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Rapid fabrication of Si_3N_4 ceramics by reaction-bonding and pressureless sintering

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ABSTRACT

Phase compositions, densification, microstructures, thermal conductivities, and mechanical properties of sintered reaction-bonded Si_3N_4 (SRBSN) and sintered Si_3N_4 (SSN) using the same additives and procedure were compared. The present results showed that the density of SRBSN with MgO-Y_2O_3 additives was much lower than that of SSN with the same additives. The Eu_2O_3-MgO-Y_2O_3 additives inhibited the densification, while the ZrO_2-MgO-Y_2O_3 additives promoted the densification. The SRBSN with relative density of 99.5% and thermal conductivity of 66.5 Wm^{-1} K^{-1} was rapidly prepared using ZrO_2-MgO-Y_2O_3 as aids. The SSN with relative density of 99.0% and thermal conductivity of 56.8 Wm^{-1} K^{-1} was fabricated using ZrO_2-MgO-Y_2O_3 additives. The comparable density and higher thermal conductivity made the SRBSN prepared rapidly from low cost Si starting powder superior over the SSN. This study suggested that the SRBSN route with a combination of nitridation catalyst and densification aids provided a promising route to fabricate cost-effective Si_3N_4 ceramics.

1. Introduction

Silicon nitride (Si_3N_4) ceramics is a class of very important structural ceramics, because of its combination of high strength, high toughness, and good wear resistance [1]. However, the fabricating cost in general is major barrier in the direct sintering of Si_3N_4 powders (SSN) because of the combination of the high cost of raw materials and post-machining process. The sintered reaction-bonded Si_3N_4 (SRBSN) has been considered as a more attractive alternative to the SSN, due to low cost Si raw powders [2,3].

Considerable studies have shown that dense SRBSN materials had comparable or even higher mechanical properties and thermal conductivity than those of the SSN materials [4–6]. For example, the SRBSN materials prepared by Zhou et al. had thermal conductivity of 100 W/m/K and bending strength of 843 MPa. [4] Therefore, the SRBSN route could be a promising method to prepare Si_3N_4 ceramics that possessed both high thermal conductivity and high strength. Generally, preparation process of dense SRBSN materials consisted of two steps: low temperature nitridation for holding long time and high temperature densification. Kusano et al. prepared the dense SRBSN materials by nitriding at 1400 °C for 8 h and subsequently post-sintering at 1900 °C [6]. The long processing time of nitridation of Si powders is an issue, which limits the development and application of SRBSN ceramic components.

In order to promote the nitridation, many additives were introduced into Si powders [7–12]. The metal additives such as copper could promote the nitridation of Si powder [7]. However, the presence of metal impurities might lead to the degradation of mechanical properties of Si_3N_4 ceramics. In recent years, Hyuga et al. studied the effect of oxides additives including ZrO_2 plus 16 other kinds of rare earth oxides on nitridation of Si powders [9–12]. Results showed that all of the oxides exhibited nitridation enhancing effect. In particular, Eu_2O_3 and ZrO_2 additions showed a larger enhancing effect than the other oxides. Based on the significant nitridation enhancing effect, ZrO_2 was employed for rapid preparation of porous Si_3N_4 or Si_3N_4/SiC ceramics via reaction-bonding process [12,13]. Simultaneously, Hyuga et al. also found that ZrO_2 additives could improve the densification of β-SiAlON ceramics via reaction-bonding and post-sintering route [14,15]. To the best of authors' knowledge, there was no report investigating the effects of Eu_2O_3 and ZrO_2 on SRBSN prepared by nitriding at low temperature and subsequent pressureless sintering at high temperature.

Therefore, the objective of present work was to evaluate the effects of Eu_2O_3 and ZrO_2 on phase compositions, densification, microstructures, thermal conductivities, and mechanical properties of SRBSN with MgO-Y_2O_3 additives prepared by nitriding at 1400 °C for 2 h and subsequent pressureless sintering at 1800 °C

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or 1835 °C for 4 h. In addition, the SSN ceramics with the same additives and procedure were prepared for comparison.

