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Effects of diazenedicarboxamide additive on the content of α-Si_3N_4 synthesized by combustion method

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Abstract

Combustion synthesis (CS) of high content of α-Si_3N_4 powders was carried out using Si and Si_3N_4 powders as reactants with the addition of diazenedicarboxamide (AC) at a relatively low N_2 pressure of 3 MPa. Effects of diazenedicarboxamide contents on the phase compositions and Si_3N_4 particle morphologies were studied. In addition, the reaction mechanisms were discussed. The results indicated that the additive diazenedicarboxamide promoted the nitridation of Si. The α-Si_3N_4 content in the combustion-synthesized products showed great dependence on the additive contents, which reached 85.21 wt% with 24 wt% diazenedicarboxamide added. N_2, CO and NH_3 produced by the decomposition of diazenedicarboxamide leaded to a change of compact porosity and the formation of micro-pores in the reactive area, which was responsible for the increasing contents of α-Si_3N_4 and the discrepancy morphology of the products.

Keywords: D. Si_3N_4; Diazenedicarboxamide; SHS; Combustion synthesis

1. Introduction

Silicon nitride (Si_3N_4) ceramics are used in a variety of structural applications such as engine components, heat exchangers, pump seal materials, ball bearings, cutting tools, and other structures subjected to high-temperature conditions due to their excellent mechanical properties at both room and high temperature, good resistance to oxidation and thermal shock, outstanding creep resistance and wear resistance [1–3]. Conventional processes of Si_3N_4 powder production, such as direct nitridation, carbothermal reduction and the decomposition of silicon imide, are characterized by high temperatures and long production periods and complicated technological cycles [3–6]. Combustion synthesis (CS), commonly known as the self-propagating high-temperature synthesis (SHS), of Si_3N_4 powder is also an attractive technology because of some unique advantages such as cost-effectiveness, self-purification, simple processes [7–9].

Recently, the fabrication of α-Si_3N_4 powder by combustion of Si powder in N_2 had been widely reported [10–14]. Most of these studies must use large contents of diluents and catalytic agents in order to increase α-phase content in the synthesized products. However, lots of additives, such as ammonium halides (NH_4Cl or NH_4F), $NaNH_2$ and NaN_3, would bring harmful materials to environment. For example, highly reactive gaseous components, such as HCl, HF, and Na-vapor would be released, which was very dangerous to machines and health. Moreover, NaN_3 itself was poisonous [13,14]. Therefore, it is desirable to develop a new and safe additive that can promote α-Si_3N_4 formation for combustion synthesis. Diazenedicarboxamide is a kind of efficient gaseous blowing agent with a low decomposition temperature. It is inexpensive, innoxious, free-pollution [15]. Meanwhile, diazenedicarboxamide can be used as the source of N_2 in combustion reaction, as N_2 is the main product decomposed by it. Because of this, the needed N_2 pressure for the combustion reaction would be efficiently decreased, which would not only increase the safety factor in industrialized produce, but also save the raw materials cost. Therefore, it is a very practical and useful work to prepare α-Si_3N_4 by combustion synthesis using diazenedicarboxamide as additive.

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Table 1
Starting material compositions and experiment conditions.

Sample	Composition (wt%)	
	$Si:Si_3N_4:AC$	P_{N2} (MPa)
S-0	50:50:0	3.0
S-1	50:50:1	3.0
S-2	50:50:3	3.0
S-3	50:50:6	3.0
S-4	50:50:12	3.0
S-5	50:50:24	3.0

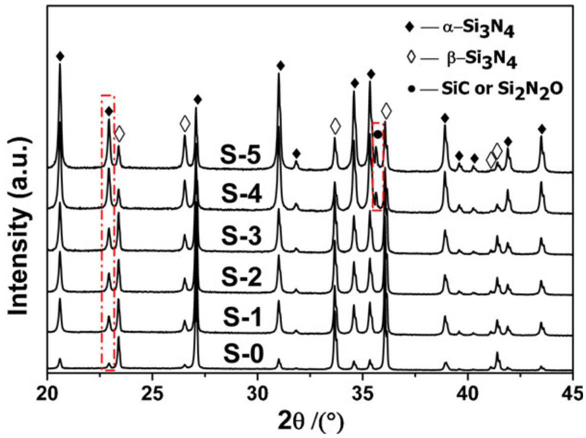


Fig. 1. X-ray diffraction (XRD) patterns of the combustion products.

In this paper, Si_3N_4 powders were fabricated by combustion synthesis using different contents of diazenedicarboxamide as additive. Effects of diazenedicarboxamide additive on phase compositions and particle morphologies of combustion products were studied. At last, reaction mechanisms were discussed in detail.

