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Work performed for
U.S. DEPARTMENT OF ENERGY
Conservation and Solar Applications
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Prepared for
Third Annual Conference on Composites
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PREPARED FROM DRY ATTRITION MILLED SILICON POWDER

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ABSTRACT

Dry attrition milled silicon powder was compacted, sintered in helium, and reaction bonded in nitrogen-4 volume percent hydrogen. Bend strengths of bars with as-nitrided surfaces averaged as high as 210 MPa at room temperature and 220 MPa at 1400° C. Bars prepared from the milled powder were stronger than those prepared from as-received powder at both room temperature and at 1400° C. Room temperature strength decreased with increased milling time and 1400° C strength increased with increasing milling time.

INTRODUCTION

NASA-Lewis has many years experience in the fine milling of metal powders. In this study, techniques of comminution previously developed for other metal powders were applied to silicon powder as a step in the production of reaction bonded silicon nitride (RBSN).

The formation of RBSN involves the reaction of two components - silicon powder and nitrogen gas. Thus, the rate and possibly the completeness of the reaction is expected to be influenced by the surface area and particle size of the silicon. Moreover, the size of the largest of the strength limiting pores in RBSN is expected to be related to the size of the largest silicon particles in the silicon powder (ref. 1). Thus, it would appear that very finely milled silicon could result in an improved RBSN.

The objective of this study was to determine the effect of dry attrition milling of silicon powder on the properties of RBSN.

Test bar shaped compacts prepared from as-received and from dry attrition milled silicon powders were reaction sintered in a nitrogen plus hydrogen atmosphere. Comparisons were made on the basis of room temperature and 1400° C bend strength, chemistry, metallography, fractography and X-ray diffraction.

EXPERIMENTAL PROCEDURE

Fine silicon powder was prepared by dry milling as described in reference 2. Milling times were 0, 1, 4, and 18 hours. All milled powders

*Member, the American Ceramic Society.

were pyrophoric, that is, self-igniting upon air exposure. Therefore, before air handling, the powders were exposed to air at a controlled rate such that the temperature of the powder bed did not exceed 200° C. Exposed powders were analyzed for oxygen, carbon, nitrogen, and iron content. Their specific surface areas were determined by the BET (Brunauer, Emmett, and Teller) method.

The dry attrition milled silicon powders were cold pressed without the use of binders into test bars 9 mm wide by 3 mm thick by 70 mm long by pressing at 170 MPa in a single acting die followed by isostatic pressing at 480 MPa. The as-received silicon powder could not be cold formed into test bars of this size without the use of a binder. However, it was possible to form larger compacts without a binder. Therefore, large bars -1.5 cm wide by 1.0 cm thick by 6 cm long, were hydropressed without a binder at 480 MPa and later diamond cut into smaller bars for testing. Representative bars were fractured prior to sintering and examined by scanning electron microscopy (SEM).

Large bars of as-received silicon powder and test bars of the milled silicon powders were sintered for four hours at 1200° C in a flowing atmosphere of purified helium. Starting weights and densities used to calculate changes during nitriding were determined after the sintering step. The large bars of as-received silicon powder were diamond cut into test bars 6 mm wide by 3 mm thick by 30 mm long.

Nitriding was done in a high purity Al₂O₃ tube with a very small flow of nitrogen plus 4 percent hydrogen. The nitriding schedule was adapted from the literature (ref. 3) and is shown in figure 1. In essence the schedule consisted of heating in 20 hours to 1150° C, a 70 hour hold at 1150° C followed by slow (6° C/hr) heating to 1390° C with no hold at maximum temperature. The sample loading and furnace description were the same as reported in reference 2.

Upon completion of nitridation, the samples were weighed and their densities determined by vacuum mercury displacement. Four point bend strengths were determined in air at room temperature and 1400° C. Six specimens were tested in each condition. Broken test bars were examined by light microscopy, and low magnification pictures and scanning electron micrographs were taken of the fracture surfaces. Each of the nitrided materials was examined by X-ray diffraction. Selected peak intensities of the phases detected were measured from the diffraction patterns. The diffraction data were analyzed by the technique developed by Gazzara and Messier (ref. 4) to determine the amount of α Si₃N₄, β Si₃N₄ and residual silicon present.

RESULTS AND DISCUSSION

Table I shows the spectrographic trace impurity analysis of the starting silicon powder. As can be seen, the major trace impurities were iron, manganese, aluminum, and calcium. Table II contains a comparison of the oxygen, carbon, nitrogen, and iron content and the surface area of the as-received and milled powders. Note that the analysis was performed after the powders were exposed to air. With increased milling time, there was

a significant increase in the oxygen content, a moderate increase in nitrogen content, and essentially no change in carbon or iron content. The steel milling hardware became coated with an adherent layer of silicon during milling which limited contact between powder and the steel, thus preventing iron contamination.

The specific surface area of the silicon powder increased from $3.0 \text{ m}^2\text{g}^{-1}$ for as-received material to $23.3 \text{ m}^2\text{g}^{-1}$ after 18 hours of milling. The surface area increased rapidly during the first hour of milling and then more gradually as milling time increased.

Figure 2 shows the effect of attrition milling on the morphology of the silicon powder as observed by SEM of fractured compacted (unsintered) specimens. The as-received powder contained a high volume percent of large particles and a small volume percent of fines. After one hour of milling, most of the large particles were reduced to a very fine size. Longer milling times (4 and 18 hr) further reduced both the size and number of the large particles.

