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# Processing and properties of sintered reaction-bonded silicon nitride with $Y_2O_3$–$MgSiN_2$: Effects of Si powder and $Li_2O$ addition

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## Abstract

The effects of Si powder and $Li_2O$ addition on the processing, thermal conductivity and mechanical properties of sintered reaction-bonded silicon nitride (SRBSN) with $Y_2O_3$–$MgSiN_2$ sintering aids were studied. Addition of $Li_2O$ provides a less-viscous liquid phase that results in a more uniform and finer pore structure in RBSN with the coarser Si powders, but the pore structure plays a less important role in the densification of RBSN. The thermal conductivity of SRBSN without porosity decreases with increased Al impurity content and also decreases with the $Li_2O$ addition regardless of the Si purity. The impurest coarse Si powder produces the lowest thermal conductivity (93 $W\,m^{-1}\,K^{-1}$) but the highest four-point bending strength ($\sim$700 MPa) and a higher fracture toughness ($\sim$10 $MPa\,m^{1/2}$). However, the purer fine Si powder produces the highest thermal conductivity (119 $W\,m^{-1}\,K^{-1}$) and highest toughness ($\sim$11 $MPa\,m^{1/2}$) but the lowest strength ($\sim$500 MPa).

*Keywords:* Sintered reaction-bonded silicon nitride; Nucleation and growth; Fracture; Toughness; Thermal conductivity

## 1. Introduction

Silicon nitride ($Si_3N_4$) is an important structural ceramic material suitable for various applications such as automotive engine parts, industrial wear parts, cutting tools, ceramic armor, etc., due to its excellent mechanical properties, good resistance to thermal shock and chemical attack, excellent creep resistance, and good tribological and wear properties [1]. The recent discovery that this material also has high thermal conductivity makes $Si_3N_4$ a promising candidate material for integrated circuit (IC) substrates and heat sinks [2–4]. However, cost is always the major barrier to commercial applications of $Si_3N_4$ ceramics. Sintered reaction-bonded silicon nitride (SRBSN) is a well-known, cost-effective $Si_3N_4$ ceramic material because of the low cost of Si raw powder, the machinability of the RBSN body and the lower sintering shrinkage [5,6]. The development of SRBSN, which combines high thermal conductivity with good mechanical properties, will undoubtedly help expand the industrial applications of $Si_3N_4$ components as both structural and functional materials.

Our previous work reported that the improvement in the thermal conductivity of SRBSN could be achieved by using coarse Si powders with lower amounts of oxygen and aluminum impurities [7], which are the two major impurities detrimental to the thermal conductivity of β-$Si_3N_4$ because of phonon scattering [8,9]. Although the use of purer coarse Si powders is beneficial for enhancing the thermal conductivity, the increase in Si particle size tends to retard densification of RBSN for two major reasons: (i) the increased grain size of $Si_3N_4$ products and (ii) the reduced amount of liquid phase [10,11]. However, complete densification is necessary to enhance the thermal conductivity and

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mechanical properties of ceramics. To achieve complete densification of SRBSN using coarse Si powders of several micrometers, or even a few tenths of a micrometer, higher amounts of sintering aids are often required [11]. However, this tends to lower the thermal conductivity because of the increased amount of secondary phases, which show thermal conductivities (~1 W $m^{-1}$ $K^{-1}$ for the amorphous phase and ~10 W $m^{-1}$ $K^{-1}$ for the crystalline phase) much lower than that of pure β-$Si_3N_4$ crystals (*a*-axis: ~180 W $m^{-1}$ $K^{-1}$; *c*-axis: ~450 W $m^{-1}$ $K^{-1}$) [12]. To minimize the negative effect of residual secondary phases on the thermal conductivity of AlN ceramics, Watari et al. [13] proposed a processing strategy that used an additional disappearing sintering aid, which provides a low-viscosity liquid phase to promote densification during the initial and middle sintering but can be removed in gaseous form from the samples during the final stage of sintering. Moreover, they reported that $Li_2O$ can serve as this kind of disappearing aid, as it can be removed in gaseous form at temperatures below 1600 °C, due to its high vapor pressure ($10^{-1}$ Pa at 1300 °C, 1 Pa at 1500 °C and 10 Pa at 1600 °C) [13]. The concurrent use of $Li_2O$ with $Y_2O_3$ and CaO resulted not only in low-temperature (1600 °C) sintering but also in improvement in the thermal conductivity of AlN ceramics, due to the pore elimination, AlN lattice purification and grain-boundary phase evaporation [13,14].

