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EFFECT OF ATTRITION MILLING ON THE REACTION SINTERING
OF SILICON NITRIDE

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ABSTRACT

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Silicon powder was ground in a steel attrition mill under nitrogen. Air exposed powder was compacted, prefired in helium, and reaction sintered in nitrogen-4 v/o hydrogen. For longer grinding times, oxygen content, surface area and compactability of the powder increased; and both α/β ratio and degree of nitridation during sintering increased. Iron content remained constant.

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INTRODUCTION

Silicon nitride (Si_3N_4) exhibits properties that make it a desirable material for high temperature engineering applications. Reaction sintered Si_3N_4 (RSSN), although lower in strength at room temperature than hot pressed Si_3N_4 (HPSN), has greater strength above about 1350°C and is more readily formed into complex shapes.

Because the formation of RSSN involves the reaction of two components, silicon metal and nitrogen gas, the rate of reaction and possibly the completeness of the reaction are expected to be influenced by the surface area and particle size of the silicon. This is one reason for using fine starting silicon powder. Another reason is that the size of the largest of the strength limiting pores in the final product may be expected to correlate with the size of the largest silicon particles in the starting powder (1). Studies have been carried out using commercially available "fine" silicon powder - $6\ \mu\text{m}$ (2) and $4\ \mu\text{m}$ (3). However, much finer powders can be rapidly prepared by attrition milling, a process in which powder is ground by repeated impact in a stirred high energy ball mill.

The primary objective of this study was to determine the effect of attrition milling of silicon powder on nitridation. A secondary objective was to determine whether a reaction between silicon and nitrogen could be promoted by milling in a nitrogen atmosphere.

Compacts prepared from as-received and attrition milled silicon powders were reaction sintered in a nitrogen plus hydrogen

atmosphere. Comparisons were made on the basis of chemistry, density, metallography, and x-ray diffraction.

EXPERIMENTAL PROCEDURE

Fine powder was prepared by grinding as-received -325 mesh silicon powder in a steel attrition mill using 0.6 cm diameter steel balls as media. The attrition mill used in this study, shown schematically in figure 1, was basically similar to a ball mill but with the energy for comminution supplied by stirring the balls rather than by tumbling. It was hermetically sealed and capable of being vacuum leak-checked. In operation it was possible to load and unload the mill without exposing the mill contents to air. The media to powder weight ratio was 40:1. Milling was performed under flowing nitrogen at a slight positive pressure for periods of 1, 4, and 18 hours. All ground powders were pyrophoric i.e. self-igniting upon air exposure. Therefore before air handling, the powders were exposed to air at a controlled rate such that the temperature and the powder bed did not exceed 200 °C. Exposure was continued until the powders showed no further tendency for self-ignition. This procedure limited the oxygen pickup to a lower value than would have been observed if the powders had been allowed to self-ignite. In addition, it provided powders that were air handleable. Exposed powders were analyzed for oxygen carbon, nitrogen, and iron content. And their specific surface areas were determined by the 3-point BET technique.

The silicon powders were cold formed without the use of binders into disks 1.3 cm in diameter and 0.5 cm high by pressing at 170 MPa in a single acting die followed by isostatic pressing at 500 MPa. Sample compacts were fractured and examined at this point by scanning electron microscopy (SEM).

Compacts of as-received and of ground silicon powders were presintered for four hours at 1150 °C in a flowing atmosphere of purified helium. Weights and densities were determined after this step.

For nitriding, the compacts were supported by 0.5 cm diameter RSSN spheres in a high purity Al203 boat and placed in the central 15 cm of a tube furnace with temperature variation of ± 2 °C over this length. The furnace was equipped with a 9.0 cm diameter high purity Al₂O₃ tube and silicon carbide heating elements. The furnace was sealed, pressurized, and leak checked; then a slow flow of purified nitrogen with 4% hydrogen was established. Heating to 1390 °C (20 °C below the melting point of pure Si) was conducted over a period of 140 hours according to the nitriding schedule selected from the literature (4) and shown in figure 2. Notice that this nitridation program consisted primarily of a 70 hour hold at 1150 °C followed by a slow continuous heating to 1390 °C without holding, thus the time at highest temperature was minimal.

