The effect of silicon purity on the strength of reaction-bonded Si_3N_4

Reaction-bonded Si_3N_4 (RBSN) is being considered for a wide variety of important high-performance applications, among them being structural components for gas turbine engines [1], turbocharger rotors [2], and various diesel engine components [3]. All of these applications require a material possessing both high strength and high Weibull modulus. In order to improve the strength and Weibull modulus, the strength-controlling defect must be identified and characterized. Various investigators have studied this problem with the consensus of opinion being that porosity, due to voids in the green compact or caused by the melting of silicon particles during nitridation, is the strength-determining factor in RBSN [4, 5]. Moulson [6], in his review article, summarizes the above mentioned defect mechanisms and also points out another type of critical defect. This defect is caused by the presence of iron impurities in the RBSN and the tendency of this defect to increase in size as the iron reacts with silicon to form iron silicides during the nitriding process. This author's experience has shown that in low-density RBSN and RBSN produced using temperature-controlled nitriding cycles, the critical defect was internal porosity [7]. However, the use of improved nitriding techniques, such as the nitrogen demand nitriding cycle and nitriding atmospheres of hydrogen–nitrogen mixtures, dramatically reduced the pore size of the RBSN [8]. It was found that the strength of this grade of RBSN was no longer governed by porosity, but rather by the presence of iron–chromium silicide inclusions [9]. These inclusions were assumed to be the result of impurities in the starting silicon powder.

This work will compare the room-temperature strength properties of RBSN produced from two different grades of silicon powder; one being an industrial grade and the other being a high-purity grade. It will show the beneficial effect of using high-purity silicon in the production of reaction-bonded Si_3N_4.

Two grades of silicon were procured from the Union Carbide Company (Niagara Falls, New York). One type of silicon was marketed as a metallurgical grade, having a nominal purity of 98% and a particle size of minus 325 mesh. This material was dry ball milled, using Burundum ball mills and media and analysed for impurities (Table I). (This material has been completely characterized in [10]). The other was a "high-purity" grade of silicon. Its analysis is also given in Table I. As noted, the overall purity is greatly improved, especially with regard to iron, aluminium, and manganese, the major impurities in the metallurgical grade.

The two grades of silicon were processed into test samples (3.1 mm × 6.3 mm × 38.0 mm). The silicon and a nitriding aid (reagent grade Fe_2O_3) were mixed together with a thermoplastic, organic binder. Samples were injection-moulded, and processed through binder burnout and nitriding.

The nitridings were performed, using a "nitrogen demand" nitriding cycle [8] along with a nitriding atmosphere composed of hydrogen/helium/nitrogen [10]. The "nitrogen demand" nitriding cycle allows the temperature of the nitriding reaction to slowly be increased to 1400° C at a rate determined by the nitriding load. At the same time, it allows the nitriding atmosphere to change dynamically during the course of the nitriding process, thereby controlling the nitriding rate and the nitriding exotherm.

The strength of the RBSN was determined in four-point bending, with fixture dimensions of 9.5 mm top span and 19.0 mm bottom span. The samples were tested with the surfaces in the as-nitrided condition. The fracture origin of each

TABLE I Impurity characterization of silicon powders* (wt %)

	Fe	Al	Ca	Mn	Ni	Cr	Mg	O_2†
Metallurgical grade	0.60/0.80	0.25	0.02–0.05	0.18	0.02	0.03–0.06	0.03	0.75
High-purity grade	0.10	0.02	0.01	0.01	0.005	0.01	0.002	0.5

*Cation impurities determined by emission spectroscopy.
†Determined by inert gas fusion technique.

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TABLE II Strength results

	Characteristic strength*	Weibull modulus	Number of samples
Normal RBSN	302 MPa	7.8	22
High-purity RBSN	345 MPa	9.2	50
% change†	+ 14.6%		
(90% confidence)	(+ 6.8 to 21.9%)	None	–

*Calculated using a maximum likelihood estimator technique [13].
†Calculated using hypothesis tests based on the Weibull distribution [14].

specimen was determined. A number of the origins were studied and analysed, using a SEM equipped with a non-dispersive X-ray analyser.

The strength results from these two RBSN materials are presented in Table II. They show that the strength of the high-purity RBSN (high-purity silicon) was 345 MPa, while the strength of the normal RBSN (metallurgical grade silicon) was 302 MPa. The strength of the high-purity RBSN was statistically found to be 14.6% higher than the normal RBSN (this increase was 6.8% to 21.9% based on a 90% confidence band). The Weibull modulus of the high-purity grade was 9.2, compared to a value of 7.8 for the normal grade. This increase, however, was not found to be statistically significant at the 90% confidence level.

