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Reaction sintered silicon nitride

Part 2 *The influence of nitrogen gas flow on strength and strength/density relationships*

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The development of strength in reaction sintered silicon nitride has been studied in a "flow" nitriding system, and it has been shown that material produced under "flow" conditions is notably weaker than material produced under "static" conditions at all degrees of conversion. It is suggested that abnormally low strengths in nominally "static" experiments may be the result of unsuspected gas "flow". The literature data on strength are discussed in the light of these observations.

1. Introduction

Reaction sintered (or reaction bonded) silicon nitride is a promising material for applications in high temperature engineering [1]. A problem associated with current fabrication of the material, however, is the inexplicable occurrence of occasional batches of material having much lower strength than is normally attainable [2]. Whilst such batches are easily detectable, the loss of a large furnace charge of accurately machined components can be costly.

Reaction sintered silicon nitride is prepared by heating silicon powder compacts in a nitrogen atmosphere to temperatures in the range 1200 to 1450° C. In one type of furnace system (Fig. 1a), nitrogen is maintained at a pressure slightly above atmospheric and enters the furnace at the same rate as the consumption of nitrogen by the silicon compacts undergoing conversion. For convenience this is termed a "static" system and is normally used at this laboratory and frequently by commercial producers of silicon nitride. In the second commonly used system (Fig. 1b) nitrogen flows continuously past the silicon compacts. The "flow" furnace is often favoured in laboratory studies because it is informative to analyse entry and exit gases.

In the preceding paper, the influence of gaseous impurities in the nitrogen on the structure and properties of silicon nitride is reported for both "static" and "flow" systems [3]. The particular experimental system seemed to exert a great influence on the properties of the material formed: for example, strengths from "flow" experiments were some 30% lower than strengths from the "static" experiments. We have, therefore, studied the development of strength in silicon nitride formed under "flow" conditions and, using strength/nitrided density and strength/weight gain relationships [4–7], compared the data with recent "static" results in an attempt to interpret the variable strength data published in the literature.

2. Experimental

Details of the two powders studied, designated B and C in keeping with a previous publication [5], are summarized in Table I. Batches of each powder were isostatically pressed at 31, 92 and 185 MN m^{-2} and heated for 5 h at 1175° C in argon to form low green density (lgd), intermediate green density (igd) and high green density (hgd) compacts, respectively. Test bars 4.57 × 4.57 × 30 mm^3 were machined from the compacts [4] and at least three bars were selected randomly

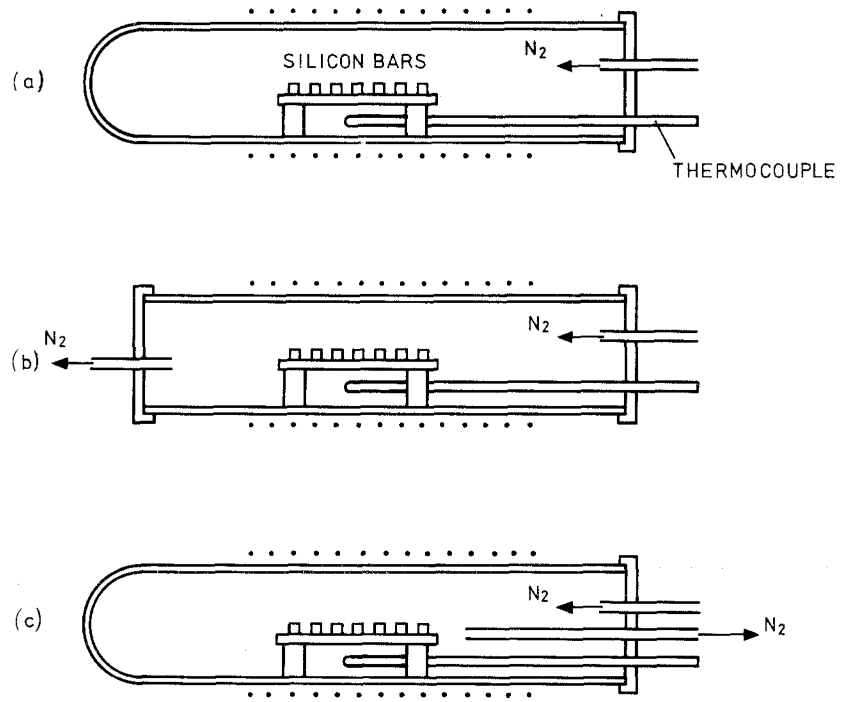

Figure 1 "Static" and "flow" nitriding systems.