After nitridation the samples were weighed and their densities determined by vacuum mercury displacement. Nitrided samples were also examined by light microscopy and x-ray diffraction. Relative

peak intensities of the phases detected were measured from the diffraction patterns.

RESULTS AND DISCUSSION

Chemical analysis and surface area of the as-received and of the ground silicon powders (after controlled air exposure) are shown in Table I. With increasing grinding time there was a significant increase in oxygen content, a moderate increase in nitrogen content, and essentially no change in either carbon or iron content. During grinding all of the steel hardware became coated with an adherent shell of silicon. The presence of this coating limited the contact between the silicon powder and the steel hardware, thus preventing iron contamination.

Surface area of the silicon powder was increased from $3.0 \text{ m}^2 \text{ g}^{-1}$ for as-received material to $23.3 \text{ m}^2 \text{ g}^{-1}$ for material ground 18 hours. The surface area increased rapidly during the first hour of grinding and more gradually thereafter. All of the ground powders were pyrophoric prior to the controlled air exposure. Figure 3 shows the effect of attrition milling on the morphology of the silicon powder as observed by scanning electron microscopy of fractured presintered compacts. The as-received powder contained a considerable volume fraction of large particles along with a relatively small amount of fines. After only one hour of grinding the majority of the large particles had been reduced to a very fine size. Continued milling for 4 and 18 hours further reduced both the number and size of the large particles. All of the ground powders

were characterized by the presence of large agglomerates of very fine particles.

As received silicon powder is difficult to compact without the use of binders; i.e., the compacts are very fragile and friable. The ground powders used in this study, however, produced well defined compacts which could be readily handled.

As shown in Table II, however, under the compaction conditions employed the powder ground 18 hours (finest powder) compacted to a lower density - (1570 kgm^{-3}) than did either the as-received (1720 kgm^{-3}) or the powders ground 1 and 4 hours (1700 to 1740 kgm^{-3}).

Nitrided density was higher for compacts prepared from ground powders - 2520 to 2560 kgm^{-3} - than for compacts prepared from as-received powder - 2120 kgm^{-3} . Figure 4, a plot of surface area versus weight gain illustrates a consistent and significant increase in percent weight gain during nitriding as surface area increase. However, the weight gain did not increase linearly with increasing surface area. This indicated that some of the grinding was redundant as may be understood from the following discussion.

Atkinson et al (5) have studied the nitridation of pure silicon powder and proposed a model involving three sequential steps: 1) Si_3N_4 nuclei form on particle surfaces, 2) the nuclei grow laterally to eventually cover the whole surface (the thickness of the Si_3N_4 coating being a function of the temperature and pressure during nitridation) and finally, 3) when the entire surface is covered by Si_3N_4 nitridation essentially stops. Although this model was formulated from observations

of nitridation of iron-free silicon powder, the same mechanisms appear to be applicable to this work.

Based on the model described above, all the silicon particles of a size as small as approximately twice the thickness of the Si_3N_4 layer (critical size) would nitride completely. Particles larger than the critical size will not nitride completely, but will have an interior of unreacted silicon surrounded by a Si_3N_4 shell. Any particles smaller than the critical size will also nitride completely, but will have been ground unnecessarily fine. Thus increased specific surface area may not result in proportionate increases in amount of nitride formation.

Figure 5 shows the relationship between initial powder surface area and density of both presintered and nitrated compacts. The importance of the fine powder size (higher surface area) in the achievement of more complete nitridation and associated, higher percent weight gain, is apparent.