The two materials were characterized with respect to density, degree of nitridation and phase composition (Table III) and were found to be identical. The difference between the two materials was found to be in the nature of the fracture origins. The fracture origins in the normal RBSN were found to be primarily inclusions composed of high concentrations of iron and chromium with an equal amount of silicon (Fig. 1). These inclusions varied in size from 60 to 130 μm and they were generally located at a depth of between 100 and 200 μm below the tensile surface. The fracture origins in the high-purity RBSN were less defined. They were often composed of low-density areas (Fig. 2a), and they often occurred at the tensile surface (Fig. 2b). However, none of the samples evaluated were found to have inclusions at the fracture origins. The composition of these origins was always the same as the surrounding matrix. The major element found was silicon with a trace of iron (assumed to be from the even distribution of the iron oxide nitriding aid).

The formation of the iron and chromium

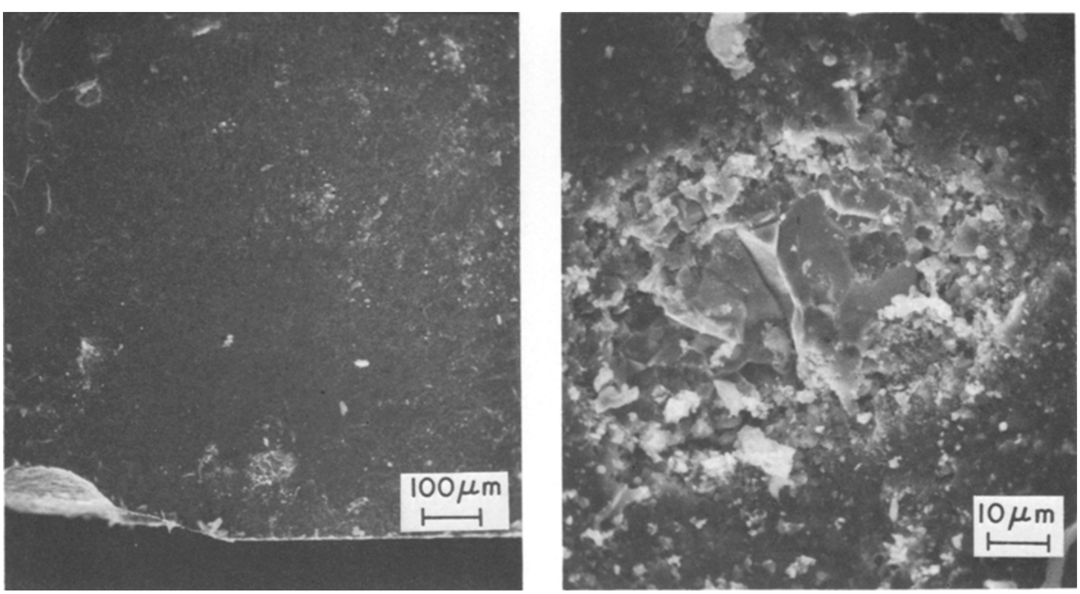

Figure 1 Typical inclusion found at the fracture origin of the normal RBSN. Analysed to be Fe, Cr, Si.