2. Experimental procedure

The raw materials used were commercially available Si (Jinan Tianqin Silicon Industry Corp. Ltd, Jinan, China), Si_3N_4 (E-10 grade, Ube Industries Ltd, Tokyo, Japan), ZrO_2 (CSG Holding Corp. Ltd., Shenzhen, China), Y_2O_3 (Fandecheng Corp. Ltd, Beijing, China), Eu_2O_3 (Fandecheng Corp. Ltd, Beijing, China), and MgO powders (Hangzhou Wanjing Corp. Ltd, China). Pure Si compact was labeled as SI sample. The compositions of Si compacts with additives were determined based on the compositions after full nitridation as Si_3N_4:MgO:Y_2O_3 = 91.4:4.8:3.8, Si_3N_4:Eu_2O_3:MgO:Y_2O_3 = 84.7:7.4:4.4:3.5, and Si_3N_4:ZrO_2:MgO:Y_2O_3 = 84.7:7.4:4.4:3.5 at mass ratios, designated as SMY, SEMY, and SZMY samples, respectively. The corresponding Si_3N_4-powder compacts with additives at same mass ratios were designated as SNMY, SNEMY, and SNZMY samples, respectively.

SRBSN and SSN were prepared using the same powder processing procedures. The starting mixtures were mixed for 18 h in a polyethylene jar using ethyl alcohol and Si_3N_4 balls, and dried by rotary evaporation. The dried powder mixtures were pressed into disks by cold isostatic pressing with an applied pressure of 200 MPa for 300s. Nitridation and subsequent pressureless sintering were conducted in a graphite resistance furnace (Shanghai Chenhua Electric Furnace Corp. Ltd., Shanghai, China) under 1 atm N_2. The pressed specimens were firstly heated to 1400 °C and isothermally held for 2 h, and then were heated to 1800 °C and isothermally held for 4 h. In addition, the SZMY, SNMY, and SNZMY samples were sintered at 1835 °C for 4 h.

Bulk densities were measured using the Archimedes method. Relative densities were calculated by dividing the measured bulk densities by a theoretical density. Phase composition was determined by X-ray diffraction (XRD, Bruker D8, Germany). In order to obtain quantitative phase analysis (QPA) results, Rietveld XRD quantification was performed using the GSAS software package and the ExpGUI interface [16]. Microstructures were characterized by scanning electron microscope (SEM, Nova NanoSEM430, The Netherlands). Oxygen content was determined by a Nitrogen/Oxygen determinator (TC600, Leco Corporation, St. Joseph, MI). Thermal conductivity (K) at room temperature was calculated from the equation [4]:

$$K = \alpha \cdot \rho \cdot C_p \quad (1)$$

where α was thermal diffusivity which was measured at room temperature by a laser flash method, ρ was the density, and Cp was specific heat (0.68 J K^{-1} g^{-1}). Hardness was measured by the Vickers indentation method(HVS-30Z, Shanghai SCTMC Co. Ltd., Shanghai)using a load of 9.8 N for 10 s on a polished surface. Test bars of 2.5 mm × 5 mm × 25 mm were cut from the sample, and fracture toughness was determined by the single-edge notched beam (SENB) test (Model 5567, Instron, USA) with 20 mm span using the crosshead speed of 0.05 mm·min^{-1} at room temperature.

