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Ceramics International 30 (2004) 121–123

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Short communication

The effect of additives on the morphology of combustion synthesized rod-like β-Si_3N_4 crystals

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Received 2 January 2003; received in revised form 25 January 2003; accepted 10 March 2003

Abstract

This paper presents the results of synthesizing rod-like β-Si_3N_4 crystals by combustion synthesis with ($Y_2O_3 + Al_2O_3$) or ($Y_2O_3 + MgO$) as additives. The Mg-doping sample forms a more uniform and regular microstructure (~10 μm) than that of the Al-doping sample(5–10 μm), while both additives had marked effects on the growth of rod-like β-Si_3N_4 crystals compared with those without additives, for the viscosity of Mg-containing liquid phase is lower than that of Al-containing liquid phase.

Keywords: D. Si_3N_4; E. Structural applications; Combustion synthesis

1. Introduction

Silicon nitride has attracted most attention among the advanced structural ceramic materials in the research and industrial community due to its overall excellent mechanical properties including high strength, high hardness, advanced wear resistance, good oxidation resistance and good thermal shock behavior at both room and high temperatures [1,2]. Wide use of silicon nitride, however, is still restricted owing to its brittle fracture. Numerous investigations have shown that the high fracture toughness is attributed to the rod-like grain morphologies, which favor crack deflection and/or bridging. Selective grain growth [1–6], which is obtained via the addition of elongated β-phase rod-like crystals, is important in obtaining high fracture toughness with fairly good mechanical properties.

It is well known that many material powders have been obtained using the technique of combustion synthesis (CS). The CS process is based on a combustion reaction in a powder system. The combustion is initiated locally in the powder bed by an outer energy source. Then the reaction starts and propagates through the bed in the form of a high temperature thermal wave. This method presents many advantages such as low processing cost, great energy efficiency, high purity of the products and a high production rate [7].

In the present work, β-Si_3N_4 rod-like crystals have been synthesized by the CS method with two different additives and the effect of the different additives on the microstructure has been investigated.

2. Experimental procedure

Si (98.92 wt.%, 6. 10 μm), Y_2O_3 (99.95 wt.%, 0.52 μm), MgO (>98%, 0.5 μm), Al_2O_3 (>99.9%, 0.5 μm), and α- Si_3N_4 (SN-E10, UBE Industries. Ltd. Tokyo, Japan; >95.5% α ratio, 1.57 wt.% oxygen, 0.55μm) as a diluent were used as starting materials for the synthesis ofβ-Si_3N_4 rod-like crystal. The samples were prepared according to the composition shown in Table 1. The mixtures were ball-milled for 24 h using Si_3N_4 balls with absolute ethanol as the milling media. The resultant slurry was dried to obtain an agglomerate-free powder mixture with a rotary evaporator in a drying box at 80 °C for at least 5 h to ensure that the powders were completely free of alcohol. The dried powders were then sieved through a 60-mesh sieve.

The experiments were performed in a cold isostatic pressure vessel under 5 MPa nitrogen pressure. Fifty-

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0272-8842/03/$30.00
doi:10.1016/S0272-8842(03)00067-1

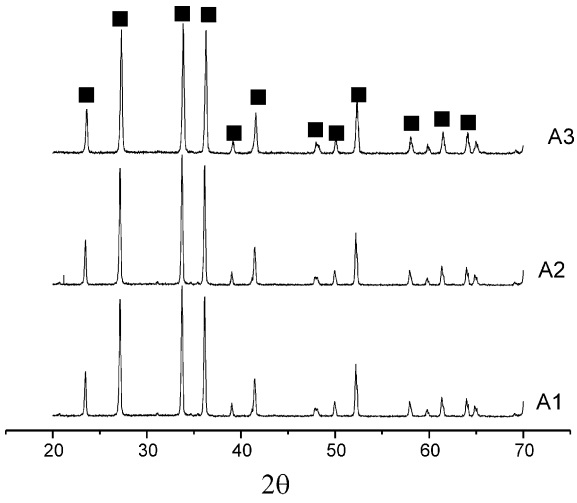
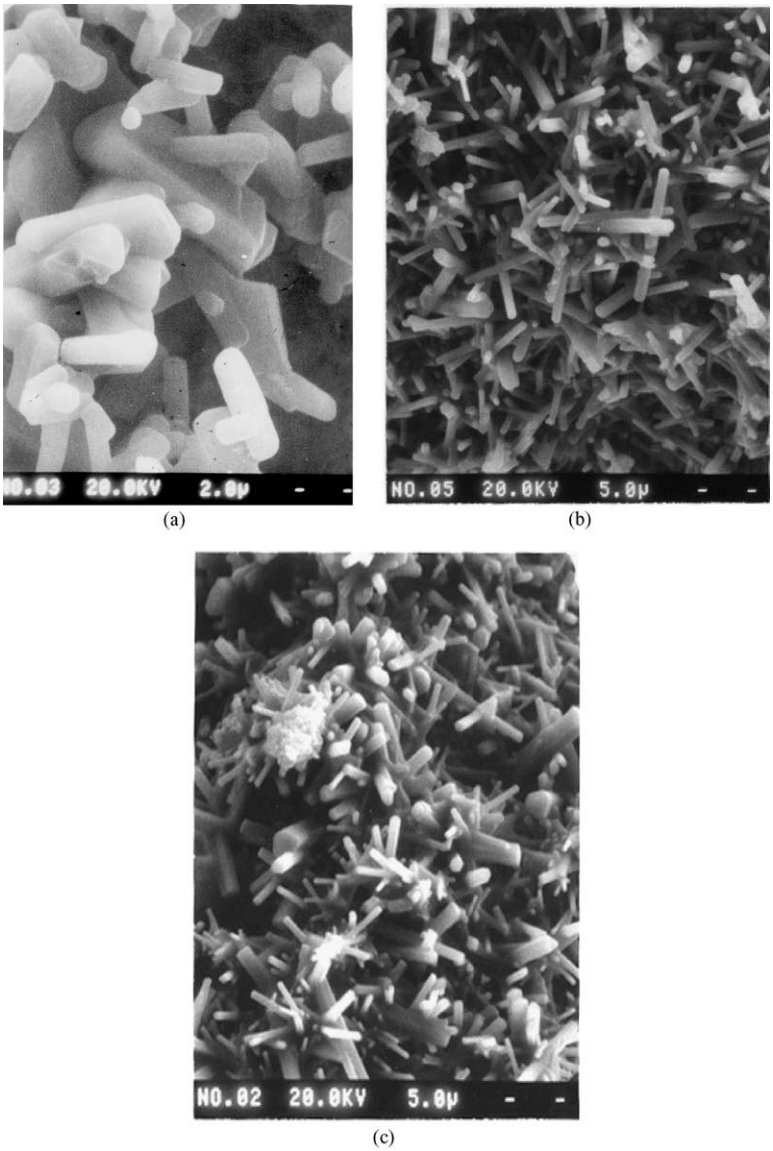