Matovic et al. [15,16] reported that the use of $Li_2O$ together with $Y_2O_3$ is also effective for achieving the low-temperature sintering of $Si_3N_4$ at 1600 °C. They showed that the rapid evaporation of $Li_2O$ starts at 1500 °C and the $Li_2O$ concentration is reduced from ~1.75 to ~0.08 wt.% after sintering for 8 h at 1500 °C, suggesting that the $Li_2O$ liquid phase is only transient. Thus, it is expected that the $Li_2O$ addition together with $Y_2O_3$ and $MgSiN_2$ would promote not only the post-sintering of RBSN but also the thermal conductivity of SRBSN with coarse Si powders. Similar to Mg and Y, Li is believed to dissolve in $Si_3N_4$ only in the presence of both Al and O [17,18]. The same authors also showed that $Li_2O$ evaporation is significantly suppressed in the case of the $LiAlSiO_4$ additive in comparison with the $LiYO_2$ additive [19]. This means that the effect of $Li_2O$ addition on the thermal conductivity of SRBSN probably depends on the Al impurity in the Si powders.

The present work is intended to study the effects of Si powder type and $Li_2O$ addition on the processing, thermal conductivity and mechanical properties of SRBSN. A mixture of $Y_2O_3$ and $MgSiN_2$ was chosen as the primary additive composition for the following two reasons: (i) to enhance the thermal conductivity [20], and (ii) to study the effect of $Li_2O$ addition on the pore structure development in RBSN and the post-sintering behavior of RBSN [21]. Three types of Si powders that revealed a significant difference in the Al impurity were chosen. Two of them were coarse and the other one was fine. The nitriding process was studied in terms of the degree of nitridation, density, α/β phase ratio, crystalline secondary phase and microstructure. The post-sintering process was studied in terms of the densification, weight loss, crystalline secondary phases and microstructure. The thermal conductivity and mechanical properties of the resultant SRBSN materials were evaluated.

## 2. Experimental procedure

Three types of commercial Si powders (Yamayishi Metal Co. Ltd., Tokyo, Japan) were used in this investigation. The characteristics of the as-received Si powders are shown in Table 1. According to the manufacturer's information, powder B was prepared from powder A using a milling process. The morphology of the powders was observed by scanning electron microscopy (SEM) (JSM-5600, JEOL Ltd., Tokyo, Japan). The oxygen contents were measured by an oxygen/nitrogen analyzer (TC-436, LECO Co., St. Joseph, MI, USA). The sintering aids are $Y_2O_3$ (purity of >99.9%, Shin-Etsu Chemical Co. Ltd., Tokyo, Japan), $MgSiN_2$ (0.63 wt.% O, 33.01 wt.% N, synthesized in our laboratory) and $Li_2CO_3$ (purity of >99%, Kojundo Chemical Lab, Saitama, Japan). The compositions of Si compacts with sintering additives were determined based on the designed compositions of the RBSN materials after full nitridation as shown in Table 2. The Si powder was mixed with the sintering additives in methanol by planetary ball milling for 2 h in a $Si_3N_4$ jar with $Si_3N_4$ balls. The slurries were dried using a rotary evaporator at a temperature of 60 °C, subsequently dried at 110 °C in vacuum, and sieved through 100-mesh screen. About 18 g of powder mixture were uniaxially pressed in a 52 mm × 43 mm stainless steel die and then cold isostatically pressed at 300 MPa. Based on the apparent dimensions and weight, all Si compacts were determined to show a green density of ~1.45 g $cm^{-3}$ or ~60% theoretical density (TD). Prior to nitridation, the Si compacts were cut in half. Thus, the Si green bodies used for nitridation had dimensions of approximately 48 mm × 20 mm × 6.5 mm. The Si green bodies were placed in a BN crucible with a BN powder (GP grade, Denki Kagaku Kogyo Co., Tokyo, Japan) bed and were nitrided in an alumina tube furnace with 1 l $min^{-1}$ high-purity nitrogen flow at 1400 °C for 8 h. The nitrided samples were placed inside a triple-crucible arrangement, which consisted of inner double crucibles of BN and an outer graphite crucible. The BN powder was used only as a powder bed. The post-sintering was performed in a graphite resistance furnace (Multi-500, Fujidempa Kogyo Co. Ltd., Japan) at 1900 °C for 12 h under a nitrogen pressure of 1 MPa with heating and cooling rates of 10 °C $min^{-1}$.

It has been generally accepted that RBSN is formed through the following reaction:

$$3Si + 2N_2 = Si_3N_4. \tag{1}$$

According to reaction (1), the extent of nitridation is determined by the following equation: