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Pressureless-sintering of reaction bonded silicon nitride containing cordierite

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Reaction bonded silicon nitride (RBSN) has been fabricated from Si powder with cordierite as a sintering aid. A nitridation rate of more than 90% was obtained in each specimen. As the amount of cordierite was increased, the nitridation rates decreased. Both α-Si_3N_4 and β-Si_3N_4 were formed during the nitridation of silicon to Si_3N_4. There were more beta crystals in the specimens with a higher cordierite content. The relative densities increased when the amount of cordierite increased. A Fracture toughness of 3.59±0.28 MPa-m$^{1/2}$ was obtained for the specimen containing 18 wt% cordierite sintered at 1800 °C for 3 hours.

Key words: Pressureless-sintering, RBSN, Nitridation, Relative density, Fracture toughness.

Introduction

Silicon nitride is readily becoming an important high temperature material in modern industry. Silicon nitride is shown to have high strength, excellent thermal shock resistance, chemical stability, and excellent creep resistance. However, the drawback with the use of silicon nitride is its high cost. This comes from the extensive processing needed to synthesize the unnaturally forming materials. Recently, the potential of using reaction-bonded silicon nitridev (RBSN) ceramics has been re-evaluated due to their low cost of fabrication. In order to improve the mechanical properties of RBSN ceramics, a technique of post sintering after nitridation (SRBSN) has been developed and the SRBSN ceramics after post sintering are now improved to those of sintered Si_3N_4 [1-4]. Also the SRBSN material has a high degree of dimensional control. Generally, to aid in the nitridation and densification of silicon metal, small amounts of powdered sintering additives can be mixed with the metal powder before the nitriding process. Extensive research in the use of sintering aids for silicon nitride has already been done in the area of alumina and yttria. These additives all increased the density significantly, but they did not decrease the nitridation time. Also, these sintering aids react with the SiO_2 layer on Si_3N_4 to produce a liquid phase slag. This liquid slag remains in the grain corners and at the grain boundaries, resulting in the degradation of high-temperature mechanical properties.

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The properties of RBSN can be affected by many processing variables [5-7]: initial silicon particle size, the purity and nitriding process, a composition and pressure of nitrogen gas ($N_2 + H_2$, $N_2 + He$, added O_2 or water vapor), pore size of the compacts and compact size [8-14]. Many studies have shown that the addition of He gas can increase the rate of nitridation and aid in the formation of a uniform distribution of microstructure throughout the specimen [15]. Also, an inhomogeneous coloration near the surface area of a RBSN sample was observed due to an interaction between the gas atmosphere and silicon nitride. By reducing the nitrogen partial pressure, the nitridation rate was improved up to 99% [16,17]. There are two methods to produce RBSN depending on the supply of nitrogen gas. One is a flow (dynamic) system, which is normally used in the laboratory since the entry and exit gas can be easily analyzed. The other is a static system, which is often used by commercial producers of RBSN. In the present study, we employed a computer-controlled graphite furnace that provides precise control of the reaction temperature and pressure. We also would like to use cordierite ($2MgO\text{-}2Al_2O_3\text{-}5SiO_2$) as a new candidate for a sintering aid, which is non-artificial and a very cheap material. The most frequently used sintering additive for silicon nitride ceramics is Y_2O_3 which contains a rare earth element. Since the price of rare earth elements increases it's meaningful to find out a cheap replacement for the expensive rare earth element.

Experimental Procedures

A schematic diagram of the experimental procedure is presented in fig. 1. The average particle size of Si

(Permascand Co., Sweden, Grade 4) was 7 μm. The impurities levels are given in table 1. 6%, 12%, and 18 wt% of cordierites ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$) (Pred Materials Co., USA) were used as sintering aids for post sintering. The D_{50} of cordierite powder used was 14 μm and the major impurities were 0.48% Fe_2O_3, 0.75% K_2O and 0.32% TiO_2. The starting materials are mixed in ethanol (pH 11) in an mono cast nylon jar after adding 5 wt% polyethylene glycol (PEG) as binder and milled for 24 hours in a planetary ball milling equipment with Si_3N_4 balls as the milling media. In each case, the resulting powder was dried and pressed to compact bodies.

