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Effects of Silicon Powder Size on the Processing of Reaction-Bonded Silicon Nitride

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Abstract

The effects of silicon powder size on the processing of reaction-bonded silicon nitride (RBSN) were investigated by using three silicon powders of 3, 6 and 12 μm in average size. The procedure for processing of RBSN body was as follows: compacting the silicon powder with uniaxial press at 72 MPa and then cold isostatic press (CIP) at 300 MPa; pre-sintering the green compact at 1200 °C in argon atmosphere for 3 hrs; then nitriding the preform body at 1500 °C in nitrogen atmosphere for 3 hrs. The physical and mechanical properties were measured. From the results, bulk density, hardness, young's modulus and flexural strength are increased with decreasing the silicon powder size. The mechanical properties vary with density, % porosity and α-Si_3N_4 content.

Key Words: Reaction-bonded silicon nitride (RBSN), RBSN, Nitridation, Mechanical properties

Introduction

Silicon nitride is an interesting structural ceramic due to its good properties. It has an excellence resistance to thermal shock and wear resistance comparing to metals(1). Thermal expansion coefficient is low and corrosion resistance is high. It also has high strength at high temperature(1). Due to these properties, silicon nitride is very good for using at high temperature.

Silicon nitride can be fabricated in many methods, such as hot pressing, hot isostatic pressing, pressureless sintering, and reaction bonding, etc. Each method presenting its own advantage. For reaction bonding method, silicon nitride can be fabricated with lowest raw material cost and processing temperature. This method is also the easiest to achieve complex and near-net shape product. However, reaction-bonded silicon nitride (RBSN) possesses high porosities, which lead to low strength. Hence RBSN is suit for the application at high temperature with low load(3). tried to make RBSN for nozzle application and studied the machine ability of RBSN. They succeeded in machining RBSN but the flexural strength of their RBSN was still low.

Most likely, the cause of low strength was from the big size (Avg. 25 μm) of the starting Si powder. In this paper, we studied the effects of the starting silicon powder size on the properties of reaction-bonded silicon nitride.

Materials and Experimental Procedure

Si powders of three mean particle sizes (3, 6, and 12 μm) were used in this experiment. The powders are commercial grade with the composition of 99.11% Si, 0.17%Fe, 0.14%Al, 0.47%Ca, 0.10%W. The size distribution and the specific surface area of the powders are shown in the Table 1.

Table 1. Characteristics of Si powder used

Powder (μm)	Particle size distribution			Specific Surface Area (m^2/g)*
	d10	d50	d90	
3	0.76	3.26	17.42	1.99
6	1.14	6.23	20.43	1.27
12	4.28	11.87	30.88	0.32

