range and $\alpha$-SiAlON crystals have adequate time to grow by consuming liquid phase. As a result, in the combustion product of YS1512-C with $Si_3N_4$/Si = 1/7, the $\alpha$-SiAlON grains develop more fully and rod-like crystals are formed; while in the product of YS1512-A with $Si_3N_4$/Si = 1/5, the grains do not grow fully and coated with much residual glassy phase.

On the other hand, of course, it should be pointed out that it is not good either if the $Si_3N_4$/Si ratio is too low. For example, in the sample of YS1512-D with $Si_3N_4$/Si = 1/9, because the amount of diluents is too small to reduce the agglomeration of metal melts effectively, the nitridation reaction of Si cannot be fully finished. At last, more residual Si exists in the combustion product, as shown in Table 1. Figure. 3d shows a typical microstructure of the combustion product of YS1512-D, where the $\alpha$-SiAlON grains show the trend of developing into prismatic rod-like shape from the liquid phase. However, most grains do not grow completely and their aspect ratios are relatively low.

As introduced before, seeding method has been proved to be effective in producing rod-like crystals in reaction sintering of $\alpha$-SiAlON. So, in this study, single-phase $\alpha$-SiAlON powder is also used as diluents instead of $Si_3N_4$ powders. At the same time, $NH_4F$ is also added in order to facilitate the nitridation of Si and growth of rod-like $\alpha$-SiAlON crystals. Figure 4 shows the variation of quantitative phase assemblage of combustion products with the addition content of $\alpha$-SiAlON and $NH_4F$. It is clear that with the increase of $NH_4F$ addition, the amount of residual Si in products decreases gradually. The residual Si completely disappears with 10 wt.% $NH_4F$ and 10 wt.% $\alpha$-SiAlON addition or with ≥5 wt.% $NH_4F$ and 20 wt.% $\alpha$-SiAlON. These results confirm the enhancement of Si nitridation by the addition of $NH_4F$, which has been reported in combustion synthesis of $\alpha$-$Si_3N_4$ powders [27]. However, it is also noticed that with the increase of $NH_4F$ addition, the content of $\beta$-SiAlON in combustion products also increases. Especially for the samples with 10 wt.% $\alpha$-SiAlON addition, when the content of $NH_4F$ reaches 10 wt.%, $\beta$-SiAlON becomes the predominant crystalline phase. This can be explained as follows: with excessive $NH_4F$ too much $\alpha$-$Si_3N_4$ will be produced very quickly, which can not be consumed timely by the formation of $\alpha$-SiAlON, and the overabundant $\alpha$-$Si_3N_4$ will transform into $\beta$-$Si_3N_4$ or $\beta$-SiAlON. In this way, the weight percentage of added $NH_4F$ should be controlled carefully and cannot be excessive.

From Fig. 4, it is also found that with the same content of $NH_4F$ added, the phase assemblages of the samples with 20 wt.% $\alpha$-SiAlON addition are always better than those with 10 wt.% $\alpha$-SiAlON, i.e. with higher content of $\alpha$-SiAlON and lower contents of $\beta$-SiAlON and residual Si. This is easy to understand, since when more $\alpha$-SiAlON is added the initial content of $\alpha$-SiAlON is higher, and at the same time more diluents can reduce the agglomeration of metal melt remarkably and improve the nitridation reaction of Si.

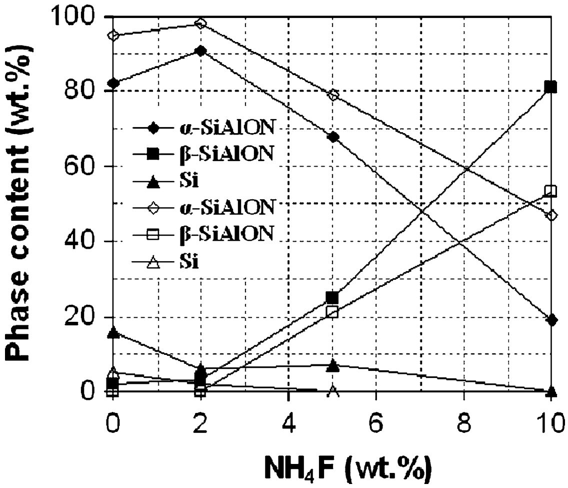
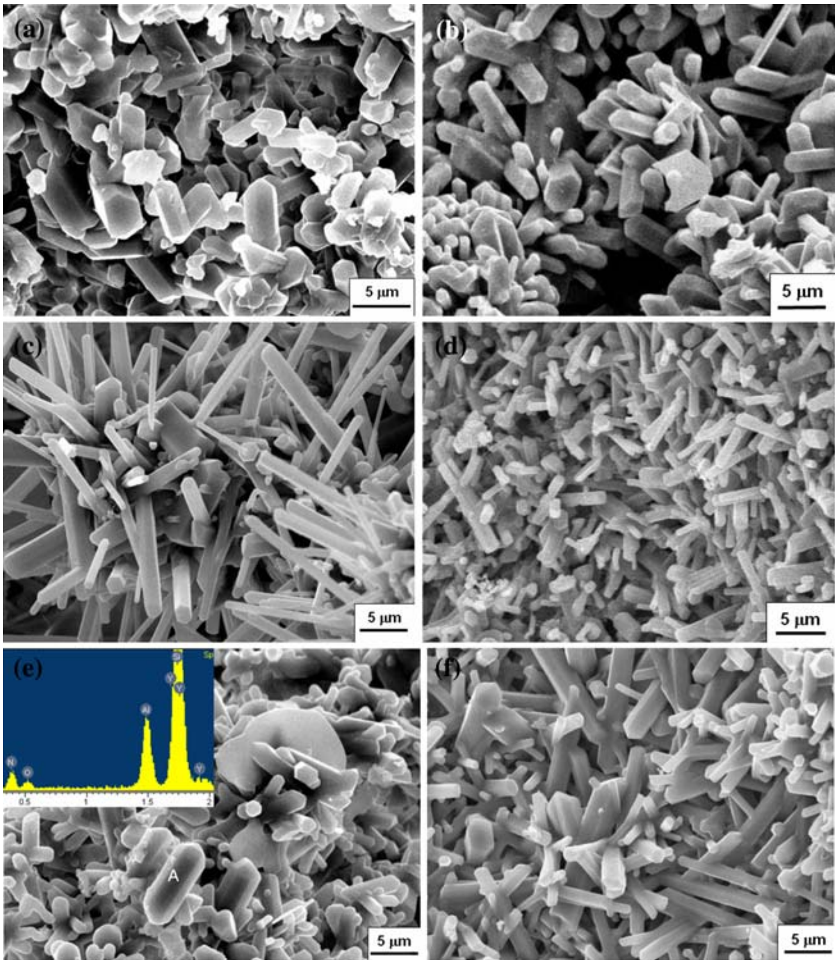