3. Results and discussion

3.1. Phase composition

Fig. 1 shows XRD patterns of SI, SMY, SEMY, and SZMY samples nitrided at 1400 °C for 2 h. The intensity of α-Si_3N_4 phase was very weak in nitrided SI sample (Fig. 1(a)). Pure Si powders were difficult to nitride at such a short time of 2 h at 1400 °C. However, the peaks of α-Si_3N_4 phase were stronger in nitrided SMY sample (Fig. 1(b)), indicating that MgO-Y_2O_3 additives promoted the nitridation. The

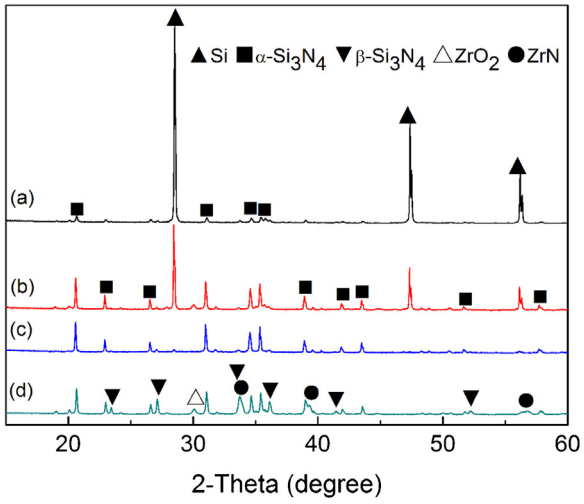

Fig. 1. XRD patterns of SI (a), SMY (b), SEMY (c), and SZMY (d) samples nitrided at 1400 °C for 2 h.

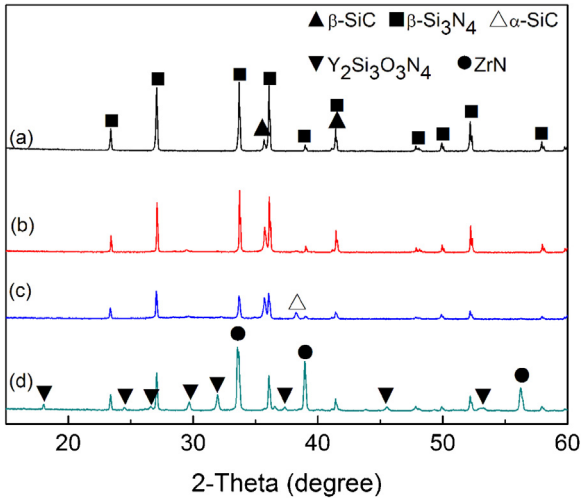

Fig. 2. XRD patterns of SRBSN ceramics at 1800 °C for 4 h including sintered SI (a), SMY (b), SEMY (c), and SZMY (d) samples.

peaks of Si phase disappeared completely in nitrided SEMY and SZMY samples. Both Eu_2O_3 and ZrO_2 additives were shown to be very effective in promoting nitridation, which was consistent with the previous results [9–12]. When ZrO_2 was added into Si powder, the reciprocal formation of ZrO_2 and ZrN was reported to effectively enhance the level of nitridation by suppressing the melting of silicon in micro-regions [17]. Only α-Si_3N_4 phase was detected in nitrided SEMY sample. In addition to α-Si_3N_4 phase, however, β-Si_3N_4 phase was observed in nitrided SZMY sample. This meant that the ZrO_2 additives could promote the α-to-β phase transformation even at such low temperature of 1400 °C, compared with Eu_2O_3. In addition, ZrO_2 and ZrN phases were observed in nitrided SZMY sample. The formation of ZrN phase was due to the reaction of ZrO_2 with Si_3N_4 [18].

Fig. 2 shows the XRD patterns of SRBSN ceramics densified at 1800 °C for 4 h including sintered SI, SMY, SEMY, and SZMY samples. Besides main β-Si_3N_4 phase, secondary SiC phase was observed in sintered SI and SMY samples. At high temperature, the Si could react with N_2 coming from sintering atmosphere and carbon coming from the graphite-rich sintering environment, respectively:

$$Si(s) + \frac{2}{3}N_2(g) \rightarrow \frac{1}{3}Si_3N_4(s) \quad (1)$$