The PEG binder was burnt out to enhance the pore channel distribution in the green compacts. After the binder burn-out operation, the compacts were subjected to nitridation in either a N_2-10%H_2 gas mixture or a N_2 atmosphere. The samples were heated in vacuum until the temperature reached 300 °C, and then the N_2-H_2 gas mixture was admitted to the desired pressure. At 1300 °C, the mixture was switched over to N_2 gas. Figure 2 shows a schematic of the computer-controlled nitriding furnace. In order to prevent a reaction between the compact and graphite and to minimize the contact area, the compacts were placed on BN-coated silicon nitride balls.

The basic nitriding reaction proceeds as follows [18]:

$$3\ Si\ (s) + 2\ N_2 = Si_3N_4\ (s) \qquad (1)$$
$$\Delta\ Ho = -723.8\ KJ/Mol$$

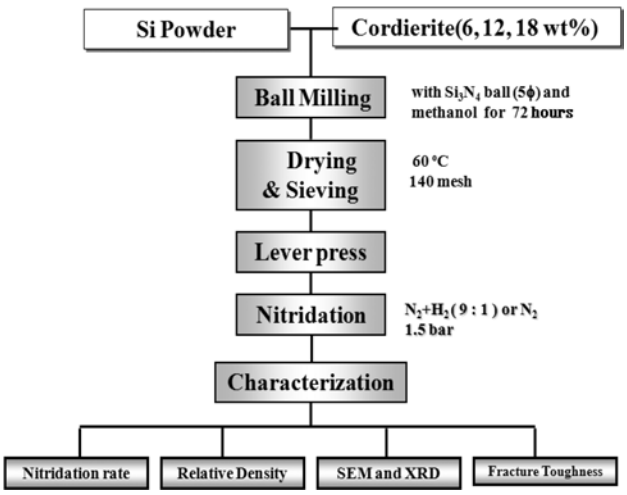

Fig. 1. Schematic diagram of the experimental procedure.

Table 1. Properties of Si powder used in this study (wt%).

Average particle size	Fe (wt%)	Al (wt%)	Ca (wt%)	C (wt%)	0% (%wt)
7 μm	0.07	0.07	0.01	0.1	0.2~1.0

The large amount of heat given off during the nitriding reaction makes close temperature control of the process difficult. To control the nitriding system, the reactants must be allowed to control the reaction rate through the rate-controlled nitriding process. This problem is one of the major obstacles to the production of high quality RBSN. Therefore, the nitriding schedule should be controlled carefully in order to avoid the fusion of silicon (Fig. 3). The microstructures of the nitride and sintering material were characterized by a X-ray diffractometer (XRD) and the analytical electron microscopy using a Scanning Electron Microscope (SEM). Room temperature-indented surfaces of nitrided material were prepared for SEM. These samples were coated with gold in order to avoid charging in the microscope.

Results and Discussions

The level of nitridation after 26 hours reaction time was obtained from the following equation:

$$\text{Level of Nitridation (\%)} = 1.5(W-W_i)/\ W_{si} \qquad (2)$$

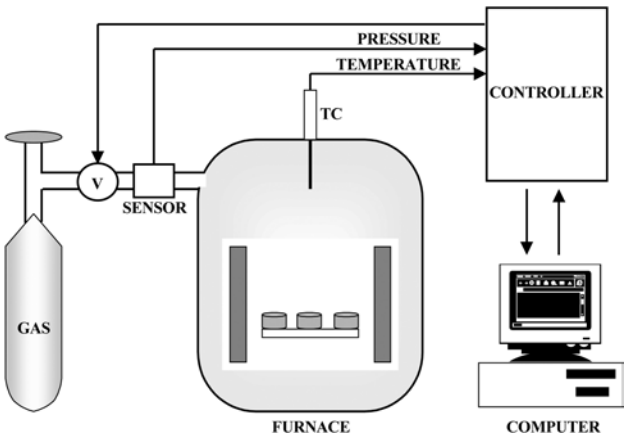

Fig. 2. Schematics of the computer controlled nitriding furnace.