Typical light micrographs of the four nitrated materials are shown in figure 6. Residual or unnitrided silicon appears as the white phase in the micrographs. Most obvious is the decreased residual silicon content with increased grinding time and the fineness of the residual porosity in the 18 hour ground material. A few large silicon particles as well as agglomerates of smaller silicon particles are still present even in the samples prepared from the 18 hour ground material. There was no appreciable difference in appearance between the surface and interior of any of the nitrated compacts which is a fair indication that nitrogen was able to get into

the interior at all times. The largest pores observed were associated with partially unreacted silicon particles as shown in figure 7, a sample prepared from ground 18 hours. The pores are the black phase in this figure. X-ray phase analysis results are listed in Table III. Only silicon, alpha Si_3N_4 , and Beta Si_3N_4 were detected by x-ray diffraction. The trend of decrease in relative amount of silicon (or the increase in nitride formation) as the grinding was increased is consistent with the weight gain and light micrographic results already presented. Of particular interest is the increase in alpha/beta- Si_3N_4 ratio with grinding time. There are at least two possible explanations for this.

Amato et al (6) and Jennings and Richman (7) showed that the increasing alpha/beta- Si_3N_4 ratio during nitridation was related to the increasing oxygen content of the powder. In this investigation the oxygen content of air exposed powder increased with grinding time (Table II); therefore it could be expected that the alpha/beta- Si_3N_4 ratio observed in this investigation would also increase with grinding time. Amato et al (ref. 6) attribute this correlation between alpha- Si_3N_4 being an oxynitride (Si11.5 N15 O0.3) (8) containing more oxygen in its lattice than beta- Si_3N_4 .

The finer particle size derived from extended grinding time may also contribute to increased alpha/beta ratio in the following manner. Jennings and Richman (7) have pointed out that lower reaction sintering temperatures favor the formation of alpha phase. Smaller silicon particles should be completely reacted at lower

temperatures. And the nitriding schedule used allowed time for reaction at low temperatures. So increased grinding time may result in increased alpha/beta ratio both by increasing the oxygen content and by reducing the silicon particle size.

CONCLUSIONS

The results of this study on the nitriding of attrition milled silicon powder lead to the following conclusions:

The surface area of silicon powder can be greatly increased by dry grinding in a steel attrition mill without iron or carbon contamination.

Using a nitriding cycle in which the melting point of silicon was not exceeded, it was possible to achieve considerable nitride formation in a compact prepared from the finest ground powder. Similar compacts made from powders containing larger amounts of unground material contained considerably more unreacted silicon.

The grinding conditions utilized did not eliminate all of the large particles present in the starting silicon powder.

The alpha to beta-Si₃N₄ ratio of nitrated compacts increased with increased grinding time of the silicon powder. This may be attributed to either (or both) an increased oxygen content or a decreased particle size of the ground silicon powder.

The attrition milling approach appears to offer potential for industrial application in the preparation of reaction sintered silicon nitride. In the final analysis, however, modulus of rupture strengths must be determined. And we are now in the process of obtaining this data.

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TABLE I. - CHEMICAL ANALYSIS AND SURFACE AREA OF SILICON POWDERS

Material	Oxygen, wt %	Carbon, wt %	Nitrogen, wt %	Iron, wt %	Surface area, m ² /g
As-received	0.60	0.03	0.004	0.62	3.0
1 hr grind	2.29	0.04	0.017	0.59	11.5
4 hr grind	2.57	0.04	0.028	0.58	14.5
18 hr grind	3.67	0.04	0.037	0.55	23.3

TABLE II. - DENSITY AND WEIGHT GAIN OF SILICON COMPACTS

Material	Sintered [*] density, kg/m ³	Nitrided density, kg/m ³	Weight gain on nitriding, %
As-received	1.72x10 ⁻³	2.12x10 ⁻³	26
1 hr grind	1.74	2.56	45
4 hr grind	1.70	2.56	50
18 hr grind	1.57	2.52	58

* 1 hr, 1150 C, helium.

