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Strength, density, nitrogen weight gain relationships for reaction sintered silicon nitride

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Linear relationships between mean strength and nitrogen weight gain are established for isostatically pressed silicon compacts nitrided to weight gains of less than 60%. For a particular silicon powder the relationship depends upon the isostatic pressure used in compact fabrication, i.e. the green density. A linear relationship between mean strength and nitrided density is also demonstrated and this is independent of green density for the particular compacts studied. The implications of these relationships are discussed and their potential value for developing high strength reaction sintered silicon nitride explained.

1. Introduction

Reaction sintered silicon nitride is an outstanding candidate ceramic for use in high temperature engineering [1]. An essential requirement of a material for such applications is that it can be fabricated in a reliable and reproducible manner to high strengths with a low strength variability. Reaction sintered silicon nitride is usually formed by heating silicon powder compacts in a nitrogen atmosphere at temperatures in excess of 1300°C for several hours, the aim of such processing being to produce a high conversion of silicon to silicon nitride. It has been our experience and that of other workers [2, 3] that the reaction kinetics for such nitriding experiments are extremely difficult to control, even in high quality laboratory experiments. These differences in nitriding kinetics can in some instances be attributed to variable low levels of cation impurities such as iron [2] and iron compounds, and nitriding atmosphere impurities such as oxygen [3]. It has also been reported that nominally identical nitriding of nominally identical silicon compacts can result in differing degrees of silicon to silicon nitride conversion [4]: reaction sintered silicon nitride materials from other sources have also shown this variable degree of conversion.

It is the purpose of this paper to show that despite the difficulty of controlling the reaction kinetics during silicon nitride formation, there are exact relationships between strength, nitrogen weight gain and nitrided density for partially reacted silicon compacts. These relationships may well prove useful as an aid to understanding the development of strength in reaction sintered silicon nitride.

2. Experimental

Silicon powder of 98% purity was sieved to remove particles greater than 75 μm diameter, the resulting powder having a mean equivalent spherical particle diameter as determined by Coulter Counter of about 25 μm and a specific surface area of approximately 0.7 m^2 g^{-1} measured by the BET method. Batches of this powder were isostatically pressed at 185 or 31 MN m^{-2} to produce high green density (hgd) or low green density (lgd) compacts, respectively. These compacts were heated in argon for 5 h at 1175°C and test bars 4.57 × 4.57 × 30 mm^3 subsequently machined from the compacts using a 46 grit alumina cup grinding wheel. The bars were nitrided at temperatures in the range 1200 to 1350°C on silicon nitride trays in a vacuum-tight mullite furnace tube. The nitrogen gas contained a maximum of 7 vpm* of oxygen and was dried over phosphorus pentoxide. The

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*Volumes per million.

TABLE I Green density, nitrided (final) density, weight gain and strength after various nitriding schedules for silicon compacts isostatically pressed at 185 MN m^{-2} (hgd) or 31 MN m^{-2} (lgd) (standard deviations are shown in brackets)

Experiment	Nominal nitriding schedule		Number of bars		Green density (Mg m^{-3})		Nitrided density (Mg m^{-3})		Weight gain (%)		Strength (MN m^{-2})	
	(h)	(°C)	"hgd"	"lgd"	"hgd"	"lgd"	"hgd"	"lgd"	"hgd"	"lgd"	"hgd"	"lgd"
1	5	1200	3	6	1.56	1.33	1.95	1.74	25.0 (0.6)	30.7 (0.8)	119 (3)	79 (7)
2	5	1200	4	8	1.57	1.32	1.88	1.64	19.9 (0.4)	23.9 (1.5)	111 (6)	81 (6)
3	5	1300	4	4	1.57	1.34	2.00	1.78	27.3 (0.7)	33.3 (1.6)	140 (3)	93 (1)
4	5	1300	4	4	1.56	1.36	2.03	1.84	30.5 (0.7)	35.8 (0.3)	147 (9)	104 (8)
5	5	1300	3	3	1.57	1.34	1.86	1.66	18.6 (0.7)	23.3 (0.7)	120 (10)	65 (17)
6	5	1300	5	6	1.58	1.32	1.81	1.55	14.5 (0.9)	17.7 (0.7)	69 (4)	45 (5)
7	5	1300	3	3	1.58	1.31	1.96	1.71	24.1 (0.9)	30.0 (2.3)	139 (5)	104 (5)
8	5	1300	3	3	1.56	1.33	1.77	1.56	12.9 (0.5)	17.7 (1.0)	90 (3)	63 (10)
9	5	1320	4	4	1.57	1.35	2.15	1.90	36.8 (1.2)	41.4 (0.9)	171 (10)	110 (5)
10	5	1350	3	3	1.56	1.35	2.37	2.06	51.8 (1.2)	52.1 (0.3)	205 (16)	143 (14)
11	5	1350	6	6	1.56	1.34	2.20	1.99	41.3 (1.2)	49.2 (1.3)	186 (10)	122 (26)
12	5	1350	3	3	1.57	1.33	2.16	1.90	37.7 (2.2)	42.6 (3.1)	154 (12)	116 (15)
13	15	1350	3	3	1.57	1.35	2.37	2.14	50.6 (1.8)	58.5 (1.7)	194 (17)	147 (7)

