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Improved thermal conductivity of sintered reaction-bonded silicon nitride using a BN/graphite powder bed

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ABSTRACT

Sintered reaction-bonded silicon nitride (SRBSN) with improved thermal conductivity was achieved after the green compact of submicron Si powder containing 4.22 wt% impurity oxygen and Y_2O_3-MgO additives was nitrided at 1400 °C for 6 h and then post-sintered at 1900 °C for 12 h using a BN/graphite powder bed. During nitridation, the BN/10 wt% C powder bed altered the chemistry of secondary phase by promoting the removal of SiO_2, which led to the formation of larger, purer and more elongated Si_3N_4 grains in RBSN sample. Moreover, it also enhanced the elimination of SiO_2 and residual $Y_2Si_3O_3N_4$ secondary phase during post-sintering, and thus induced larger elongated grains, decreased lattice oxygen content and increased Si_3N_4-Si_3N_4 contiguity in final SRBSN product. These characteristics enabled SRBSN to obtain significant increase (~40.7%) in thermal conductivity from 86 to 121 $W \cdot m^{-1} \cdot K^{-1}$ without obvious decrease in electrical resistivity after the use of BN/graphite instead of BN as powder bed.

1. Introduction

Silicon nitride ceramics are important structural materials due to their excellent mechanical properties, high chemical stability, and superior wear and thermal shock resistance [1–4]. Typically, Si_3N_4 also has a notable property of high thermal conductivity. The intrinsic thermal conductivity of β-Si_3N_4 single crystal has been estimated to be 200-320 $W \cdot m^{-1} \cdot K^{-1}$ at room temperature [5]. The excellent mechanical and thermal properties enable Si_3N_4 to be a promising substrate material for high-power electronic devices. However, polycrystalline Si_3N_4 ceramics have much lower thermal conductivity than the intrinsic value due to the existences of intergranular secondary phase and lattice imperfections including impurity atoms, vacancies, dislocations and stacking faults [6–8]. Oxygen is widely recognized as one of the most detrimental impurities to the thermal conductivity of Si_3N_4 ceramics, because oxygen can dissolve in Si_3N_4 lattice with the formation of phonon-scattering silicon vacancies [8–10]. Many studies have demonstrated that the elimination of lattice oxygen is crucial for improving the thermal conductivity of Si_3N_4 ceramics, which can be achieved by high-temperature sintering (or plus annealing) of high-purity Si_3N_4 powder compacts for a long time, using rare earth oxides (like Y_2O_3, Yb_2O_3) and magnesium compounds (MgO, $MgSiN_2$) as sintering additives [11–20]. Compared with sintered Si_3N_4 ceramics (SSN), sintered reaction-bonded silicon nitride (SRBSN) has been verified to be a better choice for industrial applications due to the lower cost and higher possibility to attain high thermal conductivity [21–23]. Therefore, a considerable amount of research effort has been made on developing high thermal conductive SRBSN [23–30].

The thermal conductivity of SRBSN was strongly affected by the particle size and the oxygen content of the starting Si powder [23,28,29]. Although the reduction in particle size of Si was beneficial for increasing the nitridation rate and the post-sintering activity, it led to a decrease in thermal conductivity of SRBSN due to the increased native oxygen content from surface oxidation [23,28]. Therefore, almost all the high thermal conductive SRBSN have been obtained using coarse and high-purity Si raw powder with low content of oxygen [23–26,30]. However, in the viewpoint of commercial application, various kinds of silicon powders including those with small particle size and high oxygen content should be considered as the starting material. Therefore, it is necessary to

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find a low-cost and simple method to remove the native oxygen more efficiently during nitridation and post-sintering, and eventually increase the thermal conductivity of SRBSN.

The thermal conductivity of Si_3N_4 ceramic can also be influenced by the processing conditions, such as atmosphere and embedding condition. Zhou et al. reported that a more reducing atmosphere during nitridation significantly improved the thermal conductivity of SRBSN doped with Y_2O_3-MgO additives by promoting the formation of β-Si_3N_4 with decreased lattice oxygen content [30]. However, the experimental details were not described and the deeper mechanism is necessary to be further investigated. Their group also reported that the thermal conductivity of SSN doped with Y_2O_3-$MgSiN_2$ additives was affected by the embedding conditions during sintering [31]. The optimum condition was that only one sample partly embedded in BN packing powder, which led to the highest thermal conductivity of 117 $W \cdot m^{-1} \cdot K^{-1}$ because of the promoted elimination of lattice oxygen and the decreased amount of secondary phase. Unfortunately, the great restriction on the number of sintered samples in this method makes it difficult to achieve high productivity. It is well-known that graphite has strong reducing ability especially at high temperature. If a graphite-containing powder bed (like BN/graphite) can be used during nitridation and post-sintering, a more reducing atmosphere would be created and significantly decrease the partial pressure of SiO(g) [32], which is possibly efficient to remove lattice oxygen and increase the thermal conductivity of SRBSN. Moreover, this new method has no special limitation on the number of samples during nitridation and post-sintering, which is suitable for mass production. However, research on the use of BN/graphite powder bed for improving the thermal conductivity of SRBSN has not been reported yet.

In the present study, we utilized submicron Si powder with an oxygen content of 4.22 wt% and Y_2O_3-MgO sintering additives as the starting materials, and a mixture of 90 wt% BN – 10 wt% C as a powder bed during nitridation and post-sintering to enhance the thermal conductivity of SRBSN. The nitridation, densification, phase composition, microstructure and thermal conductivity were systematically investigated. Moreover, the corresponding mechanism for the improvement of thermal conductivity caused by BN/10 wt% C powder bed was studied through comparing with monolithic BN powder bed.

