

Effect of diluents and NH_4F additive on the combustion synthesis of $\text{Yb } \alpha\text{-SiAlON}$

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Abstract

In this paper, $\text{Yb } \alpha\text{-SiAlON}$ crystalline powders with elongated grains were prepared by combustion synthesis. The effects of diluents and NH_4F additive on the phase composition and microstructure of combustion products were discussed in detail. It is found that proper diluents are helpful to weaken the agglomeration, improve the infiltration of N_2 , and hence facilitate the nitridation reaction. Single-phase $\alpha\text{-SiAlON}$ with elongated grains could be fabricated with advisable addition of diluents. Furthermore, adding proper amounts of NH_4F additive was also beneficial to the nitridation of Si and the development of elongated grains. However, excessive addition of $\alpha\text{-Si}_3\text{N}_4$ diluents or NH_4F additive will result in $\beta\text{-SiAlON}$ in final phase composition.

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1. Introduction

As the solid solutions of silicon nitrides, SiAlON ceramics are widely used in engineering field because of their outstanding properties. There are two well-known SiAlON polymorphs called α and β with similar crystal structures to those of α - and $\beta\text{-Si}_3\text{N}_4$, respectively. It is generally accepted that $\alpha\text{-SiAlON}$ grains mainly exist as equiaxed morphology and $\beta\text{-SiAlON}$ grains usually exist as elongated grains. This difference in microstructure results in different fracture toughness values. The poor toughness has ever been a troublesome barrier limiting the further application of $\alpha\text{-SiAlON}$ ceramics.^{1–7}

Compared with $\beta\text{-Si}_3\text{N}_4$ -based ceramics, the microstructure of $\alpha\text{-SiAlON}$ is more sensitive to the composition, the processing conditions, and the starting powders.⁸ As a result, only recently $\alpha\text{-SiAlON}$ ceramics with elongated grains

that enable in situ toughening have been developed.^{9–13} Since $\alpha\text{-SiAlON}$ is much harder than $\beta\text{-SiAlON}$, the novel tough $\alpha\text{-SiAlON}$ ceramics have a higher potential for industrial applications, especially where wear resistance is much concerned.

In view of complexity of microstructure control, seeding seems to offer an attractive solution because it can effect template growth of elongated grains. Several reports on seeding in $\beta\text{-Si}_3\text{N}_4$ -based ceramics clearly demonstrated the great potential of this method in silicon nitride ceramics.^{14–16} More recently, seeding method was also applied in $\alpha\text{-SiAlON}$ ceramics and a dramatic effect of crystalline seeds on the enhancement of resistance behaviour and fracture toughness was observed.^{17–20}

Preparation of single-phase crystalline seeds is the prerequisite for the fabrication of in situ toughened $\alpha\text{-SiAlON}$ ceramics by seeding method. Chen and coworkers^{12,21} and Zenotchkin et al.²² separately reported the synthesis of rod-like $\alpha\text{-SiAlON}$ crystals using the combustion synthesis, or by the growing of single crystal seeds from liquid. Combustion synthesis technique has been attracting the interest of many

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researchers as an energy and time-saving process. Seeding with combustion-synthesized α -SiAlON crystals will provide a convenient and low-cost method to fabricate the in situ toughened α -SiAlON ceramics with elongated grains.

In this paper, single-phase Yb α -SiAlON crystalline powders were prepared using combustion synthesis. The effects of diluents and additives on the phase composition and microstructure of the synthesized powders are discussed in detail.

2. Experimental procedure

The compositions investigated here lie in the single-phase plane²³ of Yb α -SiAlON represented by the formula $\text{Yb}_{m/3}\text{Si}_{12-(m+n)}\text{Al}_{m+n}\text{O}_n\text{N}_{16-n}$, in which $m = n = 1.2$ was selected. Starting powder mixtures were prepared by using Yb_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 (2.0 wt.% O, Fangda High-Technology Ceramics Co., China), β - Si_3N_4 (2.0 wt.% O, self-fabricated by SHS), AlN (1.0 wt.% O, self-fabricated by SHS), SiO_2 (A.R., Beijing Chemical Co., China), NH_4F (A.R., Beijing Chemical Co., China), Yb α -SiAlON (self-fabricated by SHS) according to the proportions listed in Table 1. The surface oxygen contents of the nitrides were considered.