*measured by Mastersizer analyzer

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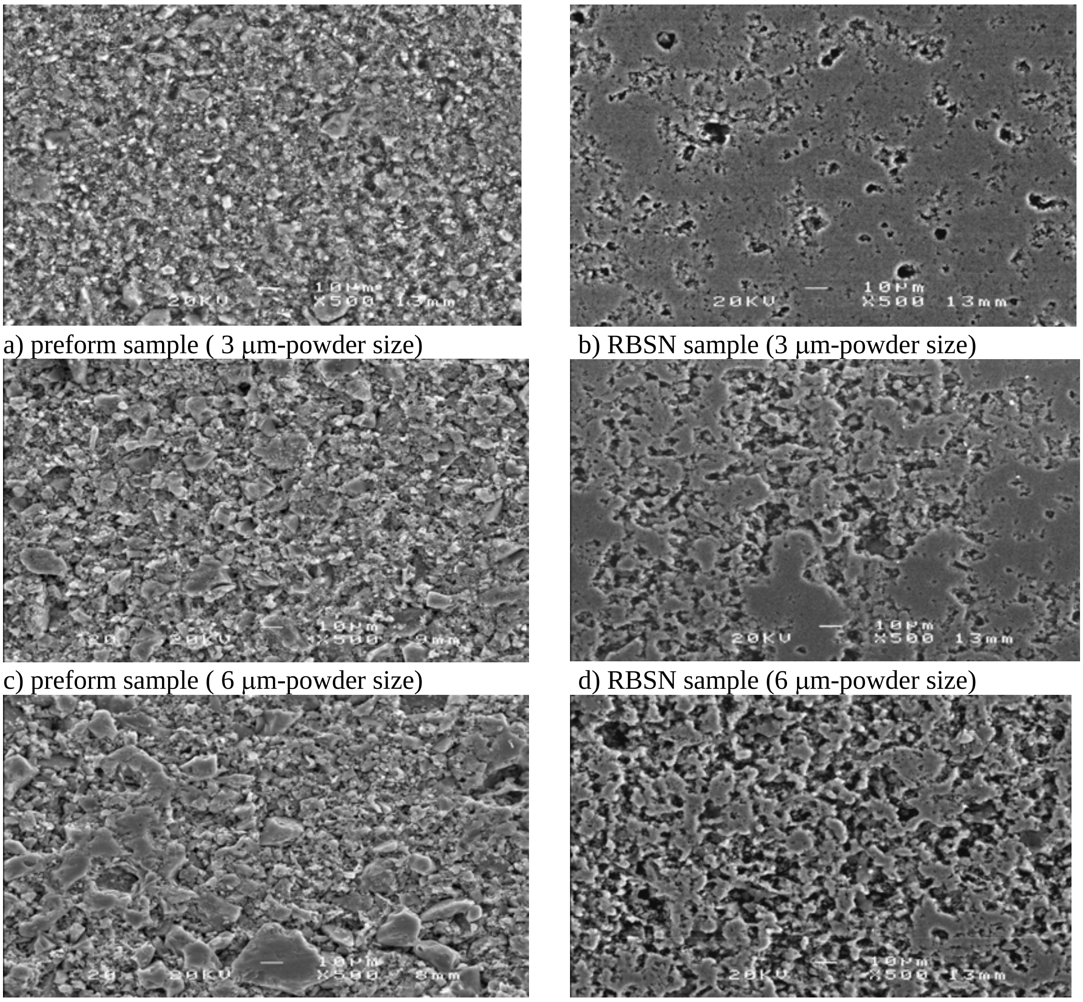
These three powder sizes were fabricated to be RBSN specimen in the following steps. The powders were mixed with 2 vol% Poly Vinyl Alcohol (PVA). The mixtures were uniaxially pressed in 4 x 6 x 34 mm stainless steel die at 72 MPa and then pressed in cold isostatic press (CIP) at 300 MPa. The green compacts were pre-sintered in Ar atmosphere at 1200 ^oC for 3 hrs. Nitridation of the preform body was done in nitrogen atmosphere at 1500 ^oC for 3 hrs.

The microstructure of RBSN specimen was investigated by SEM. The XRD with CUκα radiation was used to examine the content of α-Si_3N_4, β- Si_3N_4 and residual Si phase. The bulk density was measured by dimension measurement, Archimedes method and Ultrapycnometer analyzer. Young's modulus was measured by Grindosonic analyzer. The Vickers hardness was measured by using a load of 300 g for 10 minute. The flexural strength was measured by a three-point bending method using specimen of 3 x 5 x 25 mm^3 with cross-head speed of 0.045 mm min^{-1}.

Results and Discussion

- Microstructure

The microstructures of preform bodies (1a, 1c, 1e) and RSBN specimen (1b, 1d, 1f) from different original Si powder size are shown in Figure 1. In the preform bodies, Si powder size distribution can be seen in every sample. For the RBSN specimen, the size and amount of pores clearly increased with the increasing starting Si powder size.



a) preform sample (3 μm-powder size) b) RBSN sample (3 μm-powder size)

c) preform sample (6 μm-powder size) d) RBSN sample (6 μm-powder size)

e) preform sample (12 μm-powder size) f) RBSN sample (12 μm-powder size)

Figure 1. SEM microstructure at magnification of 500X of Preform and RBSN samples produced by various size of silicon powders

Table 2. Relative integrated intensity of α-Si_3N_4 peak, β- Si_3N_4 peak, and fraction of β intensity of RBSN sample from different raw Si powder size.