gas pressure was maintained at 7 kN m^{-2} above atmospheric, gas flow into the furnace being controlled by the rate of conversion of silicon to silicon nitride. Other silicon compacts were sometimes included in the furnace load so the contents of the furnace were not identical for every treatment. The bars were measured and weighed before and after nitriding and their strengths were determined in the as-nitrided condition in three-point bend with a span of 19.05 mm. The densities of the bars were determined from their weights and dimensions.

3. Results

Table I shows details of the nitriding schedules performed and the corresponding green densities, weight gains, nitrided densities and strengths for "hgd" and "lgd" materials.

3.1. Strength and weight gain versus maximum nitriding temperature

Whilst the data of Table I indicate a trend of increasing strength and weight gain with maximum holding temperature, the scatter is extremely large and nominally identical nitriding schedules did not produce the same weight gain or strength. In some cases, the differences involved might be related to differences in the furnace load, but in others (e.g. experiments 3 and 8 in Table I) identical furnace loads and nitriding schedules produced very different results.

Table I shows that schedules which result in low weight gains and strengths for "hgd" material produce correspondingly low values for "lgd" material. High green density bars (hgd) have lower weight gains but higher strengths than low green density bars (lgd) nitrided in the same experiment.

3.2. Strength versus weight gain

Fig. 1 shows a plot of strength versus weight gain for "hgd" and "lgd" materials. Straight lines have been fitted to each set of data using the method of least squares. The line for "hgd" material is represented by the equation

$$\sigma = 3.03W + 50.74$$

where σ is the mean strength in MN m^{-2} and W is the weight gain in per cent. The correlation coefficient for the data was 0.959.

The line for "lgd" material is represented by the equation

$$\sigma = 2.26W + 18.56$$

and the correlation coefficient was 0.962. Clearly the strength of "hgd" material is more sensitive to weight gain than that of "lgd" material.

3.3. Strength versus nitrided density

Mean strengths are plotted against nitrided

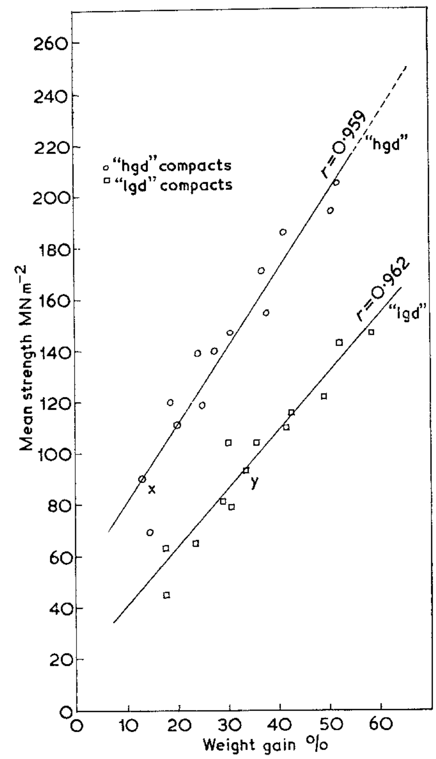

Figure 1 Strength versus weight gain for high green density (hgd) and low green density (lgd) compacts. The straight lines are the least squares fit and *r* is the correlation coefficient.