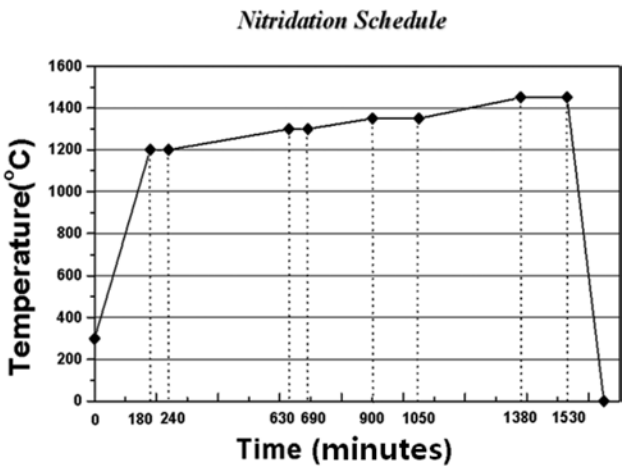

Fig. 3. Nitriding schedule used in this study.

where W is the weight of the specimen after the nitridation reaction, W_i is the weight before nitridation and W_{si} is the weight of Si before nitridation. Phase analysis was performed by XRD using Cu Kα radiation and a Ni filter. The α/β Si_3N_4 ratio after nitridation was calculated by the Gazarra and Messier equation [19].

Peak height ratios from the X-ray diffractometer were used to determine the relative changes in phase content in the compacts during the nitridation and sintering processes. This α-β phase transformation occurs because the β phase is believed to be the stable form of Si_3N_4 at temperatures above 1400 °C.

$$\alpha\text{-}Si_3N_4 = \langle I_\alpha(210)/L_\alpha(210)\rangle / \langle I_\beta(210)/L_\beta(210) + I_\alpha(210)/L_\alpha(210)\rangle \quad (3)$$

The results of nitridation experiments with increasing cordierite content are shown in figure 4. The nitridation rates ranged from 90 to 95%. As the amount of cordierite increased, the nitridation rates decreased. The rates were a little bit lower than the values in the Y_2O_3-Al_2O_3 system(more than > 99 %). With the presence of MgO, the glass viscosity was low and the transport of material was rapid. In this system, the kinetics of densification was generally faster than the kinetics of the dissolution process. With Y_2O_3, the glass viscosity is higher and the transport of materials through the glass phase is slow [20]. Therefore, higher nitridation rates can be expected in the Y_2O_3-Al_2O_3 system.

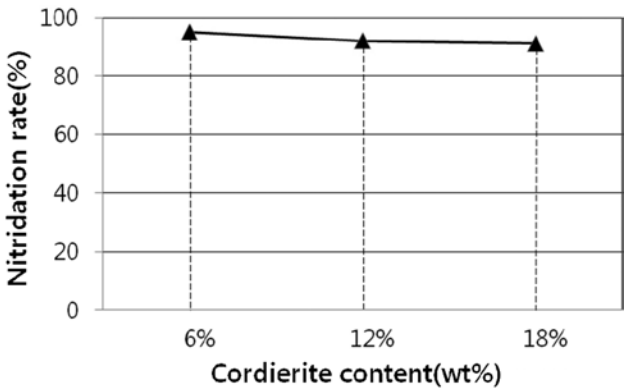

Fig. 4. Nitridation rate as a function of the cordierite content.

