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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

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

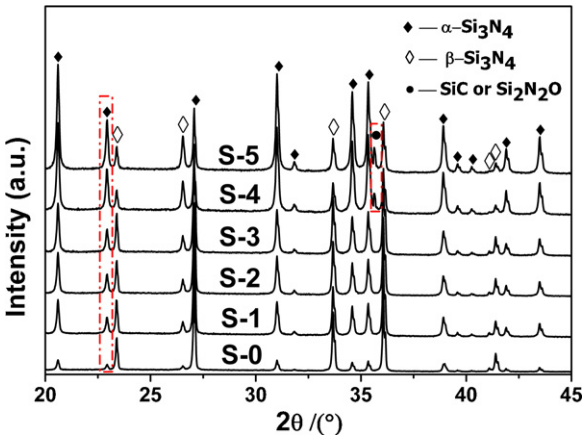

Fig. 1. X-ray diffraction (XRD) patterns of the combustion products.

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.

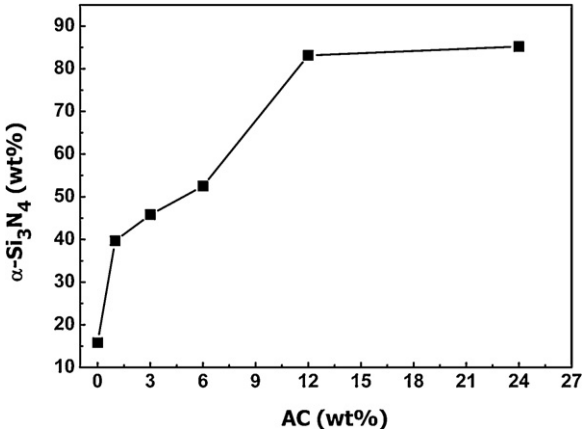

Fig. 2. Variation of α-Si_3N_4 contents with different percentages (wt%) of diazenedicarboxamide.