TABLE 1 Properties of starting silicon powders

Properties	Powder B	Powder C
Median particle size* (μm)	6	25
Max particle size* (μm)	40	75
Specific surface area† ($m^2 g^{-1}$)	2.7	0.7
Impurity content (wt %)		
Iron	0.74	0.65
Aluminium	0.78	0.28
Calcium	0.28	0.27
Titanium	0.06	0.06
Other cations	<0.02	<0.01
Oxygen	2.5	0.5

*Particle sizes measured by Coulter Counter.
†Specific surface areas by the BET method.

from each compact for all nitriding experiments. The test bars were nitrided in a closed end mullite tube (capacity ~ 3 litres) at temperatures in the range 1300 to 1375° C on silicon nitride trays using a gas "flow" system of the type illustrated in Fig. 1c. This system approximates that of Fig. 1b although the exact gas flow characteristics will be significantly different. The alumina exhaust tube in Fig. 1c was 50 mm from the specimen tray to induce substantial gas "flow" in the region of the specimens. The gas pressure was maintained at about 7 kN m^{-2} above atmospheric, but allowed to flow from the furnace at a rate of 100 ml min^{-1} in seven nitriding experiments but at only 10 ml min^{-1} in an eighth. The nitrogen gas contained a maximum concentration of 7×10^{-6} volumes oxygen per unit volume and $\sim 3.5 \times 10^{-5}$ volumes of water vapour per unit volume. The contents of the furnace, weight and type of silicon, were nominally identical for all experiments although in some cases roughly shaped bars were used in place of accurately machined specimens. The densities of the bars were determined from their weights and dimensions before and after each experiment and strengths were determined in the as-nitrided condition in three-point bend with a span of 19.05 mm.

3. Results

Table II shows the nitriding schedules, green and nitrided densities, weight gains and strengths for bars nitrided with gas flow rates of 100 and 10 ml min^{-1}. In general, for each powder, hgd bars show lower weight gains than igd bars which in turn are lower than lgd bars. Compacts of powder B show higher weight gains for equivalent nitriding schedules than compacts from powder C. The weight gains under "flow" conditions are considerably lower than those recorded using the same

TABLE II Green density, nitrided density, weight gain and strength after various nitriding schedules of silicon compacts prepared in flowing nitrogen

Expt. schedule	Nitrogen flow (ml min^{-1})	Powder	Compact	Green density (Mg m^{-3})	Nitrided density (Mg m^{-3})	Weight gain (%)	Mean strength (MN m^{-2})
(1)	100	B	lgd	1.24	1.62	30.7 ± 1.2	32 ± 3
5 h 1300° C			igd	1.33	1.73	30.4 ± 0.7	36 ± 2
			hgd	1.40	1.81	29.3 ± 0.8	48 ± 1
		C	lgd	1.34	1.40	4.6 ± 0.3	5 ± 1
			igd	1.48	1.54	4.2 ± 0.2	13 ± 2
			hgd	1.57	1.63	4.4 ± 0.2	22 ± 4
(2)	100	B	lgd	1.25	1.90	51.7 ± 1.8	74 ± 5
5 h 1330° C			igd	1.33	2.01	51.0 ± 0.6	86 ± 7
			hgd	1.41	2.10	49.2 ± 0.7	99 ± 5
		C	lgd	1.34	1.45	8.3 ± 1.1	9 ± 1
			igd	1.49	1.61	8.1 ± 0.6	16 ± 2
			hgd	1.56	1.67	6.8 ± 0.3	25 ± 1
(3)	100	B	hgd	1.40	2.24	60.1 ± 0.3	154 ± 9
15 h 1350° C		C	hgd	1.57	2.13	35.5 ± 1.9	89 ± 12
(4)	100	B	lgd	1.25	2.00	59.6 ± 2.3	73 ± 10
15 h 1360° C			igd	1.33	2.13	60.2 ± 1.2	110 ± 8
			hgd	1.40	2.25	60.1 ± 1.0	139 ± 7
		C	lgd	1.35	2.17	60.1 ± 1.9	85 ± 5
			igd	1.47	2.34	58.6 ± 0.4	108 ± 11
			hgd	1.58	2.47	56.5 ± 0.8	151 ± 6
(5)	100	B	hgd	1.40	2.25	60.2 ± 0.4	146 ± 6
15 h 1375° C		C	hgd	1.57	2.50	59.2 ± 0.8	144 ± 17
(6)	100	B	hgd	1.40	Rough bars – no data		
10 h 1350° C		C	hgd	1.56	2.09	33.9 ± 1.7	59 ± 12
(7)		B	hgd	1.40	Rough bars – no data		
15 h 1375° C	100	C	hgd	1.57	2.48	58.9 ± 0.6	125 ± 8
(8)		B	hgd	1.41	2.23	58.1 ± 0.3	150 ± 8
15 h 1350° C	10	C	hgd	1.58	1.77	12.0 ± 0.8	51 ± 4