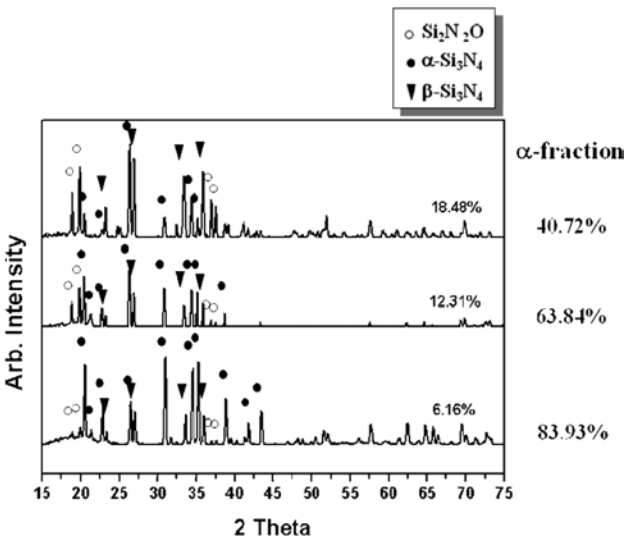

Fig. 5. XRD patterns as a function of cordierite content after RBSN.

Figure 5 shows the X-ray results of specimens after nitridation. The α-β Si_3N_4 ratio was calculated based on equation (3). The (210) plane was selected to minimize the effect of grain size and the preferred orientation. A structure-related parameter (L) was obtained for each plane, and $L_\alpha(210)$ and $L_\beta(210)$ were 6.79 and 11.21 respectively. There were more beta crystals in the specimens with a higher cordierite content. The reason was probably that the amount of liquid glass in the higher cordierite content samples was large enough to produce more beta Si_3N_4. Also the total amount of Si_3N_4 formed during the nitriding process was small so that it was easier to transform from alpha to beta Si_3N_4. The Si_2N_2O peak was also observed in each specimen. Formation of Si_2N_2O is enhanced when the Si_3N_4 formed after the nitridation reacts with SiO_2 from the liquid phase, which suggests that the large amount of SiO_2 in cordierite favors the formation of Si_2N_2O. It was believed that Si_2N_2O grows from a liquid phase, which has been saturated with the dissolved nitrogen [21,22]. Sintered densities are plotted against added cordierite contents at different sintering temperatures in figure 6. The sintered densities at 1750 °C and 1800 °C increased when the amount of cordierite increased. Also a higher sintering temperature ensures a higher density. The density value sintered at 1800 °C with 18% cordierite is 3.0 gcm^{-3}. When we remind the theoretical density of silicon nitride is 3.2 and that of Si_2N_2O is lower a sintered density of 3.0 gcm^{-3} seems to be near theoretical density.

Figure 7 shows a SEM micrograph of a polished and

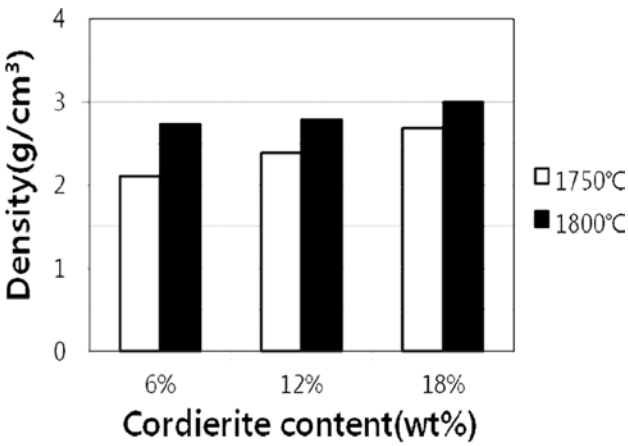

Fig. 6. Density of each specimen as a function of the cordierite content and sintering temperature.