TABLE III. - RELATIVE X-RAY PEAK INTENSITIES IN
NITRIDED SILICON COMPACTS

Material	Amount of phase present			
	Residual Si	$\alpha\text{Si}_3\text{N}_4$	$\beta\text{Si}_3\text{N}_4$	α/β ratio
As-received	77	13	10	1.3
Ground 1 hr	68	23	9	2.6
Ground 4 hr	40	44	16	2.8
Ground 18 hr	14	72	14	5.1

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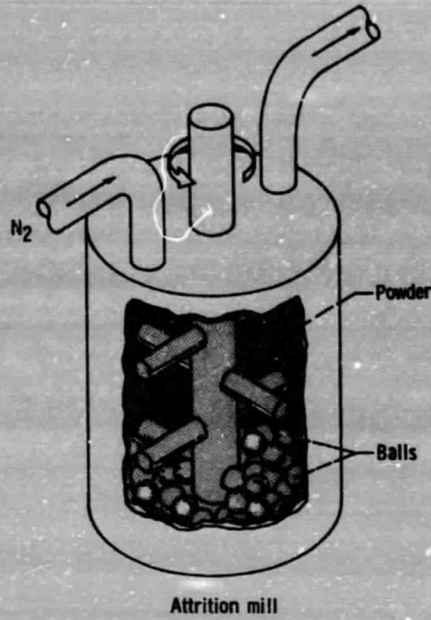


Figure 1. - Attrition mill (schematic).

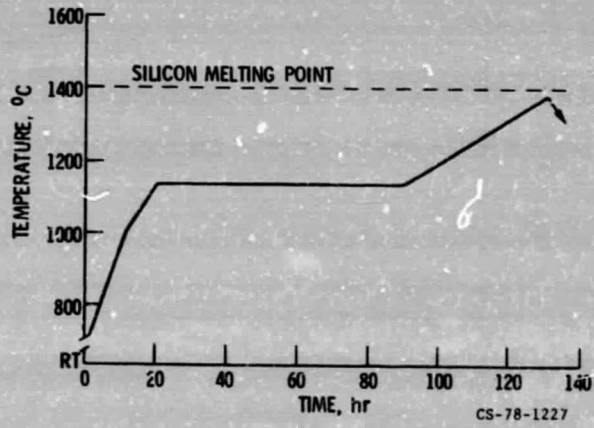


Figure 2. - Nitriding schedule.



Figure 3. - As received and attrition milled silicon powder; SEM; X10 000.

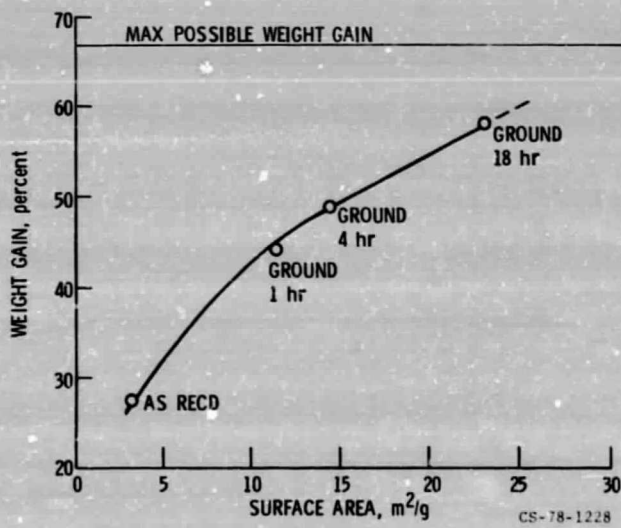
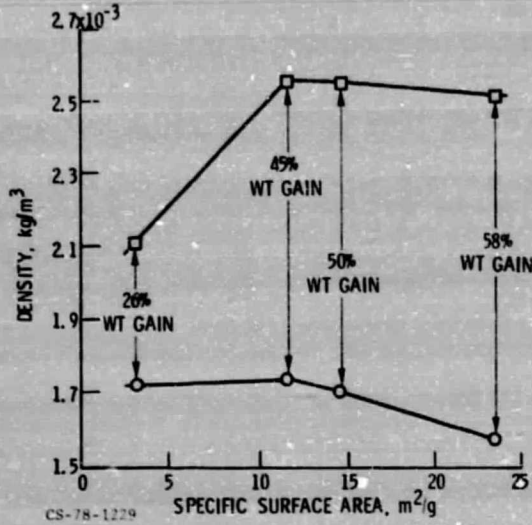