2. Experimental procedure

The starting materials were high-purity Si powder (Sicomill Grade 4, 99.99%, D_{50} = 4.0 μm, Vesta Ceramics, Ljungaverk, Sweden) with an oxygen content of 0.63 wt%, Y_2O_3 (Grade C, 99.99%, D_{50} = 0.7 μm, H.C. Stark, Goslar, Germany) and MgO (99.99%, D_{50} = 3.6 μm, Sigma-Aldrich Co., St. Louis, MO, USA). In order to improve the nitridation rate and post-sintering activity, Si powder was crushed in ethanol by planetary milling at 300 rpm for 12 h using Si_3N_4 balls and jars. After drying, the as-received Si powder obtained a decreased D_{50} of 0.36 μm and an increased oxygen content of 4.22 wt%. Then, Si, Y_2O_3 and MgO powders, as well as Si_3N_4 milling media, were poured into a polyethylene bottle and ball-milled in ethanol for 24 h. The starting composition was determined as Si_3N_4:Y_2O_3:MgO = 93:2:5 at molar ratio based on the assumption that Si powder could be fully transformed into Si_3N_4 after nitridation. After vacuum drying and sieving, the powder mixture was uniaxially dry-pressed into pellets (Φ18 mm × 5 mm and Φ50 mm × 5 mm) in steel dies, followed by cold isostatic pressing at 200 MPa.

Powder bed was employed during both nitridation and post-densification processes, and two kinds of bed were respectively designated: (1) the monolithic BN powder (Grade GP, mean particle size of ~9 μm, Denka Co. Ltd., Tokyo, Japan) bed for Sample S1; (2) a mixture bed of 90 wt% BN and 10 wt% C (Graphite, Synthetic, mean particle size of ~7.5 μm, Sigma-Aldrich Co., St. Louis, MO, USA) for Sample S2. The Si compacts were firstly placed on Si_3N_4 balls (as an intermediate layer), which lay on BN or BN/graphite powder bed in a BN-coated graphite crucible, and then nitrided at 1400 °C for 6 h under a nitrogen pressure of 0.1 MPa. Subsequently, the RBSN samples were entirely embedded in their corresponding powder bed in a BN crucible and post-sintered at 1900 °C for 12 h under a nitrogen pressure of 1 MPa. All the heat-treatment processes were carried out in a graphite resistance furnace.

The degree of nitridation was determined by measuring the weight gain of the nitrided compact, and the detailed method was described by Zhu et al. [23]. The phase compositions were identified by X-ray diffractometry (XRD; D/Max 2500, Rigaku, Tokyo, Japan) using Cu $K\alpha$ radiation. The quantitative analysis of α- and β-Si_3N_4 phases was conducted based on the method reported by Gazzara and Messier [33]. Bulk densities (ρ) were determined by the Archimedes method, and the theoretical density was calculated according to the rule of mixtures using density values of 3.19 $g \cdot cm^{-3}$ for Si_3N_4, 5.01 $g \cdot cm^{-3}$ for Y_2O_3 and 3.58 $g \cdot cm^{-3}$ for MgO. The surfaces of post-sintered samples were grinded and polished to 1 μm finish using diamond abrasives. The microstructures were observed using scanning electron microscopy (SEM; JSM-5800, JEOL, Tokyo, Japan). Lattice oxygen contents were determined by a hot-gas extraction method and the procedures were reported by Kitayama et al. [9]. Thermal diffusivities (α) at room temperature were measured on disk specimens with a dimension of Φ10 mm × 2 mm using the laser-flash method (LFA 467 Hyperflash, NETZSCH Instruments Co. Ltd., Selb, Germany). Before measurement, the surfaces of disks were sputter coated with a 60 nm thick layer of gold, followed by a subsequent coating of spraying colloidal graphite. Thermal conductivity (κ) was calculated according to the relation of $\kappa = \rho C_p \alpha$, using a constant value of 0.68 $J \cdot (g \cdot K)^{-1}$ for the specific heat (C_p) of Si_3N_4 in this work. The large-size samples (Φ40 mm × 2 mm) were used for electrical resistivity measurement and electrodes were formed on both sides of the disks by platinum sputtering. The bulk resistivity (ρ_v) at room temperature was determined using a high-resistance meter (Agilent 4339A, Agilent Technologies Inc., Santa Clara, CA, USA) under applied electric-field strength of 100 $V \cdot mm^{-1}$.

3. Results and discussion

Table 1 summarized the nitridation results of Si compacts at 1400 °C for 6 h. It was shown that the nitridation degree (91.08%), relative density (72.08%), linear shrinkage (1.54%) and lattice oxygen content (0.224 wt%) of Sample S2 were all slightly lower than those of Sample S1, which was probably associated with the variation of chemical equilibrium in the more reducing atmosphere created by the BN/graphite powder bed. Besides, both of the RBSN samples exhibited fairly high $\beta/(\alpha+\beta)$ phase ratios of ~100% and exceeded the values reported previously [23–30]. The possible reasons were given as follows: Firstly, the ultra-fine particle size

Table 1
Nitridation results of the Si compacts at 1400 °C for 6 h.

Sample	Nitridation degree (%)	$\beta/(\alpha+\beta)$ (%)	Bulk density ($g\ cm^{-3}$)	Relative density (%)	Linear shrinkage (%)	Lattice oxygen content (wt%)
S1	93.16	100	2.39	73.94	1.79	0.296
S2	91.08	100	2.33	72.08	1.54	0.224

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