TABLE III Strength/nitrided density relationships

Powder	Reference	Nitriding conditions	Linear regression	Correlation coefficient r
B	This work	Flow	$\bar{\sigma} = 193\rho_n - 296$	0.970
B	[5]	Static	$\bar{\sigma} = 211\rho_n - 260$	0.952
C	This work	Flow	$\bar{\sigma} = 127\rho_n - 183$	0.980
C	[6]	Static	$\bar{\sigma} = 178\rho_n - 228$	0.919

temperature schedules but "static" gas conditions [4, 5].

The strength/nitrided density data for bars prepared from powder B are plotted in Fig. 2, together with data for bars prepared from powder B nitrided under "static" conditions [5]. Fig. 3 shows similar information for bars prepared from powder C. Straight lines have been fitted to these data by the method of least squares and the relevant equations and correlation coefficients are shown in Table III. For both powders there are significantly different strength/nitrided density

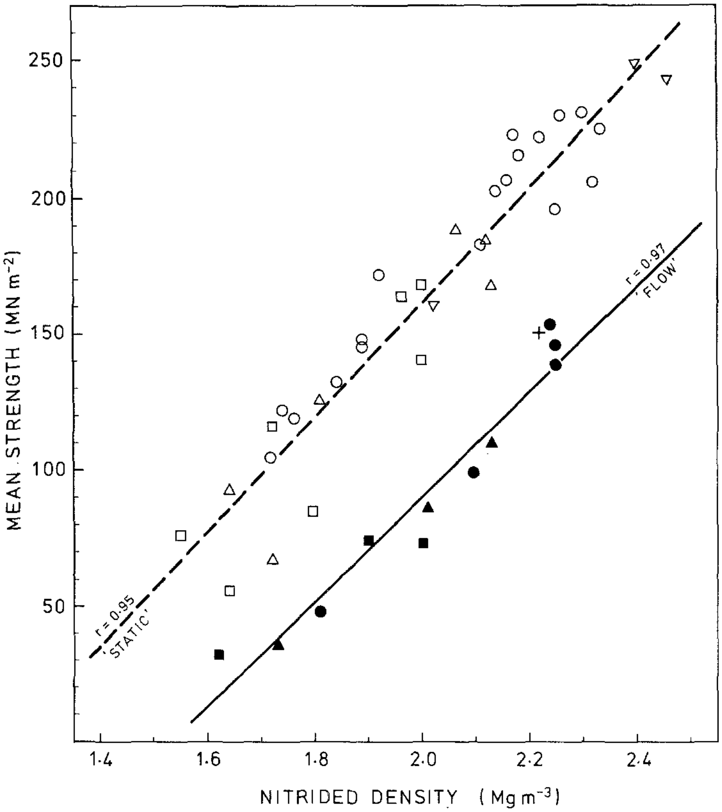

Figure 2 Mean strength versus nitrided density for compacts of powder B. Open symbols represent compacts nitrided under "static" conditions [5]. Closed symbols represent compacts nitrided under "flow" conditions at a flow rate of 100 ml m^{-1}. Straight lines are linear regressions and r is the correlation coefficient. □ ■ "lgd" compacts; △ ▲ "igd" compacts; ○ ● "hgd" compacts; ▽ compacts pressed at 400 MN m^{-2}; + "hgd" compact nitrided at a flow rate of 10 ml min^{-1}.