2. Experimental procedure

Starting powder mixtures were prepared by using Si powder (purity >99.9 wt%, Fushun Al Factory, China), Si_3N_4 (α-ratio >80 wt%, self-fabricated by SHS) and diazenedicarboxamide (AC, $d > 15 \pm 5$ μm, Hangzhou HI-TECH Fine Chemical Co., Ltd., China) according to the proportions listed in Table 1.

Raw materials were attrition milled for 1 h using steel balls as the milling media with a ball/charge weight ratio of 8:1. The mixed powders were sieved through a 200 mesh screen. Then, the reactant mixtures were packed in a porous graphite crucible which was 35 mm in diameter and 150 mm in length. The crucible was then placed into a stainless steel combustion reaction chamber. After evacuation, the reaction chamber was inflated with high-purity N_2 to 3.0 MPa. The combustion reaction was triggered by passing an electric current through a tungsten coil closely above the sample.

The phase composition was determined by X-ray diffraction (XRD; Cu Kα, Rigaku, Japan). The microstructure of combustion products was observed by scanning electron microscopy (SEM; JSM-6460LV, JEOL, Japan).

3. Results and discussion

3.1. Effects of diazenedicarboxamide contents on the phase compositions of products

Fig. 1 shows the X-ray diffraction (XRD) patterns of the combustion products from S-0 to S-5. It can be seen that for all combustion products, no diffraction peaks of residual Si are found, which demonstrates that complete nitridation of Si is achieved. Samples of S-0–S-3 consist of α-Si_3N_4 and β-Si_3N_4, yet S-4 and S-5 contain not only two above phases but also SiC or Si_2N_2O. The presence of these impurities in S-4 and S-5 can be associated with the reactions of C and O decomposed by diazenedicarboxamide with Si or N_2. An increase in the high of diffraction peaks of SiC or Si_2N_2O for S-4 and S-5 can also be related to a change in the using contents of diazenedicarboxamide (see the right dashed rectangle in Fig. 1). At the same time, we can also see that for all samples, the diffraction peaks of α-Si_3N_4 are increasing markedly with contents of diazenedicarboxamide increasing. This suggests that amount of α-Si_3N_4 in products increases with more diazenedicarboxamide adding in the starting materials.

The α-Si_3N_4 contents of the corresponding products are calculated according to Gazzara and Messier method [16], and the variation curve of α-Si_3N_4 contents with different percentages of diazenedicarboxamide is shown in Fig. 2. It is found that the value of α-Si_3N_4 increases with the increase of diazenedicarboxamide content. However, a sharply increase in the content of α-Si_3N_4 is obtained when amount of diazenedicarboxamide is less than 12 wt% and it only increases from 83.1 wt% to 85.2 wt% with adding diazenedicarboxamide from 12 wt% to 24 wt% for S-4 and S-5, respectively. The amount of diazenedicarboxamide additive almost attains its maximum value, as increasingly SiC and Si_2N_2O would be found in the final products with further adding it in the starting materials.

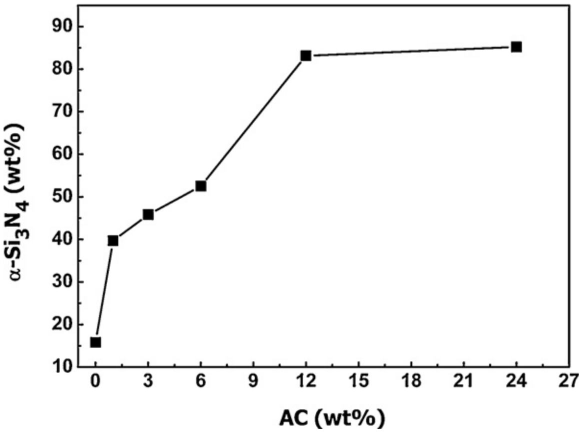


Fig. 2. Variation of α-Si_3N_4 contents with different percentages (wt%) of diazenedicarboxamide.

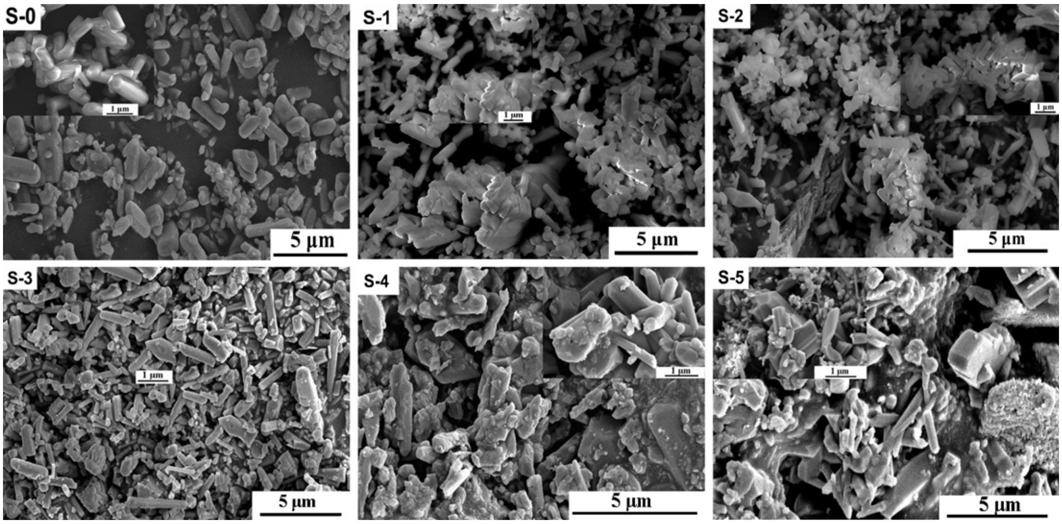


Fig. 3. Scanning electron microscope (SEM) photographs of combustion products synthesized using different percentages (wt%) of diazenedicarboxamide in starting materials.

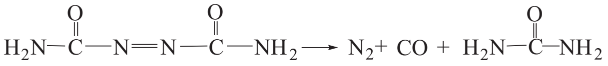
3.2. *Effects of diazenedicarboxamide contents on particle morphologies of combustion synthesis products*

The scanning electron microscope (SEM) photographs of combustion products are shown in Fig. 3. We can see that there are three kinds of particles with different morphologies contained in every sample: rod-like particles, coalescent grains and small blocks. Most of particles in S-0 synthesized by starting materials without diazenedicarboxamide are rod-like shape, while the amount of rod-like particles decreases with increasing diazenedicarboxamide in samples from S-1 to S-5. S-4 and S-5 contain lots of blocks and small amount of rod-like particles, which is very different with other samples. This different could be related to that SiC or Si_2N_2O coat around the Si_3N_4 particles, which leads to the growth of blocks because of adhering and agglomerating. Therefore, coalescent particles and blocks increase in the final products with more diazenedicarboxamide added. However, the morphologies of rod-like particles in S-4 and S-5 are similar with it in S-0, such as having smooth surface, agglomerated together with one side, being hexagonal rod-like prisms (see inset images in S-0, S-4 and S-5). These rod-like prisms with pyramidal faces on top and bottom usually are β-Si_3N_4 particles which always grow in Si melts. Consequently, addition of diazenedicarboxamide leads to the agglomeration and growth of product particles.

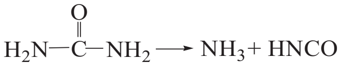
3.3. *Effects of diazenedicarboxamide additive on the reaction of Si and N_2*

Diazenedicarboxamide is always used as a gaseous blowing agent that releases lots of N_2 when it is heated beyond 200 °C which is its decomposition temperature. Diazenedicarboxamide has a high frothing volume and gas evolution rate, and the relation of frothing volume with time is shown in Fig. 4. It can be seen that after an introduction period of decomposition, diazenedicarboxamide sharply decomposes and releases large amounts of gas, and the highest frothing volume is about 250 mL/g [15].

N_2 is the main gas decomposed by diazenedicarboxamide, and other products are CO and NH_3. The decomposition equations of diazenedicarboxamide are shown from Eqs. (1)–(3) [15]. The combustion temperature that comes from the reaction of Si with N_2 is much higher than the decomposition temperature of diazenedicarboxamide, which would lead to a quick decomposition and to sharply raising of the pressure after the reactants are successfully ignited. Therefore, large amount of gas produced and the increasing pressure would affect Si–N_2 reaction seriously.



$$H_2N-\overset{\overset{O}{\|}}{C}-N=N-\overset{\overset{O}{\|}}{C}-NH_2 \longrightarrow N_2 + CO + H_2N-\overset{\overset{O}{\|}}{C}-NH_2 \tag{1}$$



