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Effect of Si addition on the mechanical and thermal properties of sintered reaction bonded silicon nitride

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ABSTRACT

Advanced silicon nitride (Si_3N_4) ceramics were fabricated using a mixture of Si_3N_4 and silicon (Si) powders via conventional processing and sintering method. These Si_3N_4 ceramics with sintering additives of $ZrO_2 + Gd_2O_3 + MgO$ were sintered at 1800 °C and 0.1 MPa in N_2 atmosphere for 2 h. The effects of added Si content on density, phases, microstructure, flexural strength, and thermal conductivity of the sintered Si_3N_4 samples were investigated in this study. The results showed that with the increase of Si content added, the density of the samples decreased from 3.39 g/cm^3 to 2.92 g/cm^3 except for the sample without initial Si_3N_4 powder addition, while the thermal diffusivity of the samples decreased slightly. This study suggested that addition of Si powder, which varied from 0 to 100%, in the starting materials might provide a promising route to fabricate cost-effective Si_3N_4 ceramics with a good combination of mechanical and thermal properties.

1. Introduction

Because of its excellent mechanical strength, good thermal shock behavior, as well as high heat resistance, silicon nitride (Si_3N_4) ceramic has been considered as a promising candidate material for power electronic ceramic substrate [1–3]. This is true especially for application conditions with violent vibration and high thermal mechanical loading, where a good mechanical property with high reliability is critically needed [4]. As to overcome the high degree of covalent bonding between Si and N, several processing approaches have been developed to fabricate Si_3N_4 ceramics and components, such as hot-pressing sintering, hot-isostatically-pressing sintering, gas-pressure sintering and so on. However, all these sintering approaches developed are relative high cost, which has become a main obstacle to the wide acceptances and applications of silicon nitride ceramics [5–7]. To achieve low cost, simplicity, and suitability to fabricate Si_3N_4 products with complex shapes, pressureless sintering could be an ideal way to the production of silicon nitride ceramics [8]. Sintering aids such as rare earth oxides[9] and/or metallic oxide[10] were in general used in the pressureless sintering with a sintering temperature around 1800 °C in nitrogen atmosphere. Silicon nitride ceramics with relative density as high as 99% and flexural strength around 900 MPa achieved by this method have been previously reported [9,10].

Although the pressureless sintering can help to decrease the production cost of Si_3N_4 ceramics to some degree, the production cost is still quite high for products with good physical and mechanical properties due to the use of high purity Si_3N_4 powder. To overcome the high cost of high purity Si_3N_4 powder, a forming method named sintered reaction bonded silicon nitride (SRBSN), which uses silicon (Si) powder as raw material, was developed [6,11–13]. Many of Si_3N_4 ceramic products have been realized for a wide range of applications through the use of the relative cheaper Si raw powders [5]. It is well known that the reaction between silicon and nitrogen is an exothermal reaction process [13]. Because of the huge amount of heat generate during the reaction process, melting of silicon is readily to initiate and therefore partial reaction will be difficult to avoid. If the reaction rate is not well controlled in the fabrication of Si_3N_4 ceramic substrates, there would be a great propensity for distortion or crack to develop in the samples. Thus, so far there are some cases that have employed SRBSN approach to fabricate the Si_3N_4 substrates [14].

It is very likely that the pore-channel structures in the compact could be easily closed by the early formation of Si_3N_4, which consequently would probably inhibit further nitridation of the compact. Therefore, researchers began to employ raw Si_3N_4 powers as the initial diluents in the SRBSN process [11,12,14–17]. It was reported that the introduction of Si_3N_4 diluents could help to avoid the violent exothermic nitridation reactions. Also, the initial Si_3N_4 dilu-

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ents could promote the densification of the products, and affect the resulting thermal conductivity and the mechanical properties. Hirao et al. reported that by seeding β-Si_3N_4 particles and sintering at 1850 °C for 1–6 h under 0.9 MPa N_2 pressure, the fracture toughness could be improved from 6.3 to 8.7 MPa $m^{1/2}$ and the fracture strength could reach up to 1 GPa [18]. Also, Soo Young Lee et al. reported that the fracture toughness of seeded Si_3N_4 was improved up to 35% compared to the baseline Si_3N_4 after sintering at 1850 °C for 2 h under a nitrogen pressure of 0.5 MPa [19]. In addition, Joo-Sin Lee also studied the microstructure development and mechanical properties of SRBSN ceramics, and reported that Si_3N_4 ceramics with fracture strength of 1100 MPa and fracture toughness of 7.2 MPa $m^{1/2}$ were obtained by sintering at 1900 °C for 3 h under 2 MPa N_2 pressure [11]. Recently, Young-Jo Park reported that Si_3N_4 ceramics fabricated with Si_3N_4 added as the diluents exhibited thermal conductivity 75 W/mK by sintering reaction-boned process at 1900 °C for 6 h under the static N_2 pressure of 0.9 MPa [14].