**Fig. 4** Effect of the addition of α-SiAlON and $NH_4F$ on the phase assemblage of combustion products. The filled and unfilled symbols stand for the samples with 10 and 20 wt.% α-SiAlON, respectively

The addition of α-SiAlON and $NH_4F$ also affect final grain morphology of the combustion products. The initially added α-SiAlON powders act not only as diluents but also as seed crystals. During the dissolution-reprecipitation process, these seed crystals have the advantages in both particle size and thermodynamic stability for surviving the dissolution compared with silicon nitride particles. Therefore, the extra-added seed crystals can provide more efficient nucleation sites for the formation of new -9α-SiAlON phase. The added $NH_4F$ will decompose during the combustion reaction and release gases, which makes the samples looser and facilitates the development of rod-like crystals by providing sufficient space for growth. Because of these advantages, rod-like α-SiAlON crystals can be acquired with proper addition of α-SiAlON and $NH_4F$.

Figure 5 shows the SEM micrographs of combustion products with the addition of α-SiAlON and $NH_4F$. It is clear that, from the sample A10F0 to A10F10 (from a to d in Fig. 5), with the gradual increase of $NH_4F$ content, more rod-like crystals are observed. Of course, it should be noticed that for the samples A10F5 and A10F10, the products are not single-phase α-SiAlON but the composite of α- and *β*-SiAlON. With 20 wt.% α-SiAlON addition, rod-like crystals can be obtained even without $NH_4F$ addition, and the rod-like crystals develop better with a faceted

**Fig 5** Grain morphology of the samples with the addition of α-SiAlON and $NH_4F$: (**a**) A10F0, with the addition of 10 wt.% α-SiAlON; (**b**) A10F2, with the addition of 10 wt.% α-SiAlON and 2 wt.% $NH_4F$; (**c**) A10F5, with the addition of 10 wt.% α-SiAlON and 5 wt.% $NH_4F$; (**d**) A10F10, with the addition of 10 wt.% α-SiAlON and 10 wt.% $NH_4F$; (**e**) A20F0, with the addition of 20 wt.% α-SiAlON; (**f**) A20F2, with the addition of 20 wt.% α-SiAlON and 2 wt.% $NH_4F$. The inset EDS result in (**e**) is for the crystal marked with ''A''



shape and higher aspect ratios with 2 wt.% $NH_4F$ added simultaneously.

Since the rod-like α-SiAlON crystals are expected to be used as seeds, their stability at elevated temperatures should be examined. For this purpose, two samples (YS1209 and YS1512-A) of the as-synthesized α-SiAlON powders are slightly pressed and then heat-treated at 1800 °C for 1 h. The phase assemblages of the samples after heat treatment (referred to as YS1209-HT and YS1512-A-HT) are reported in Table 1. It is found that after heat treatment, the α-SiAlON phase is stable and single-phase α-SiAlON can be obtained, where the minor residual Si has been nitridated. This reveals the high stability of combustion-synthesized α-SiAlON powders and their great potential for seeding to fabricate in situ toughened α-SiAlON ceramics.

## Conclusion

Yttrium-stabilized α-SiAlON powders with rod-like crystals were fabricated by combustion synthesis. Effect of the addition of $Si_3N_4$ diluents, α-SiAlON seeds, and $NH_4F$ additive on the phase assemblage and grain morphology of combustion products were discussed in detail. The appropriate addition of α-SiAlON seeds and $NH_4F$ could improve the anisotropic growth of rod-like crystals. However, if too much $NH_4F$ was added, the phase purity of products would be decreased obviously and more *β*-SiAlON was produced. In order to examine the stability at elevated temperatures, the as-synthesized α-SiAlON powders were heat treated at 1800 °C and the results showed that after the heat treatment single-phase α-SiAlON was obtained, revealing the high stability of combustion synthesized α-SiAlON powders.

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