Each mixture of raw materials was planetary milled in absolute ethanol (Beijing Chemical Co., China) for 24 h using agate containers and agate balls. The obtained slurry was then dried in an oven at 70 °C for 8 h. Subsequently, the powder mixture was put in a porous crucible and then placed into the CS chamber, which was reported elsewhere.²⁴

Evacuation was performed up to a vacuum of 10^{-4} MPa. Then the powder mixture was ignited with a tungsten coil under 2 MPa N_2 pressure and the combustion temperature was recorded with a W–Re3/W–Re25 thermocouple inserted into the sample, which was connected to a data acquisition system.

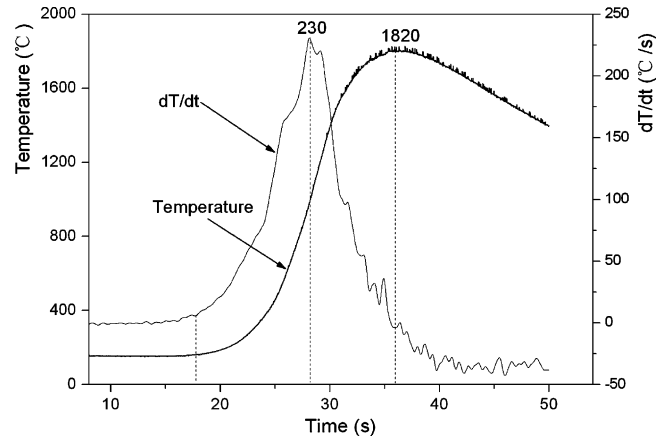


Fig. 1. Typical temperature–time history during combustion synthesis of Yb α -SiAlON.

The phase composition was determined by X-ray diffraction (XRD; $\text{Cu K}\alpha$, 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).

3. Results and discussion

3.1. Effects of diluents

High reaction temperature and fast heating or cooling rates are the main characteristics of combustion synthesis. Fig. 1 shows the temperature variation curve for the sample SA3, which represents the typical temperature–time history in combustion synthesis of Yb α -SiAlON. It can be seen that once the combustion reaction starts, the temperature increases very dramatically to the maximum of 1820 °C in about 15 s, and the highest heating rate reaches 230 °C/min. Owing to this high reaction temperature and fast heating rate, the Al and Si particles in raw materials will melt and agglomerate in a short time, inhibiting the infiltration of N_2 and further

Table 1
Starting compositions of the samples

| Sample codes | Compositions (wt.%) | | | | | | | | |
|--------------|-------------------------|-------|------------------------------------|-----------------------------------|-------|-------|----------------|------------------|-----------------------|
| | Yb_2O_3 | Si | α - Si_3N_4 | β - Si_3N_4 | Al | AlN | SiO_2 | α -SiAlON | NH_4F |
| SA1 | 16.48 | 42.16 | 23.92 | | 11.29 | 3.51 | 2.63 | | |
| SA2 | 16.20 | 38.68 | 28.22 | | 11.10 | 3.45 | 2.34 | | |
| SA3 | 15.80 | 33.68 | 34.28 | | 10.83 | 3.37 | 2.04 | | |
| SA4 | 15.19 | 25.53 | 44.12 | | 10.41 | 3.24 | 1.50 | | |
| SB1 | 15.80 | 33.68 | | 34.28 | 10.83 | 3.37 | 2.04 | | |
| SC1 | 15.98 | 34.07 | 34.68 | | 13.20 | | 2.06 | | |
| SC2 | 14.96 | 31.88 | 32.46 | | | 18.76 | 1.93 | | |
| SF0 | 14.59 | 46.71 | | | 12.01 | | 6.67 | 20 | 0 |
| SF1 | 14.14 | 45.25 | | | 11.63 | | 6.46 | 20 | 2.5 |
| SF2 | 13.69 | 43.79 | | | 11.26 | | 6.25 | 20 | 5 |
| SF3 | 12.78 | 40.87 | | | 10.50 | | 5.83 | 20 | 10 |

nitridation reaction. In order to eliminate this agglomeration, α - Si_3N_4 or β - Si_3N_4 and AlN with relatively high melting points were added as diluents into raw materials. The experiments showed that the characteristics and the added amounts of diluents affected the phase composition and microstructure of the combustion products considerably.