Previous studies showed that good properties such as mechanical properties and thermal conductivity could be achieved with the addition of Si_3N_4 seed powder as one of the starting raw materials. However, most of the experiments were conducted either under the condition of high N_2 pressure and/or high temperature, which could possibly lead to the increase of the difficulty and/or cost of manufacturing of the products. On the other hand, the melting of Si powders could readily occur due to the fact that the nitridation of Si powders is an exothermic reaction, which could possibly result in over-heating above the melting point of Si. Hyuga et al. reported that the addition of ZrO_2, which mostly played the role of catalysis, could facilitate the nitridation rate of Si powder [20–22]. Furthermore, as reported in previous study that the addition of Gd_2O_3 could be beneficial to enhance the mechanical properties [23,24]. For the purpose of reducing the manufacturing cost, and avoiding the melting of Si, Si_3N_4 ceramics were prepared using a mixture of Si_3N_4, Si powders and ZrO_2 + Gd_2O_3 + MgO additives via conventional powder processing with the sintering conditions of 1800 °C and 0.1 MPa in the present study. The effects of Si powder contents on microstructure as well as physical and thermal properties were systematically investigated and reported.

2. Experimental procedure

The raw materials used in this study were Si_3N_4 (E-10 Grade, Ube industries Ltd., Tokyo, Japan), Si (purity > 99.999%, Tianqin Silicon industries Ltd., Jinan, China), Gd_2O_3 (purity > 99.5%, Baotou, China), MgO (purity > 99.5%, Jingrui Corp., Xuancheng, China), and ZrO_2 (purity > 99.5%, Jingrui Corp., Xuancheng, China). The amount of sintering additives in the Si_3N_4 and Si compact was calculated in order to yield a fully nitrided compact with a nominal composition of Si_3N_4:Gd_2O_3:MgO = 90:8:2 mass ratio. The amount of ZrO_2 added as the catalyst for nitridation process was 1/10 of Si. The mass ratios of Si to Si_3N_4 raw material were 0:100%, 25%:75%, 50%:50%, 75%:25%, and 100%:0, respectively. These specimens are designated as 0Si, 25Si, 50Si, 75Si, and 100Si, respectively, in this study.

In order to homogeneously mix the powders, ethanol was added to each powder mixture and the slurry was then planetary milled for 8 h using silicon nitride balls. After drying and sieving, the mixed powder was uniaxially pressed in a 50 mm × 50 mm stainless-steel die and then cold-isostatically pressed at a pressure of 200 MPa. The nitridation of Si:Si_3N_4 green compacts in a BN crucible was carried out in a graphite resistance furnace (ZT-90-22, Chenghua Electric Furnace Co. Ltd., Shanghai, China) at 1400 °C for 2 h under a N_2 pressure of 0.1 MPa, and the nitrided disks were then sintered at 1800 °C with 0.1 MPa N_2 pressure for 2 h.

The bulk density was measured using the Archimedes method. X-ray diffraction (XRD) patterns of the green body and the post-sintered samples were obtained using a Bruker D8 X-ray diffractometer. Microstructure of the post-sintered materials was characterized using scanning electronic microscope (SEM, Nova NanoSEM430, The Netherlands) on the polished and plasma etched (with a 90% CF_4 gas) surfaces. The flexural strength of the samples was measured in a four-point flexure test fixture (WDW-100E, Shijin Corp., Jinan, China) with inner and outer span of 10 mm and 20 mm, respectively. The dimensions of the test bend bars were 25 mm in length, 2 mm in width, and 1.5 mm in height. The Fracture toughness was evaluated by the single edge notched beam (SENB) method using a universal machine (Model 5567, Instron, USA) with a 20 mm span and the cross head speed of 0.05 mm min^{-1} at room temperature.

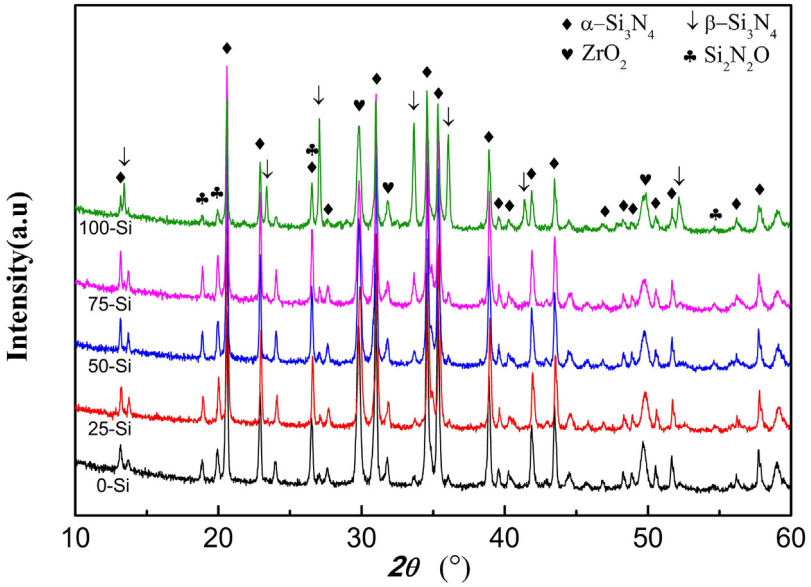

Fig. 1. XRD patterns of the samples nitrided at 1400 °C for 2 h under 0.1 MPa N_2 pressure.

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