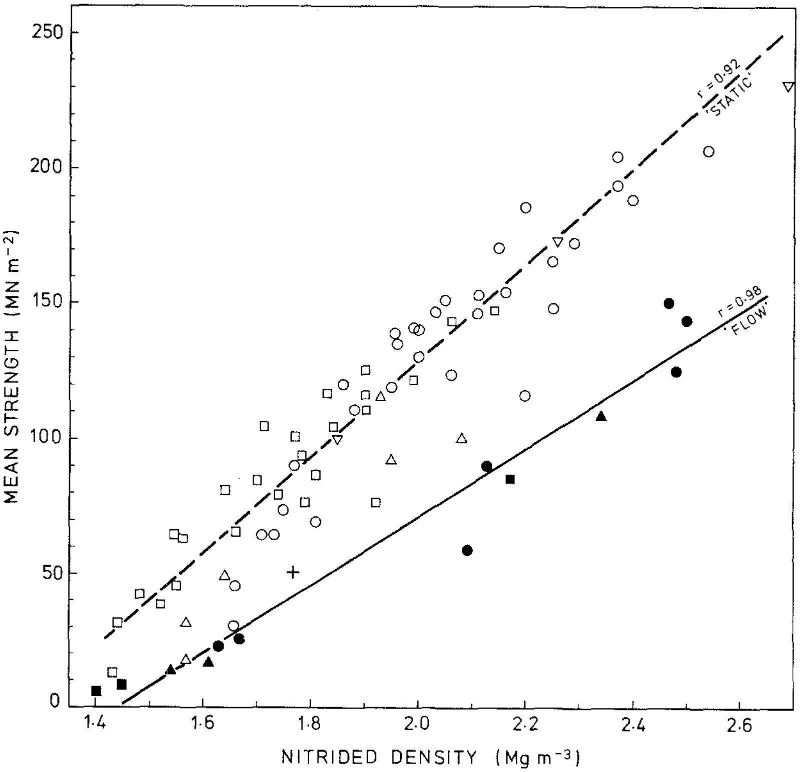

Figure 3 Mean strength versus nitrided density for compacts of powder C. Open symbols represent compacts nitrided under "static" conditions [6]. Other details equivalent to key in Fig. 2.

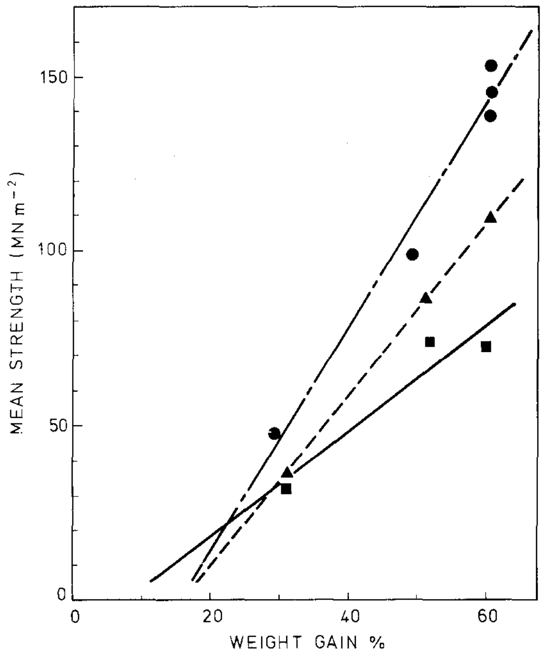

Figure 4 Mean strength versus weight gain for compacts of powder B. ■ "lgd" compacts; ▲ "igd" compacts; ● "hgd" compacts.

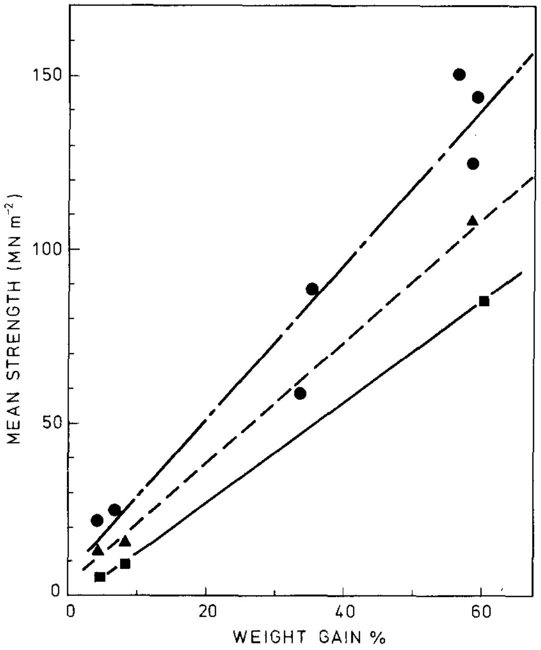

Figure 5 Mean strength versus weight gain for compacts of powder C. Key as for Fig. 4.

relationships for "static" and "flow" conditions: at a particular nitrided density "flow" conditions produce a weaker material than "static" conditions.