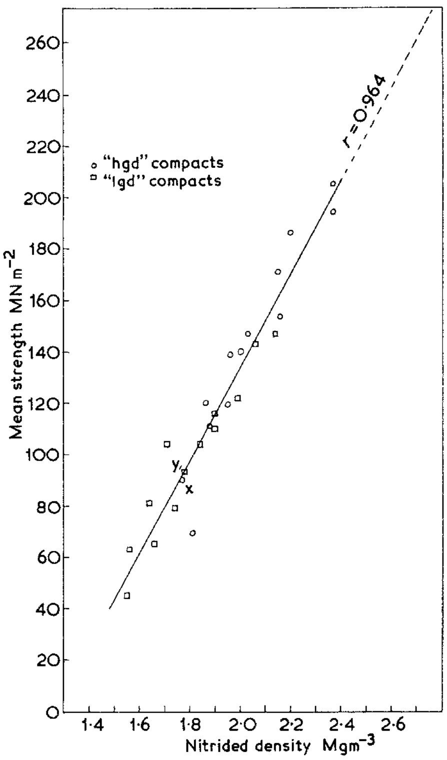

Figure 2 Strength versus nitrided density for high green density (hgd) and low green density (lgd) compacts. The straight line is the least squares fit and *r* is correlation coefficient.

densities for both materials in Fig. 2. The data for both types of material can be represented by a single straight line

$$\sigma = 181\rho_n - 227$$

where σ is the mean strength in MN m^{-2} and ρ_n is the nitrided density in Mg m^{-3}. The correlation coefficient for these data was 0.964.

4. Discussion

4.1. Structure of compacts before nitriding

For a given powder, the isostatic pressure during the formation of compacts will determine the size of the spaces between silicon particles so that "lgd" material will contain larger interparticle voids than "hgd" material. Let us assume that the sintering which occurs during the 5 h treatment at 1175°C in argon (given to all compacts) produces a structure in which all the porosity is in the form of spherical holes of a particular diameter dependent upon the original size of interparticle voids in the as-compacted powder. Let us also assume that both materials contain the same number of holes per unit volume, the difference in density resulting from larger diameter holes in the "lgd" material compared to the "hgd" material.

From Table I, the densities of "lgd" and "hgd" materials prior to nitriding are 1.33 Mg m^{-3} and 1.56 Mg m^{-3} respectively. Taking the density of silicon to be 2.33 Mg m^{-3} the ratio (ldg to hdg) of the volume of pores in the two materials is 42.5 to 33.3 i.e. 1.29. In a model material of the type described above the ratio (lgd to hgd) of the surface area of the pores would be $1.29^{2/3}$ i.e. 1.19. This figure compares closely with the mean ratio of weight gains for "lgd" and "hgd" materials in Table I (1.19 ± 0.08) which suggests there are similarities in the character of the green structures of the two materials despite their differing densities.

4.2. Strength versus nitrided density and composition

It is of interest to compare "hgd" material from

TABLE II Structure and composition of materials x and y before and after nitriding

Material	Green density (Mg m^{-3})	Green structure		Weight gain (%)	% conversion	Nitrided structure			Nitrided density (Mg m^{-3})	
		Vol % Si	Vol % pores			Vol % Si	Vol % Si_3N_4	Vol % pores	Theoretical	Measured
x "hgd" Experiment 8	1.56	67.0	33.0	12.9	19.3	54.1	15.8	30.1	1.77	1.77
y "lgd" Experiment 3	1.34	57.5	42.5	33.3	49.9	28.8	35.3	35.9	1.80	1.78

experiment 8 with "lgd" material from experiment 3 (Table I). These materials have similar nitrided densities (1.77 and 1.78 Mg m^{-3} respectively) and similar mean strengths (90 and 93 MN m^{-2} respectively) and are marked x and y in Figs. 1 and 2.