In the combustion reaction, Al will react with N_2 firstly because of its lower melting point and energy barrier for nitridation compared with those of Si.¹² The heat released during the nitridation of Al provides adequate energy for the subsequent reaction. This analysis explains why the sample SC2 was not successfully ignited, unlike the other samples. Because in the starting composition of SC2 no Al powder was added and AlN was used as the only Al source, resulting in the lack of energy at initial stage, the combustion reaction could not be maintained.

Fig. 2 shows the XRD results of the combustion products, from which the detailed effects of diluents on the final phase composition can be discussed.

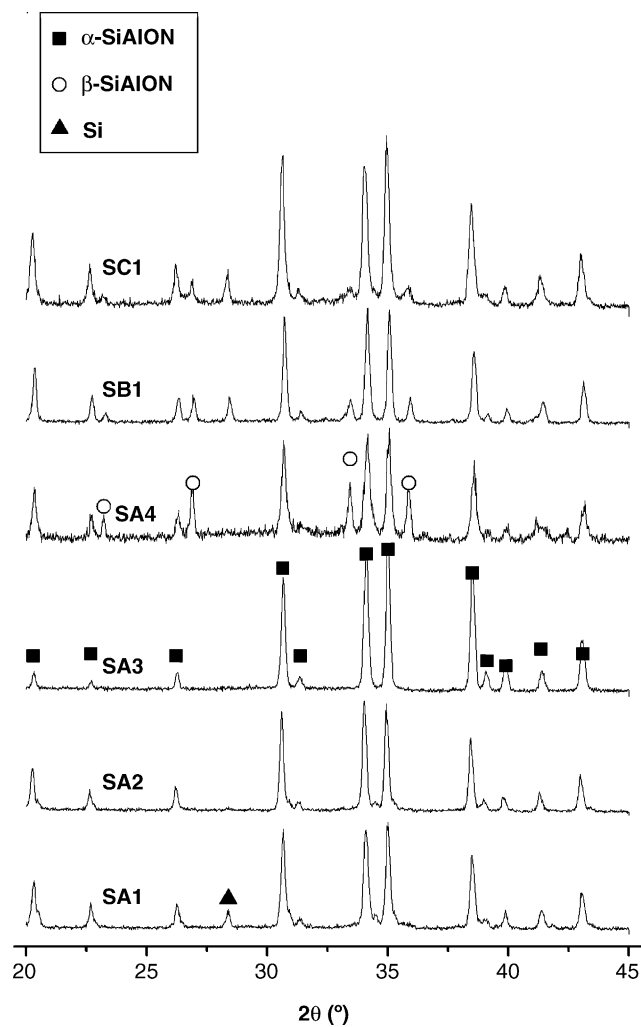


Fig. 2. XRD results of the combustion products with different kinds and contents of diluents.

At first, although when too much AlN is added the absence of Al results in the failure of ignition as described above, proper quantity of AlN is necessary for preparing the single-phase α -SiAlON. The starting compositions of SA3 and SC1 were similar, except that no AlN was used in the latter. Consequently, the combustion product of SA3 was pure α -SiAlON but β -SiAlON and residual Si were both found in the product of SC1.

Secondly, the structural characteristics of Si_3N_4 diluents have an obvious effect on the final phase composition of combustion products. The sample SA3 and SB1 have the same chemical composition, except for the difference in crystalline morphology of Si_3N_4 diluents: α - Si_3N_4 in SA3 and β - Si_3N_4 in SB1, respectively. From Fig. 2, it can be found that β - Si_3N_4 in SB1 lead to the β -SiAlON in final phase composition. This is because, that the additive Si_3N_4 particles act not only as diluents eliminating the agglomeration but also as crystalline seeds providing nucleation sites. Due to the similarity in crystal structure, the energy barrier for the nucleation of β -SiAlON on β - Si_3N_4 particles is lower than that of α -SiAlON. In this way, the β - Si_3N_4 diluents facilitate the nucleation of β -SiAlON and improve its formation. This result is rather dissimilar compared to the hot-pressing of α -SiAlON using β - Si_3N_4 as a raw material.¹⁰ In this later case, the sintering reaction is thermodynamically determined and the reactant system is kept in an equilibrium state approximately. Therefore, there is adequate time for the dissolution, mass transportation, and reprecipitation processed to occur, and hence the intermediate phases can fully transform into the final stable phase (α -SiAlON). However, in combustion synthesis the reaction process is kinetically determined and the reaction system is in non-equilibrium conditions because of the dramatic temperature variation rate and considerably short reaction time. With β - Si_3N_4 used as reactant, much β -SiAlON will be formed by coherent nucleation because of lower interfacial energy and strain energy. But in latter reaction period, the as-formed β -SiAlON can not be fully consumed lacking enough time and remains in final products.^{25–27}