RBSN sample size (μm)	Relative Integrated Intensity of α-Si_3N_4 peak	Relative Integrated Intensity of β- Si_3N_4 peak	$\frac{I_{\beta(210)}}{I_{\beta(210)} + I_{\alpha(210)}}$
3	1180	215	0.15
6	1437	377	0.21
12	2473	728	0.23

XRD result shows α-Si_3N_4 (210) peak at 2θ = 2.54 and β- Si_3N_4 (210) peak at 2θ = 2.49. The XRD result does not show the Si phase peak which implies that there is no or only little residual Si phase in the microstructure. Table 2, shows the relative integrated intensity of α and β Si_3N_4 peaks, and fraction of β intensity of RBSN sample from different raw Si powder size. Figure 2 is the calibration curve used to obtain weight fraction of β-Si_3N_4 from the fraction of β intensity.

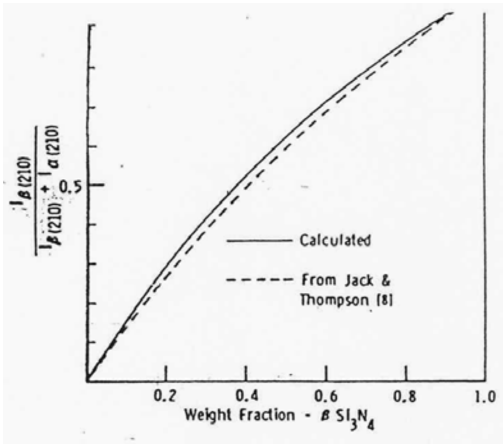


Figure 2. Calibration curve show relationship between fraction of integrated intensity of β-Si_3N_4 and weight fraction of β-Si_3N_4[4].

Table 3. The percentage α-Si_3N_4 and β- Si_3N_4 of RBSN samples

Starting Si Powder size (μm)	α-Si_3N_4 (%)	β- Si_3N_4 (%)
3	90	10
6	86	14
12	83	17

Table 3 shows the amount of phases present in the microstructure of RBSN samples obtained from Table 2. and Figure 2. The smaller the starting Si powder size was the higher α/β Si_3N_4 ratio. This is due to the surface area effect. The most fundamental difference between the mechanism that lead to the formation of the alpha and the beta phases is that the former results from reaction of silicon with molecular nitrogen, and the latter forms when silicon reaction with active nitrogen that may be atomic nitrogen[5]. The role of particle size or surface area is interlinked with the other reaction variables. Because even small amount of oxygen can remove active nitrogen as shown in reaction 1 and 2, most surface reaction will produce α-Si_3N_4. The initial product will influence later product and therefore high surface area (small particle size) will generally imply high α/β Si_3N_4 ratio. Also, high surface area will mean that a high percentage of products will be formed before unreacted silicon is sealed from the nitrogen,[5].

$$N + O_2 \rightarrow NO + O \qquad [1]$$
$$N + NO \rightarrow N_2 + O \ : \Delta H^{o}_{298} = -313 \text{ kJ} \qquad [2]$$

The molecule of nitrogen promoted α-Si_3N_4 phase, which the nitrogen promoted β-Si_3N_4 phase instead. Therefore, α-Si_3N_4 was formed at surface area where the reaction occurred. This resulted in increasing in of α/βratio[5]. The previous work[6]has recently found that α-Si_3N_4 and β- Si_3N_4 can be formed in any size of powder. However, the ratio of β/(α+β) depends on the powder size. Samples produced from the large particle size have higher transformation rate of α-Si_3N_4 to β-Si_3N_4 compared with the samples produced from the smaller particle size. This is because in large particle size there is a small amount of silica covering the surface and the distribution of additive is likely to be more heterogeneous than in the small particle size sample. As a result, liquid phase is formed and increasing the amount of β-Si_3N_4.

Table 4. Physical properties of Preform and RBSN bodies from different raw Si powder size.