Fig. 1. XRD patterns of combustion products (■: β-Si_3N_4).

gram samples were packed in a porous graphite crucible (ϕ-5 cm) were buried by igniting 5mm depth titanium powders placed on the top of them. The ignition was carried out using a tungsten coil. The combustion wave temperature was measured with a W/Re thermocouple protected by a 2 mm layer of BN, which was inserted into the center of the powders. Phase analysis of the

Table 1
Composition and combustion condition of samples

Sample No	Composition of samples/wt%					Combustion condition
	Si	Si_3N_4	Y_2O_3	Al_2O_3	MgO	PN_2/MPa
A1	50.0	50.0	0.0	0.0	0.0	5
A2	46.4	46.4	4.8	0.0	2.4	5
A3	46.4	46.4	4.8	2.4	0.0	5



(a) (b) (c)

Fig. 2. SEM photographs of combustion products with different additives. (a) A1 sample, (b) A2 sample, (c) A3 sample.

combustion products was performed by using X-ray diffractometry (XRD). The morphologies of combustion products were studied by using scanning electron microscopy (SEM).

3. Results and discussions

XRD analysis of the combustion products showed that both the samples are composed of only β-Si_3N_4 as shown in Fig. 1. The results indicate that the Si powders have been fully nitrided under high nitrogen pressure and α- Si_3N_4, which had been added as a diluent and has also been completely converted into β-Si_3N_4.

Fig. 2 shows the SEM micrographs of the combustion products under 5 MPa nitrogen pressure with two different additives.

It is well known that the (Y_2O_3 + MgO) and (Y_2O_3 + Al_2O_3) act as sintering aids for silicon nitride to form a liquid phase and to accelerate the α to β phase transformation and grain growth via the dissolution-reprecipitaton [8–10]. In the present experiment, it is proposed that the (Y_2O_3 + MgO) and (Y_2O_3 + Al_2O_3) had the same role as that in the sintering process of silicon nitride. We note that the combustion wave temperatures of the two samples, as measured by a W/Re thermocouple, was over 2000 °C, which is considerably higher than both the melting point of Si [11] and the eutectic point of the Y_2O_3–SiO_2–Al_2O_3–Si_3N_4 system and the Y_2O_3–SiO_2–MgO–Si_3N_4 system. Therefore, a Y–Si–Al–O–N liquid or Y–Si–Mg–O–N liquid could be formed that could be beneficial for the α–β phase transformation and the β-Si_3N_4 grain growth. Moreover, it is reported [12] that the liquid Si can act as suitable liquid solvent for Si_3N_4 and assists in the α to β phase transformation. However, the marked increase of the β-Si_3N_4 grain in aspect ratio [Fig. 2 (b), (c)] suggests that the Y–Si–Mg–O–N and Y–Si–Al–O–N liquids plays the predominant role in the growth of β-Si_3N_4 grains compared with those without this liquid as in the sample A1 [Fig. 2 (a)].

The microstructure of A2 is more uniform and regular than that of A3 as shown in Fig. 2 (b, c). The length of β-Si_3N_4 grains in A2 is about ~10 μm, while that of A3 varied from 5 to 10 μm. The difference in the microstructure of sample A2 and A3 is due to the difference in liquid viscosities thus causing different grain growth rate of the width and length directions of β-Si_3N_4 crystals. Comparing Mg-containing glass, the viscosity of Al-containing glass is higher, making diffusion more difficult. Thus, the grain growth is hindered, especially in the length direction. This accounts for the non-uninformed microstructure of the Al-containing sample.

4. Conclusions

This work shows that β-Si_3N_4 whiskers can be synthesized by the nitridation of silicon powders with (Y_2O_3 + Al_2O_3) or (Y_2O_3 + MgO) as an additive using a CS method. Both additives had marked effects on the growth of rod like β-Si_3N_4 crystals compared to samples without additives. The Mg-containing sample is more prone to forming uniform and regular microstructure because of its lower liquid phase viscosity.

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