$$H_2N-\overset{\overset{O}{\|}}{C}-NH_2 \longrightarrow NH_3 + HNCO \tag{2}$$

$$H-N=C=O \rightleftharpoons HO-N=C \longrightarrow N_2 + NH_3 + CO \tag{3}$$

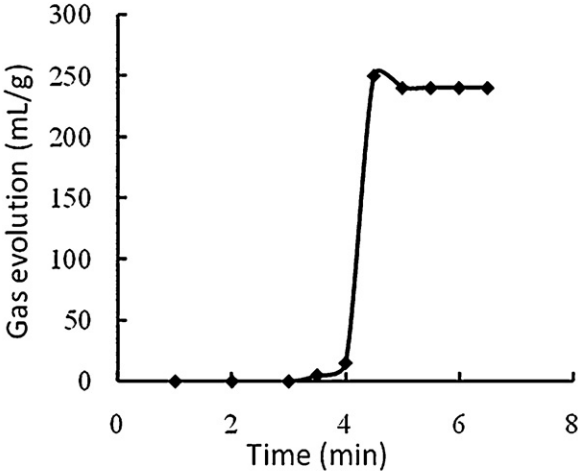


Fig. 4. Characteristic curve of diazenedicarboxamide gaseous blowing agent.

NH_3 produced by the decomposition of diazenedicarboxamide promotes the reaction of Si with N_2 via the following reactions, seeing Eqs. (4)–(8). N_2 decomposed by NH_3 could be used as reactant for combustion reaction. Meanwhile, H_2 that come from Eq. (4) would promote the transfer of Si, which is advantage for synthesis of Si_3N_4, especially for α-Si_3N_4 [3].

$$2NH_3(g) \rightarrow N_2(g) + 3H_2(g) \quad (4)$$

$$Si + (1/2)H_2(g) \rightarrow SiH \quad (5)$$

$$Si + 2H_2(g) \rightarrow SiH_4 \quad (6)$$

$$3SiH_4 + 4NH_3(g) \rightarrow Si_3N_4(s) + 12H_2(g) \quad (7)$$

$$3SiH_4 + 2N_2(g) \rightarrow Si_3N_4(s) + 6H_2(g) \quad (8)$$

CO decomposed by diazenedicarboxamide provides lots of C and O for the reaction system. C and O would affect the reaction followed many factors. On the one hand, many impurities, such as SiC or Si_2N_2O, would be found in the final products, which had been confirmed by Fig. 1. On the other hand, the presence of oxygen greatly increases the percentage of α-phase Si_3N_4 in the final product. This could be attributed to the formation of gaseous SiO which in turn forms the α-phase (see Eqs. (9)–(11)) [17]. The role of oxygen, documented well every where, is simply that of encouraging the Si to be carried to the reaction site in the vapor state and the oxygen needs not necessarily enter the resulting structure, although in some cases it may.

$$2Si(g) + CO(g) \rightarrow SiC(s) + SiO \quad (9)$$

$$3SiO + 2N_2(g) \rightarrow Si_3N_4(s) + (3/2)O_2(g) \quad (10)$$

$$2Si(g) + O_2(g) \rightarrow 2SiO \quad (11)$$

Lots of N_2 would be released according to Eqs. (1), (3) and (4). The amount of released N_2 is so large and the release rate is so quick that it would affect not only the pressure of N_2 and also the porosity of reactant compact. P_{N2} sharply increased in several seconds when the reactants were ignited, which provided enough N_2 for the reaction and promotes the infiltration of N_2 from the surface of green body to the center. Because of the quick release of gas from the reaction area, lots of micro-pores would be found and the porosity of compact would be increased, which were beneficial to diffusion of N_2 from around to the reaction positions. Meanwhile, N_2 was easily provided to react with very unit Si powder when diazenedicarboxamide and starting materials were uniformly mixed. This mode of supplying N_2 led to less depending on infiltration for combustion synthesis, which ensured that all of Si particles achieved complete nitridation. The reactions of Si–N_2 are listed from Eqs (12)–(14) [18].

$$3Si(s) + 2N_2(g) \rightarrow Si_3N_4(s) \quad (12)$$

$$3Si(l) + 2N_2(g) \rightarrow Si_3N_4(s) \quad (13)$$

$$3Si(g) + 2N_2(g) \rightarrow Si_3N_4(s) \quad (14)$$

4. Conclusion

High levels of α-Si_3N_4 powders were prepared by combustion synthesis using diazenedicarboxamide as additives at a relatively low nitrogen pressure of 3 MPa. Content of α-Si_3N_4 in combustion products increased with increasing the percentage of diazenedicarboxamide in reactants. More than 83.1 wt% of α-Si_3N_4 was formed when 12 wt% diazenedicarboxamide was added in the starting materials, but more impurities, such as SiC or Si_2N_2O, would be found. Products synthesized using less than 12 wt% diazenedicarboxamide as additive contained most of rod-like prisms, yet products including some impurities mainly consisted of small blocks that as if were coated by a little of SiC or Si_2N_2O. N_2, CO and NH_3 decomposed by diazenedicarboxamide promoted the complete nitridation of Si and the preparation of α-Si_3N_4 due to the formation of micro-pores and a change of porosity.

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