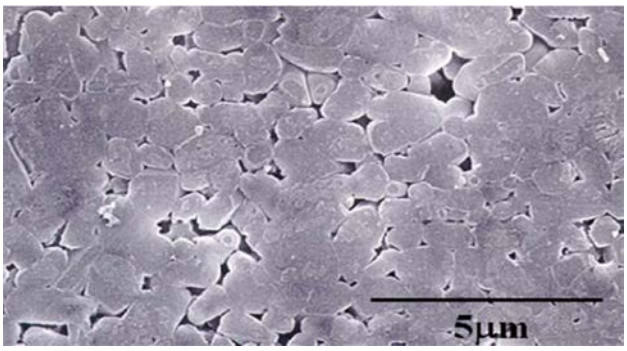

Fig. 7. SEM micrograph of a polished and then etched surface of a specimen containing 18 wt% cordierite.

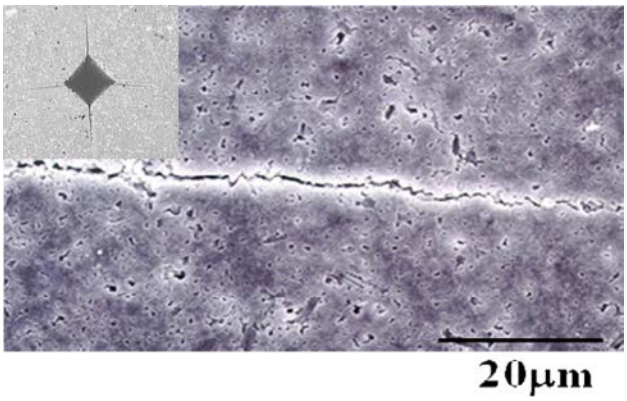

Fig. 8. SEM micrograph of an indentation mark and crack of a specimen containing 18 wt% cordierite.

etched specimen sintered at 1800 °C for 3 hours. The addition of hydrogen to the nitriding atmosphere appears to be beneficial. Si_3N_4 grains were uniformly distributed throughout the sample. Lin [23] showed that small additions of hydrogen resulted in an increase in the SiO concentration in the nitriding atmosphere. The presence of SiO has been postulated to be critical to the nitriding reaction [24]. Theoretically, two possible nitriding reactions occur, one involving the reaction of silicon and the other involving the reaction of gaseous SiO with nitrogen. The reaction involving SiO takes place within the pore space of the compact, resulting in the formation of a uniform, fine grained Si_3N_4 network.

Figure 8 shows a SEM micrograph of a polished and etched surface of a sample containing 18 wt% cordierite sintered at 1800 °C for 3 hours. The indentation mark was used to calculate the fracture toughness of 3.59 ± 0.28 MPa $m^{1/2}$. This value was somewhat lower than that of the conventionally sintered silicon nitride. This may have to do with the very large amount of cordierite added and Si_2N_2O formed. Since the grain morphology of Si_2N_2O is equiaxed its grains may not provide toughening mechanisms such as crack deflection and/or crack bridging. Addition of cordierite provides enough liquid phase to allow near full densification, although the large amount of SiO_2 in cordierite leads to the formation of Si_2N_2O. Since Si_2N_2O has a better oxidation resistance than Si_3N_4 the sintered reaction bonded silicon nitride having a mixture of Si_3N_4 and Si_2N_2O might provide better oxidation resistance.

Conclusions

Sintered Reaction Bonded Silicon Nitride (SRBSN) has been fabricated from Si powder with cordierite as a sintering aid.

A nitridation of more than 90% was obtained in each specimen. As the amount of cordierite was increased, the nitridation rates decreased. Both α- and β-Si_3N_4 were formed during the nitridation of silicon to Si_3N_4. There were more beta crystals in the specimens with higher cordierite content since the amount of liquid phases needed for the transformation of alpha to beta silicon nitride was large enough. The Si_2N_2O peak was also observed. It is believed that Si_2N_2O grows from a liquid phase.

The sintered densities increased when the amount of cordierite was increased. Also a higher sintering temperature ensures the higher density.

A fracture toughness of 3.6 MPa · $m^{1/2}$ was obtained for the specimen containing 18 wt% cordierite sintered at 1800 °C for 3 hours.

Acknowledgement

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