Finally, the content of diluents in the starting composition is also very important in determining the final phase composition. Single-phase α -SiAlON could be prepared with appropriate α - Si_3N_4 diluents in SA2 and SA3, while too much or little diluents lead to the remnant β -SiAlON or Si. As diluent, the added α - Si_3N_4 powder can weaken the agglomeration of Al and Si melt and enhance the infiltration of N_2 , beneficial to further nitridation reaction. If the added amount of diluent is too small to restrain the agglomeration, the further nitridation of Si will be limited by the absence of N_2 and some un-reacted Si remains. Excessive amount of diluent is also disadvantageous to obtain the single-phase product. A large amount of diluents will decrease the reaction temperature remarkably by absorbing more heat energy, which is harmful to the formation of α -SiAlON. At the same time, too much diluent results in the overabundance of α - Si_3N_4 at early reaction stages. If the α - Si_3N_4 material can not be consumed timely, it will transform into β - Si_3N_4 at mediate temperatures accounting

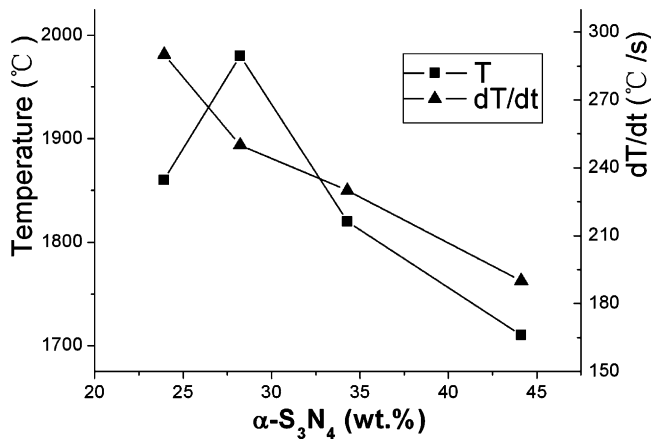


Fig. 3. Effects of the content of $\alpha\text{-Si}_3\text{N}_4$ diluent on the combustion temperature and heating rate.

for the formation of $\beta\text{-SiAlON}$. Therefore, the complete nitridation of Si can only be achieved and the single-phase $\alpha\text{-SiAlON}$ can only be successfully fabricated in the presence of the right added amount of $\alpha\text{-Si}_3\text{N}_4$ as diluent.

The diluents affect not only the phase composition but also the microstructure of the combustion products. Generally speaking, the final grain morphology in combustion products is determined by the nucleation and grain growth. According to related studies,^{9–13} the development of elon-

gated $\alpha\text{-SiAlON}$ grains can be favoured if (a) very few nuclei are available, and (b) the kinetics of crystal growth is fast.⁸ In combustion synthesis of $\alpha\text{-SiAlON}$, fast heating rate is helpful to limit the nucleation and high temperature is beneficial to grain growth. Fig. 3 shows the combustion temperatures and heating rates of the samples with different contents of diluent $\alpha\text{-Si}_3\text{N}_4$. In the sample SA2 with proper content of diluent, the combustion temperature reached 1980 °C (see Fig. 3) and the heating rate was relatively fast, and accordingly, elongated grains were obtained, as shown in Fig. 4a. From the XRD and EDS results, it can be concluded that these elongated grains are Yb $\alpha\text{-SiAlON}$. On the contrary, in the sample SA4, overabundant $\alpha\text{-Si}_3\text{N}_4$ diluent debased the reaction temperature (1710 °C) and decreased the heating rate (167 °C/min), which is not favourable for the development of elongated grains. Additionally, plentiful $\alpha\text{-Si}_3\text{N}_4$ particles provide more nucleation sites and thereby in the later process the space for grain growth is deficient. A substantive amount of grains can only grow into equiaxed morphology because they will impinge each other before developing into elongated shape, as shown in Fig. 4b.