A comparison of the composition and structure of these two materials before and after nitriding is given in Table II. To derive these data, the density of silicon was taken as 2.33 Mg m^{-3} and that of silicon nitride as 3.20 Mg m^{-3}. It was assumed that 100% conversion of silicon to silicon nitride would produce a weight gain of 66.7%; no allowance has been made for the small amount of mass transport which occurs within the furnace. The lattice volume expansion associated with the conversion of silicon to silicon nitride has been assumed to be 23% (the exact values are 21.5% for β-Si_3N_4, 21.75% for α-Si_3N_4 and 27% for α-$Si_{11.5}N_{15}O_{0.5}$ [5]). An important implication of our relationship between strength and nitrided density is that two materials such as x and y in Table II of the same nitrided density but with different compositions and structures exhibit similar mean strengths. The Griffith relationship $\sigma_f = \sqrt{(E\gamma/\pi C)}$ (where σ_f is fracture strength, E is Young's modulus, γ is fracture surface energy and C the effective flaw size) can be used to examine the implication of the similarity in strength of such dissimilar structures. It seems unlikely that the values of E, γ and C will be the same for both materials, particularly as E is so different for silicon (110 GN m^{-2}) and silicon nitride (310 GN m^{-2}). However, since their strengths are equivalent, the quantity $E\gamma/C$ must be the same for both materials. This suggests that there exists a subtle relationship between E, γ and C and the structure of the partially nitrided compacts, differences in one parameter between the two materials being compensated by corresponding differences in one or both of the other parameters.

4.3. Strength versus weight gain

A close correlation between weight gain and strength for "hgd" and "lgd" materials is shown in Fig. 1. Different relationships between weight gain and strength exist for the two materials and it is noted that "hgd" material is more sensitive to percentage weight gain than "lgd" material.

A given percentage nitrogen weight gain for "hgd" material corresponds to the conversion of a larger weight of silicon than is the case for an equivalent percentage weight gain for "lgd" material. The effect of the newly formed silicon nitride will be two-fold. Firstly it represents the formation of a stronger, stiffer phase which will contribute greater strength to the structure compared to the silicon which it has replaced. Secondly its formation represents a reduction in the void space in the material reducing the size of defects in the structure. Thus "hgd" material acquires a greater volume fraction of strong material which effectively reduces its pore size to a greater degree than is the case for "lgd" material for a given percentage weight gain.

4.4. Variability of strength

The strengths reported in this work are mean values from a minimum of three tests. Standard deviations are quoted in Table I and the small scatter is noted. This implies the frequent occurrence of the strength controlling defect in the structure especially in the case of a three-point bend test where only a small volume of material experiences the maximum stress. This observation supports the ideas discussed above where the microstructure, i.e. pore size, controls material strength.

4.5. Strength and weight gain versus maximum nitriding temperature

Whilst excellent correlations have been shown between strength and nitrided density and strength versus weight gain it is important to stress the lack of control of the nitriding process which is apparent from Table I. A wide scatter in weight gains was obtained from nominally identical experiments, and the differences could not be related to differences in the furnace load (Section 3.1). Despite this wide scatter it is noted that the ratios of weight gain of "hgd" material to "lgd" material in each of the thirteen experiments are roughly constant, i.e. an experiment producing a low weight gain for "hgd" material produced a correspondingly low weight gain for "lgd" material. Since the green bars for any particular experiment were selected at random we conclude that some unknown factor, probably a furnace atmosphere effect, is influencing reaction kinetics. The effect of the changes in reaction kinetics which occurred during these treatments was to move the relevant data points up or down the lines derived in Figs. 1 and 2. The fact that such clear relationships have been established is extremely important since it provides a means of comparing materials in situations where the fine control of nitriding kinetics is not possible.

4.6. Variations in starting powder

The data reported in this paper are for green compacts made from the same starting powder isostatically pressed at different pressures before heating for 5 h at 1175°C in argon. Some data have been obtained for compacts fabricated from a different silicon powder. Whilst straight line relationships exist between strength and weight gain, and strength and nitrided density for this different powder, these lines are significantly different from those reported in Figs. 1 and 2.

It seems likely, therefore, that each unique silicon powder will produce its own unique linear relationship between strength and weight gain provided the silicon compacts have identical green structures. Further, each unique silicon powder will produce its own unique linear relationship between strength and nitrided density for silicon compacts of differing green density, provided the pre-nitriding fabrication process does not change certain critical particle properties which may include particle size and shape, and surface composition.