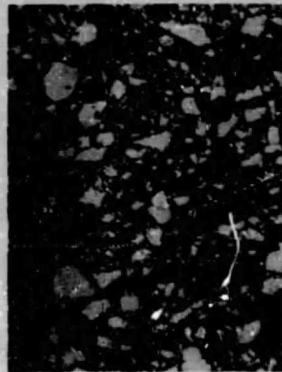
Figure 4. - Nitridation weight gain as a function of silicon powder surface area for compacts prepared from as-received and ground powders.

- NITRIDED 140 hr IN NITROGEN-4% HYDROGEN
- PRESINTERED 4 hr AT 1150° C IN HELIUM

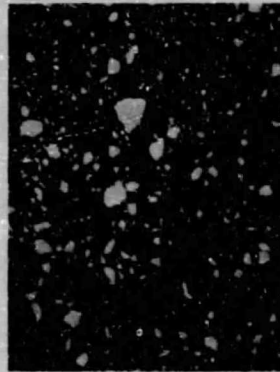


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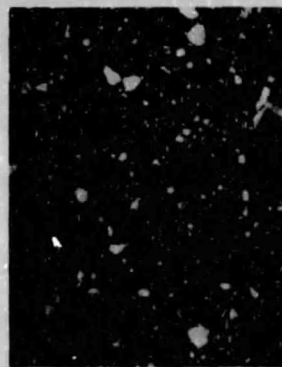
Figure 5. - Relation of presintered and of nitrided compact densities to specific surface area of starting powders.



AS RECEIVED 40 μm



GROUND 1 hr 40 μm



CS-78-1229 GROUND 4 hr 40 μm



GROUND 18 hr 40 μm

Figure 6. - Microstructure of nitrided compacts prepared from "as received" and from attrition milled silicon powder.

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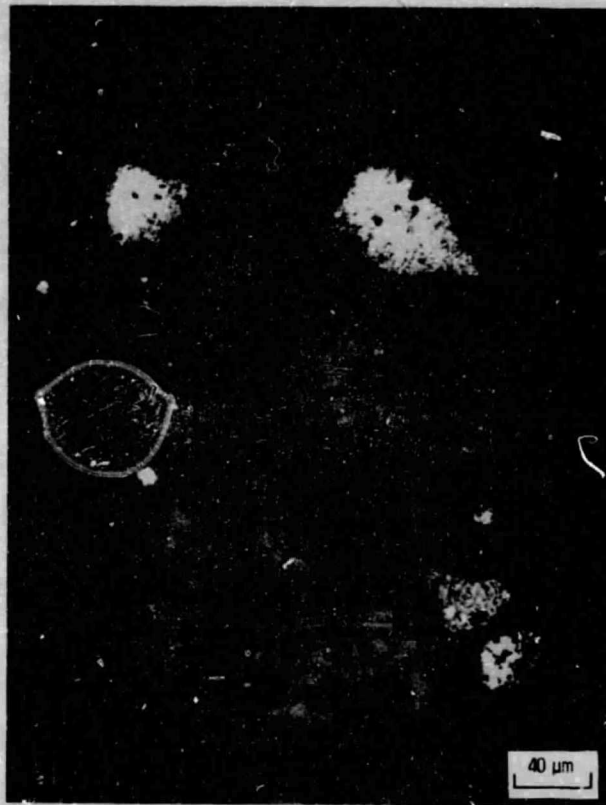


Figure 7. - Porosity associated with unreacted silicon present in nitrided sample prepared from silicon powder ground 18 hours; X250.