3.2. Effect of NH_4F additive

In the fabrication of $\alpha\text{-Si}_3\text{N}_4$ powders by combustion synthesis, ammonium halides are often added in order to control

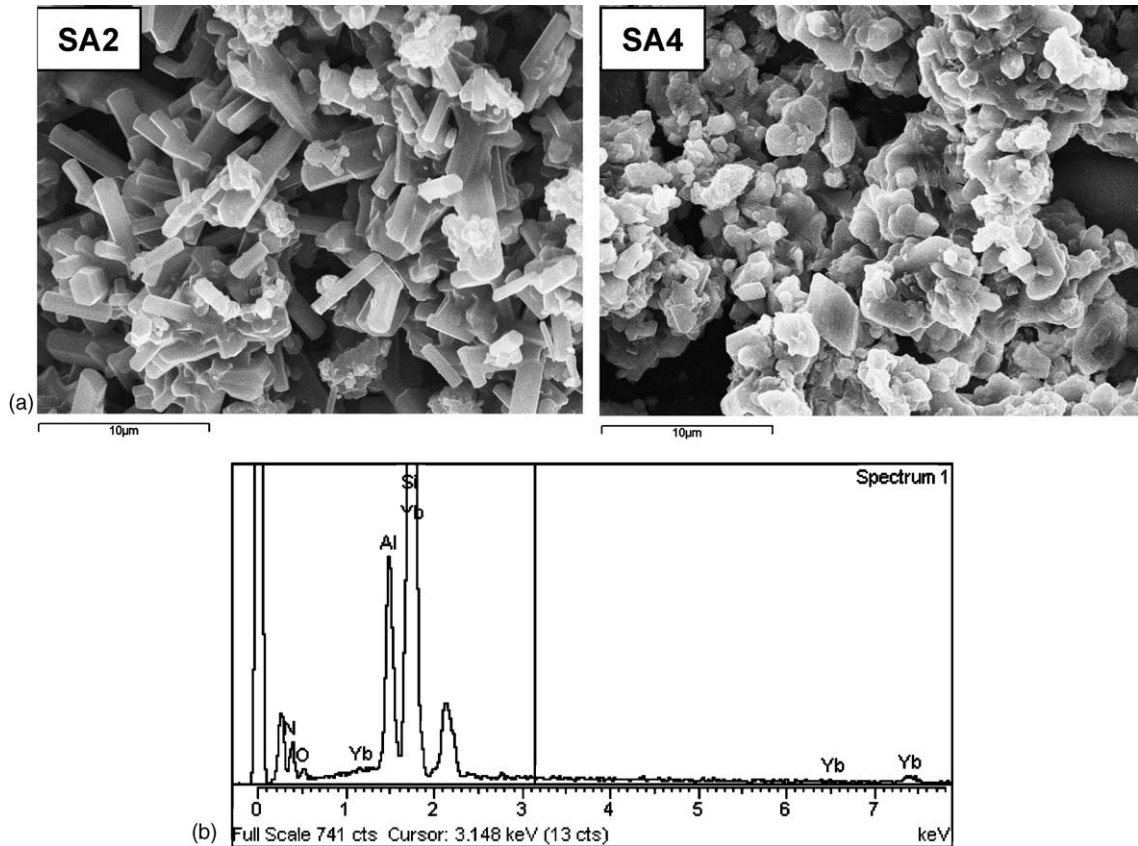
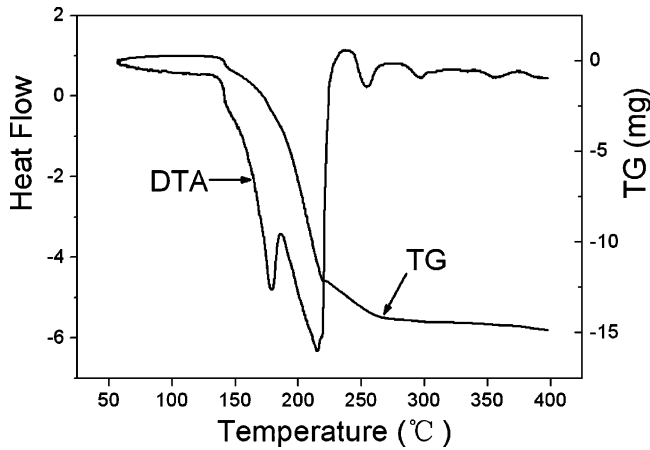
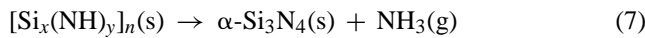
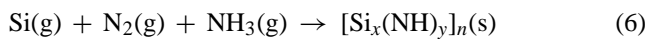
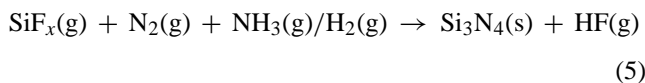
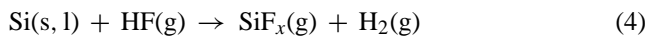
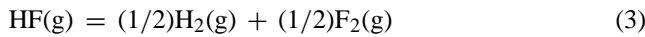
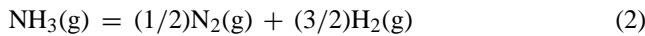
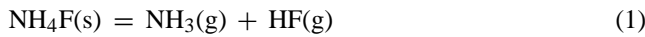