Figs. 4 and 5 show strength versus weight gain data for powders B and C respectively. At equivalent weight gains, strengths from "flow" experiments are considerably lower than strengths from "static" experiments [4, 5]. It is noted, however, that there is still a trend of steeper strength weight gain lines for higher green density bars.

4. Discussion

4.1. General observations

The data show that the difference in the relationships between strength and nitrided density for "static" and "flow" conditions is accompanied by a change in the rate of the reaction. The extremely slow rates of conversion in "flow" experiments are outside the range of scatter of the conversion rates in "static" experiments [4]. Attention is also drawn to the strength/weight gain relationships shown in Fig. 4, and the fact that compacts of powder B apparently show no significant improvements in strength until a weight gain of greater than 10% is achieved.

X-ray diffraction data have shown higher proportions of β-silicon nitride in materials prepared from both powders under "flow" conditions, consistent with the data for powder C reported in the preceding paper. A detailed analysis of the structure and composition of these materials will be presented elsewhere [8].

It is interesting to speculate on the implications of these observations in terms of the nitriding process. It is likely that gas "flow" will modify the removal of surface silica from the silicon at an early stage in the reaction as well as influencing the conversion of silicon to silicon nitride in a more direct manner by modifying the gas composition in the region of the reacting test bars. That gas flow can have such an influence on the properties of reaction sintered silicon nitride is of importance in the planning of research into the mechanisms of nitridation because, whilst "static" systems are more economical for commercial production, "flow" systems are generally preferred in research studies. It is, therefore, important that the reasons for the observed differences between the two types of system are understood.

4.2. Variations in strength/density relationships

It has been suggested that, for a particular powder, small changes in "static" nitriding conditions can produce a change in the strength/nitrided density relationship [6]. It is noted that the lower bound line of Fig. 1 of [6] lies close to the "flow" line in Fig. 3 of this paper. It is probable that gas turbulence or "flow" in a nominally "static" experiment (e.g. as a result of a leak) could produce the observed discrepancies since it has been shown [3] that the chemical contamination effects of a leak (e.g. increasing the oxygen or water vapour content of the nitriding gas) are relatively unimportant. In our laboratory the furnace is evacuated to 10^{-6} bar to test for leaks. During nitriding the furnace tube operates under a slight excess pressure (7 kN m^{-2}) so that newly developed small leaks would not be detected and have hitherto been considered unimportant. Another potential leak could occur through the alumina thermocouple sheath which extends into the hot zone (see Fig. 1), since these become permeable with age. Experiment 8 (Table II) indicates that even very slow flow rates (10 ml min^{-1}) can have a large effect on the properties of the silicon nitride produced.

It was suggested in [6] that the presence of compacts of fine silicon powders in the nitriding furnace may have been the cause of different strength/nitrided density relationships for the two groups of experiments performed under "static" conditions. A large quantity of fine powder would effectively increase the flow rate of nitrogen into the furnace since fine powders react more rapidly than coarse powders.

4.3. Reassessment of the literature

In the light of the above observations it is of interest to examine the strength values of reaction sintered silicon nitride that have been reported in the literature. The occurrence of occasional low strength batches of material at this laboratory [2] may be attributed to "flow" conditions which result from small leaks or are caused by a large volume of silicon in the furnace (Section 4.2). Messier and Wong [9] have recently compared their own strength data with that in the literature and conclude that the particle size of the silicon powders used is the main factor influencing strength. Whilst particle size is an important factor [5] it appears that nitriding conditions are probably more important in many cases. The strength of 160 MN m^{-2} reported by Messier and Wong [9] for a powder of 37 μm maximum particle size, nitrided to a density of 2.48 to 2.49 Mg m^{-3} is low compared to our strength data (see Table IV). For strict comparison we must make a correction of between 13% [2] and 20% [10] for the fact that Messier and Wong used a four-point bend test, so their strength lies in the range 180 to 192 MN m^{-2} in terms of a three-point bend test. Our powder B is similar to Messier and Wong's powder since it has a maximum particle size of 40 μm. However, Fig. 2 shows that silicon nitride prepared from this powder nitrided to a density of 2.50 Mg m^{-3} under "static" conditions should have a strength of about 270 MN m^{-2} [5]. Even the coarse powder C with a maximum particle size of 70 μm results in a material with a strength of 220 MN m^{-2} when nitrided to a density of 2.50 Mg m^{-3} under "static" conditions (Fig. 3) [4]. It is noted, however, that Messier and Wong [9] perform their experiments under "flow" conditions and comparison of our