Particle size (μm)	Preform Bulk density (g/cm^3)		RBSN Bulk density, (g/cm^3)		RBSN Porosity (%)	Number of samples
	ρ	STD.	ρ	STD.		
12	1.58	.0230	2.18	.0995	21.30	10
6	1.60	.0088	2.38	.0026	14.08	10
3	1.60	.0073	2.61	.0316	5.78	10

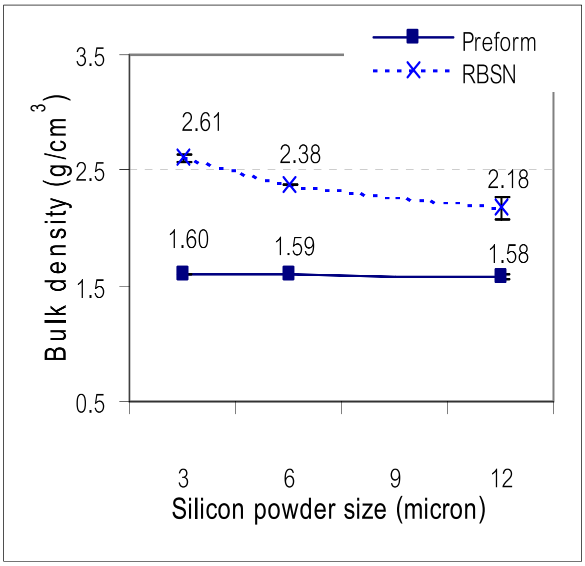


Figure 3. Effects of silicon powder size on bulk density

- Density

Table 4. and Figure 3. show the effect of the raw silicon powder size on the bulk densities of the preform body and the RBSN specimen. As the silicon powder size decrease, the bulk densities of both preform body and RBSN sample increase. This is due to smaller particle size has higher surface area and higher driving forces for sintering. Effect of smaller particle size on the increasing bulk density in preform body is less comparing to the RBSN sample. In the preform body, density increases only by sintering or diffusion and the diffusion rate is low because of the relatively low sintering temperature. In the RBSN sample, density not only increases by diffusion but also by nitriding reaction and the later has more effect. Finer Si powder provides more surface area for nitridation and shorter diffusion path to complete the reaction.

- Mechanical properties

Table 5. Mechanical properties of Preform bodies from different raw Si powder size.

Particle size (μm)	Young's Modulus, E (GPa)		Flexural strength (MPa)		Vickers Hardness (HV)		Number of samples
	E	STD	σ	STD.	HV	STD.	
12	9.45	0.91	22.05	5.55	98.03	6.74	5
6	20.75	.051	32.12	2.19	137.94	11.98	5
3	25.66	0.84	42.33	6.88	167.18	11.21	5

Table 6. Mechanical properties of RBSN bodies from different raw Si powder size.

Particle size (μm)	Young's Modulus, (GPa)		Flexural strength, (MPa)		Vickers Hardness, (HV)		Number of samples
	E	STD.	σ	STD.	HV	STD.	
12	121.64	5.92	104.03	16.12	403.24	74.18	5
6	145.66	9.39	147.50	11.01	680.47	136.16	5
3	198.63	3.45	250.79	33.52	971.06	141.04	5

Mechanical properties of preform bodies and RBSN bodies are listed in Table 5 and Table 6, respectively. The Young's modulus, flexural strength and hardness of both preform and RBSN samples are increased with decreasing Si raw powder size.

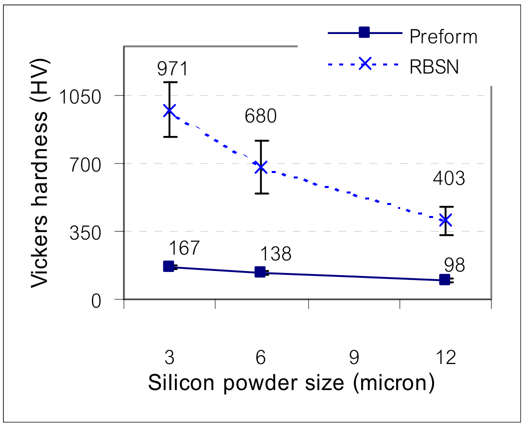


Figure 4. Effects of silicon powder size on hardness of Preform and RBSN samples.

Figure 4. shows the effect of Si powder size on the Vickers hardness test. It is clearly shown that hardness of silicon nitride samples decreased with increasing particle size. This is because the fine powder produced the denser preform and RBSN samples. It should be noted that the powder size has more significant effect on hardness for the RBSN samples compared with the preform samples. This is due to finer particle size has much more effect on the density of RBSN sample than preform samples as mention in the previous section. Apart from the denser samples, it also found that α-Si_3N_4 phase presented in the RBSN samples gives higher hardness than that of β-Si_3N_4 phase.