Fig. 4. Effect of the content of $\alpha\text{-Si}_3\text{N}_4$ diluent on the microstructure of final products (the EDS result is for an elongated grain in SA2).

Fig. 5. TG and DTA curves of NH_4F .

the reaction process.²⁸ For example, NH_4F was proved to have a catalytic effect on the nitridation of Si as follows:



In this study NH_4F was also used as an additive to enhance the nitridation reaction. At the same time, the as-synthesized single-phase Yb $\alpha\text{-SiAlON}$ was added as crystalline seeds to simplify the nucleation control.

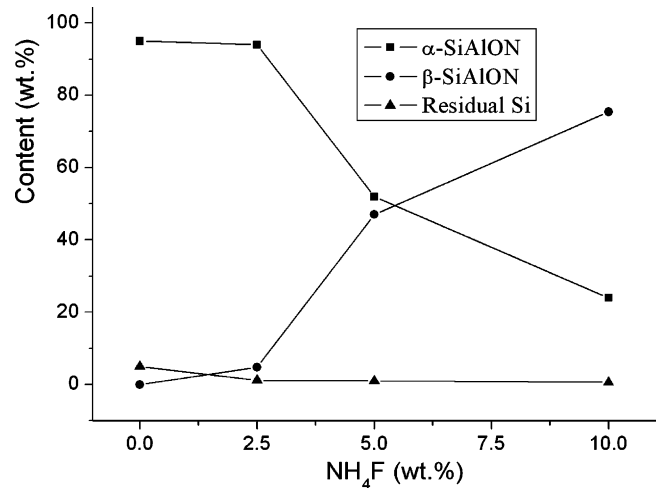
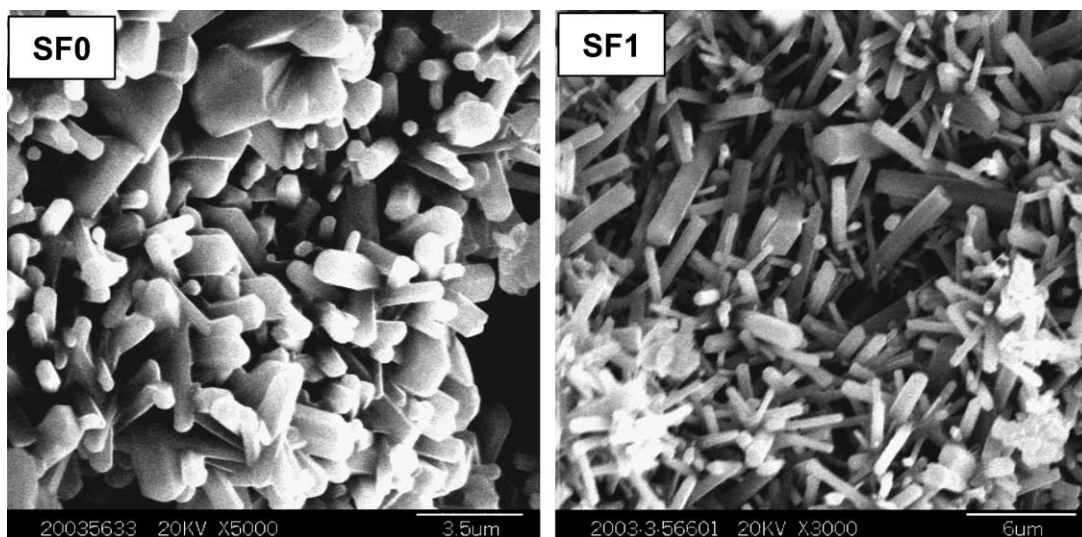
Fig. 6. Effect of NH_4F addition on the phase content of combustion products.