TABLE IV Comparison of recent strength data for reaction sintered silicon nitride

Source	Powder particle size (μm)		System	Density (Mg m^{-3})	Strength (MN m^{-2})
	mean	max			
Present data	6	40	Flow	2.35	155†
	6	40	Flow	2.50	185†
Messier and Wong [9]	-	37	Flow	2.48–2.49	180–192*
Jones and Lindley [5]	6	40	Static	2.35	235†
	6	40	Static	2.50	270†
	6	40	Static	2.61	300†
Jones and Lindley [4]	25	70	Static	2.50	220†
	25	70	Static	2.63	240†
Dalgleish and Pratt [11]	3	25	Flow	2.35	165
	3	25	Flow	2.61	292
	8	64	Flow	2.63	247

*Strength converted from four-point to three-point bend values.
†Strengths extracted from strength/density relationships.

"flow" data indicates a strength of 185 MN m^{-2} at a density of 2.50 Mg m^{-3} for powder B (Fig. 2). This strength is in close agreement with the data of Messier and Wong and suggests that the influence of nitriding conditions have outweighed the importance of particle size in their comparisons.

Dalgleish and Pratt [11] discuss the importance of silicon particle size, compaction pressure and nitriding schedule on the fracture strength of silicon nitride prepared in "a stream" of purified nitrogen. Table IV includes those materials which they describe as produced predominantly at low temperature i.e. where silicon melting has been minimized. Their results are compatible with the influence of nitriding conditions discussed above. For example, our finest powder (6 μm mean particle size) compacted and nitrided under "flow" conditions to a density of 2.35 Mg m^{-3} exhibits a strength of 155 MN m^{-2} which is slightly lower than the value of 165 MN m^{-2} for their finer powder (3 μm mean particle size) nitrided to the same density. The information in Table IV shows that, despite the use of a coarser silicon powder, we should be able to produce a slightly stronger material at a density of 2.61 Mg m^{-3} (300 MN m^{-2} compared to 292 MN m^{-2}) by using "static" rather than "flow" nitriding systems. It is suggested that if compacts of the type produced by Dalgleish and Pratt were nitrided under "static" rather than "flow" conditions, strengths in excess of 350 MN m^{-2} might be achieved. Although other workers do not provide details of their nitriding process it is suspected that differences in nitriding conditions account for many of the observed variations in strength.

Evans and Davidge [12] have shown that defects resulting in low strength can occur when large silicon particles melt during nitriding. This type of defect can be eliminated as the cause of low strength in our "flow" experiments because the bars were nitrided at temperatures well below the melting point of silicon (~1420° C). This observation, together with the fact that our data indicate that compacts of powder C nitrided for 50 h at 1350° C in flowing high purity nitrogen will be almost completely converted to silicon nitride, allows us to be sure that the melting of silicon was not the cause of the low strengths recorded for material produced under "flow" in nitrogen containing 5 x 10^{-6} volumes of oxygen per unit volume in the preceding paper [3]. Messier and Wong [9] and Dalgleish and Pratt [11] both discuss the conditions under which strength is controlled by defects caused by the melting of silicon particles when significant nitride formation occurs above the melting point of silicon. It is likely, however, that these conditions will be different in "flow" and "static" experiments since reaction rates are significantly changed and interparticle void sizes are probably different due to changes in the reaction mechanism.

5. Conclusions

(1) The flow of nitrogen gas around silicon compacts during nitriding has been shown to have a significant influence on the strength of the resulting reaction sintered silicon nitride. Under "flow" conditions silicon reacts more slowly and the resulting silicon nitride is notably weaker than material produced under "static" conditions at all equivalent degrees of conversion.

(2) Unsuspected gas "flow" in nominally "static" experiments may be a reason for lower than normal strengths in reaction sintered silicon nitride.

(3) The variable strength data in the literature for silicon nitride can be explained in many instances in terms of the detail of the particular nitriding processes which in most cases outweighs the influence of changes in the particle size of the silicon.

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