4.7. Materials nitrided to higher weight gains

Some of the data reported so far and the derived relationships have been for partially nitrided "hgd" compacts with a maximum silicon to silicon nitride conversion of 78%. It is of interest to consider other data accumulated at this laboratory for "hgd" silicon compacts prepared from the same powder and in the same manner as described in Section 2, but nitrided for longer times (up to 100 h) at similar or higher temperatures where the silicon to silicon nitride conversion has been in the range 82 to 99%. The data considered here are confined to materials where the formation of strength controlling defects by the melting of large silicon particles [6] has been avoided by careful control of the nitriding schedule. This is achieved by either restricting the maximum nitriding temperature to 1350 °C or ensuring that 90 to 95% conversion occurs at 1350 °C before the nitriding temperature is increased above the melting point of silicon (~ 1420 °C) [4].

The mean strength of compacts nitrided to silicon conversions of greater than 82% and final densities in excess of 2.44 Mg m^{-3} range from 204 to 251 MN m^{-2} but there is a tendency for mean strengths to be lower than extrapolations of our strength/weight gain or strength/nitrided density relationships suggest. It is noted, however, that a number of data points with weight gains greater than 60% have mean strengths in good agreement with these extrapolations.

In cases where lower strengths are recorded, it seems likely that the strength is controlled by flaws other than the largest effective pore present in the material. In these situations pore sizes are becoming progressively smaller as weight gain increases so that other types of flaw present in some batches of material could become strength controlling. If this is the case it follows that the relationships derived from the present work could simplify the comparison of various starting powders and green silicon compact microstructures. The derived relationships would permit the elimination of the confusing effects that occur at high weight gains and also eliminate the need to compare materials having identical weight gains, percentage conversion or nitrided density. It remains important, however, to identify and eliminate the flaws which become strength controlling at the higher weight gains.

A linear extrapolation of the strength versus weight gain relationship for "hgd" material indicates a mean strength of 253 MN m^{-2} for a completely nitrided compact (66.7% weight gain). A similar extrapolation of strength versus nitrided density to a density of 2.63 Mg m^{-3} (100% conversion of a compact with a green density of 1.58 Mg m^{-3}) shows a corresponding mean strength of 248 MN m^{-2}. Both of these extrapolated numbers compare closely with the maximum mean strength of 251 MN m^{-2} we have ever recorded for "hgd" material tested with as-nitrided surfaces. Consequently, the potential of a particular silicon compact (in terms of the character of the starting powder, compact density and pore structure) to ultimately form a high strength reaction sintered silicon nitride can be assessed unambiguously by using short nitriding times corresponding to weight gains of less than 60%.

5. Conclusions

(1) The factors which control the nitriding kinetics of silicon powder compacts are not sufficiently well understood that materials can be nitrided consistently to a given weight gain below about 60% by repeating nominally identical fabrication procedures. Evidence suggests that small variations in the furnace atmosphere are an important factor as the non-reproducibility could not be directly attributed to variations in structure or composition of the compacts.

(2) A close positive correlation has been established between strength and weight gain for weight gains of less than about 60% for material isostatically pressed at 185 MN m^{-2}. Compacts isostatically pressed at 31 MN m^{-2} from the same powder also exhibited a good positive correlation between these parameters but the dependence was different. The material with the higher green density exhibited a greater change in strength for a given weight gain.

(3) A good positive single correlation between strength and final density but independent of green density has been demonstrated for the two materials studied.

(4) When the silicon to silicon nitride conversion exceeds about 82% there is a tendency for the strength of some batches of "hgd" material to fall below that predicted by extrapolation of the derived strength/weight gain and strength/nitrided density relationships. This may be the result of a change in the nature of the strength controlling flaws at these high levels of conversion.

(5) The maximum mean strength derived by extrapolation of the established strength/weight gain and strength/nitrided density relationships are in close agreement with the maximum observed mean fracture strength for "hgd" compacts.

(6) Use of the relationships between strength/weight gain and strength/nitrided density could simplify the development of optimum starting powders and/or pre-nitriding treatments in efforts to improve the strength of reaction sintered silicon nitride.

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