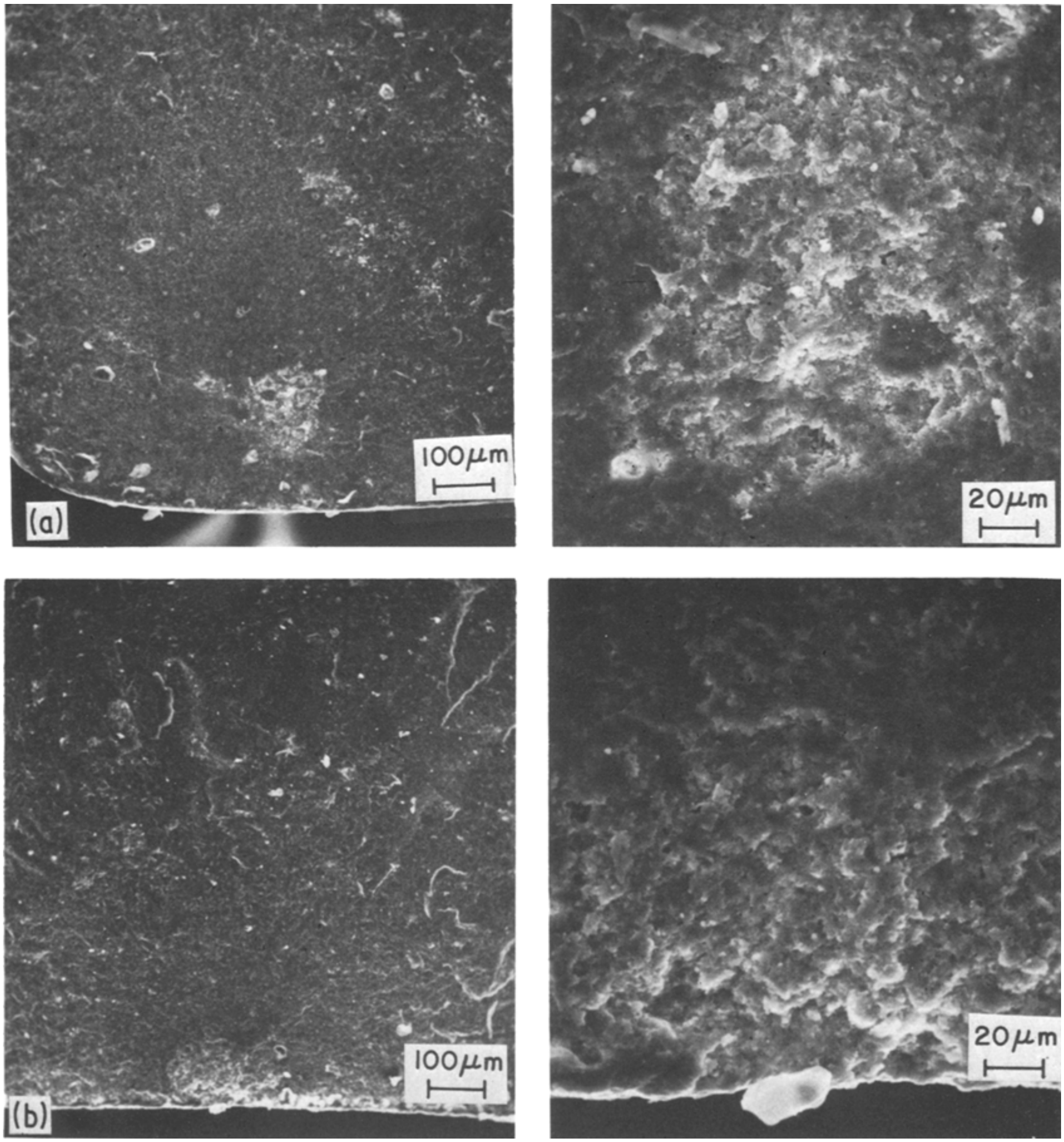

Figure 2 (a) Low-density area at the fracture origin of the high-purity RBSN. Analysed to be Si with a trace of Fe. (b) Tensile surface origin in the high-purity RBSN.

silicide inclusions could occur during the nitriding reaction. Iron will react with silicon to form a series of iron silicides, with FeSi being formed at about 1210° C, while chromium silicide forms at about 1335° C [11]. Both are well within the range of nitriding temperatures. However, the silicides could also have been present in the silicon. It has been estimated that up to two thirds of the iron impurity in the normal grade silicon could have been present in the form of silicides [12]. Iron oxide was added to both materials. However, this was added in the form of fine powder. The iron was found to be uniformly distributed and probably does not affect the quality of the RBSN.

The high-purity silicon contained little iron and chromium and no silicides. The high-purity silicon also was processed using an addition of 2.5 wt% iron oxide as a nitriding aid, as was the normal

TABLE III Characterization of nitrided test specimens

	Density ($g\,cm^{-3}$)	% nitrided*	Phase composition		
			% α-Si_3N_4	% β-Si_3N_4	% Si†
Normal RBSN	2.7	99	75	25	0
High-purity RBSN	2.7	99	75	25	0

*Based on weight gain data, corrected for residuals from binder burnout and the amount of nitriding aid and impurity composition.
†Weight percentages.

grade, but no iron silicide inclusions were observed. The high-purity RBSN was processed, using equipment identical to that used to process the normal grade, and no contamination was observed. It must, therefore, be concluded that the starting silicon powder was the source for the silicide inclusions, which were the strength-limiting flaws in the normal grade RBSN. By improving the quality of the silicon powder used to produce reaction-bonded Si_3N_4, the quality of the RBSN can also be significantly improved.

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