Fig. 5 shows the TG and DTA curve of NH_4F . It can be seen that above 250°C NH_4F has been fully decomposed approximately. During the decomposition of NH_4F , N_2 will be released as a reaction product, improving N_2 supply and the nitridation reaction. In addition, as an intermediate product $\text{SiF}_x(\text{g})$ provides another way for the nitridation of Si, and thus the formation of Si_3N_4 is accelerated. The phase content of combustion products from SF0 to SF4 is shown in Fig. 6, from which it can be seen that residual Si is basically eliminated by adding NH_4F . It is also visible that when the added amount of NH_4F is low (≤ 2.5 wt.%), the final product is mainly $\alpha\text{-SiAlON}$, but a rather increase of $\beta\text{-SiAlON}$ phase in the combusted product occurs with further addition of NH_4F . This can be explained as follows: with excessive added amounts of NH_4F too much $\alpha\text{-Si}_3\text{N}_4$ will be produced, which can not be consumed timely in the formation of $\alpha\text{-SiAlON}$, and the overabundant $\alpha\text{-Si}_3\text{N}_4$ will transform into $\beta\text{-Si}_3\text{N}_4$ or $\beta\text{-SiAlON}$.

Fig. 7. Effect of NH_4F addition on the microstructure of combustion products.

Moreover, appropriate NH_4F addition can improve the grain growth of $\alpha\text{-SiAlON}$. The additive NH_4F promotes the nitridation of Si and increases the reaction rate, so the heat-releasing rate and the formation rate of $\alpha\text{-Si}_3\text{N}_4$ is increased. That is to say, in equal time unit a larger amount of heat energy is released and more $\alpha\text{-Si}_3\text{N}_4$ is produced with additive NH_4F . Consequently, the dissolution of $\alpha\text{-Si}_3\text{N}_4$ particles can be enhanced, leading to a high instantaneous supersaturation degree. In this way, the difference in chemical potential between the liquid phase and the added crystalline seeds is enhanced and thereby a rather high driving force will be created. This high driving force accelerates the mass transportation and reprecipitation on surface of the crystalline grains, promoting a rapid anisotropic grain growth. At the end, well-developed elongated grains can be obtained successfully.

Fig. 7 exhibits the SEM images of the sample SF0 and SF1 without and with 2.5 wt.% NH_4F additive, respectively. It is clear that more elongated grains with higher aspect ratio and more perfect morphology were acquired, confirming the advantageous effect of NH_4F on the development of elongated grains Yb $\alpha\text{-SiAlON}$ in combustion synthesis.

4. Conclusions

1. Single-phase Yb $\alpha\text{-SiAlON}$ crystalline powders could be fabricated by combustion synthesis, and under proper conditions, the $\alpha\text{-SiAlON}$ grains can be developed into elongated morphology.
2. The diluents in starting materials are beneficial to weaken the agglomeration and improve the nitridation of Si. The phase composition and microstructure of final products were considerably affected by the chemical and structural characteristics and contents of diluents.
3. The NH_4F used as additive accelerated Si nitridation and formation of $\alpha\text{-Si}_3\text{N}_4$, and thus improved the growth of elongated grains. However, too much NH_4F is harmful and leads to a rather increase of amount of $\beta\text{-SiAlON}$ in the combusted products.

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