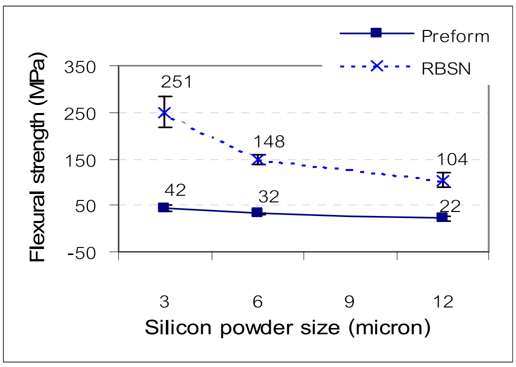


Figure 5. Effects of silicon powder size on flexural strength of Preform and RBSN samples.

The relationship between flexural strength (σ) and percentage of porosity can be expressed in equation 3[(7)].

$$\sigma = \sigma_0 \exp(-nP) \qquad [3]$$

where σ_0 and n are constant and P is the volume fraction of porosity of sample. The result from this experiment shown in Figure 6 agrees with the relationship in equation 3.3, where the flexural strength exponentially decreases with percentage of porosity. σ_0 and n in this experiment which give the R^2 of 0.9971 are 378.28 MPa and 4.37 respectively.

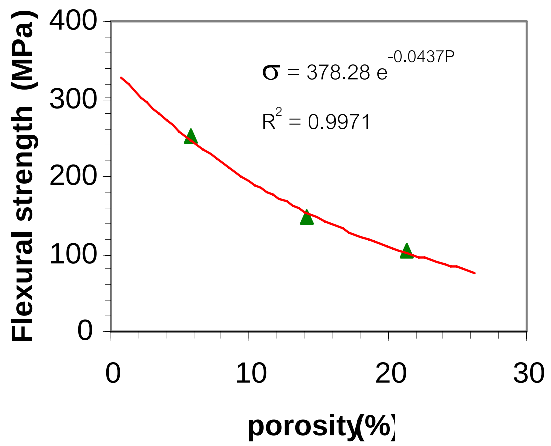


Figure 6. Flexural Strength versus percentage of porosity of RBSN samples

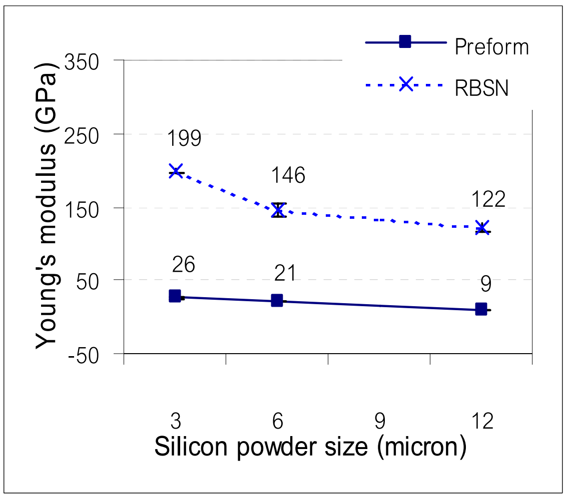


Figure 7. Young's modulus of Preform and RBSN samples at various powder size

Young's modulus versus silicon powder size is plotted in Figure 7. The results show that Young's modulus reduces with increasing powder size. The perform samples has a very low Young's modulus of approximately 9-26 GPa while RBSN samples has a much higher Young's modulus of 122-199 GPa.

The relationship between Young's modulus and percentage of porosity can be expressed in equation 4(7). [William, 1994]

$$E = E_o (1-1.9 P + 0.9 P^2) \qquad [4]$$

where E_o is modulus of elasticity of the non-porous material and P is the volume fraction of porosity of sample. From equation 3.4 RBSN samples has very high density resulting in high Young's Modulus value. The more amounts of porosities, the lower the Young's Modulus values.

Conclusions

In the processing of RBSN, smaller raw Si powder size will lead to the following results:

1. higher density or lesser porosity in both preform and RBSN samples.
2. higher α/β Si_3N_4 ratio in RBSN samples.
3. higher hardness, flexural strength, and Young's modulus in both preform and RBSN samples.

RBSN with high flexural strength of 251 MPa can be made from the raw Si powder having the average particle size of 3 μm.

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