The finest powder (milled 18 hr) compacted to a lower density (1.60 g/cc) than did the as-received powder or the powders milled one and four hours ($1.71\text{-}1.75 \text{ g/cc}$) (see table III). Nitrided density was consistently higher for the milled powders ($2.51\text{-}2.58 \text{ g/cc}$) than for the unmilled powder (1.96 g/cc). The weight gain during nitriding, shown in table III, also increased with milling time probably as a result of the higher surface area associated with the attrition milling process.

X-ray examination of nitrided samples prepared from as-received and from milled silicon powders revealed the presence of only $\alpha\text{Si}_3\text{N}_4$, $\beta\text{Si}_3\text{N}_4$, and residual silicon. Analysis of X-ray diffraction data indicated that the residual silicon content decreased with increased milling time (table IV); both the $\alpha\text{Si}_3\text{N}_4$ content and the α/β ratio increased with increased milling time. The decrease in the residual or unreacted silicon content is consistent with both the weight gain data already described as well as with the light microscopy results to be described later. The increased $\alpha\text{Si}_3\text{N}_4$ and α/β ratio with increased milling time is believed (as discussed in ref. 2) to be associated with the higher oxygen content and/or finer size of the milled powder.

Polished sections of the nitrided materials were examined by light microscopy. Typical microstructures are shown in figure 3. It is obvious that there was a decrease in the size and amount of large unreacted silicon particles (the white areas) as milling time was increased. The microstructures indicate both the potential of dry attrition milling for producing a fine silicon powder and a possible problem. Some large silicon particles were retained even in the longest time of milling used - 18 hours. The average particle size of the material milled 18 hours was $<1 \mu\text{m}$, but some particles as large as $40 \mu\text{m}$ remain. In addition, all dry milled powders show evidence of large agglomerates of fine particles.

The fracture surfaces of test bars broken at room temperature were examined at low magnification optically and at higher magnification by SEM. A large amount of residual silicon was present on the fracture surface of bars prepared from as-received silicon powder, the white phase in figure 4(a). SEM examination, figure 4(b), showed that the fracture progressed through areas of large pores, silicon nitride and unreacted silicon (see arrows). Fractured silicon appears as smooth planar surfaces; fractured silicon nitride has a rougher appearance.

The fracture surfaces of RBSN prepared from milled silicon powder were more homogeneous in appearance. There was much less residual silicon present on the fracture surface of bars prepared from silicon powder milled for 18 hours (fig. 4(c)) and SEM examination (fig. 4(d)) revealed that the pores were smaller and more uniformly distributed.

A search for fracture initiation sites was conducted by SEM. Unreacted silicon particles were found at the apparent fracture initiation sites in all samples examined.

Bend strengths were determined by four-point loading. All samples were tested with as-nitrided surfaces. Room temperature tests employed 1/3 point loading and 1400° C 1/4 point loading. The crosshead speed was 0.05 cm/sec. The bend strength data is presented in figure 5 and represents the average of six tests for each condition. Room temperature strength for specimens prepared from as-received silicon averaged almost 100 MPa. Bars prepared from material milled one hour had an average strength of 210 MPa, and the room temperature strength decreased with increased milling time. At 1400° C the strength increased with increased milling time and the specimen prepared from material milled 18 hours averaged 220 MPa.

Analysis of the bend strength data indicates fairly clearly that RBSN prepared from milled powder and nitrided by the schedule used in this study is stronger than RBSN prepared in a comparable manner from as-received powder. It is believed that this strength difference is related primarily to the smaller silicon particle size of the milled powders which in turn leads to increased weight gain (greater degree of nitridation) and decreased residual silicon after nitriding.

Another trend evident in the data is the increase in strength with increased milling time for the 1400° C tests. This trend may be attributed to the decreased residual silicon and increased α/β ratio in RBSN prepared from powder milled 18 hours. What is more difficult to understand is that this trend is reversed at room temperature. The strength of all RBSN prepared from milled powder is greater than that of RBSN prepared from as-received powder, but shorter milling times gave higher strengths. These results suggest that the strength limiting factors for high and low temperature strength differ. However, because several factors vary simultaneously (e.g., density, residual silicon content, oxygen content, weight gain, and α/β ratio) it is not possible from the data available to unambiguously determine which were responsible for the trends observed.

CONCLUDING REMARKS

The dry attrition milling technique employed in this work consistently produced powder with the undesirable characteristic of retained large silicon particles. Increasing grinding time did decrease the number and size of the large particles, but only very slowly. The retained large particles appeared to be associated with numerous finer silicon particles in tightly bound agglomerates which may have conferred protection during milling to the large particles. This characteristic of dry milled powder was not changed by moderate changes in the dry milling procedure. For example, in unpublished work by the authors, it was found that the addition of limited

amounts of oxygen to the nitrogen milling atmosphere or the addition of FeO or carbon to the silicon powder charge had no effect on the retention of large silicon particles. Thus the dry attrition milling process as employed here can be of only limited value.

From the strength measurements of RBSN prepared from milled silicon it is apparent that particle size reduction can lead to an improved product. However, if silicon powder free of large retained particles is to be produced the milling procedure should be different. A method in which the desired fine particles are continuously removed from the milling circuit while large particles are retained for further comminution would be more appropriate. Examples of such processes are jet milling and pin milling combined with air classification.*

An alternative under investigation is a wet milling process in which formation of agglomerates may be avoided during milling. Another approach, to the authors' knowledge not currently under investigation, is the manufacture of silicon powder of initially fine size.

SUMMARY

This study dealing with the evaluation of reaction bonded silicon nitride (RBSN) prepared from minus 325 mesh silicon powder dry attrition milled for 0, 1, 4, and 18 hours indicates that dry attrition milling results in:

1. A fine high surface area silicon powder
2. An as-nitrided microstructure that is more uniform than that observed in specimens prepared from as-received silicon powder
3. Bend strengths at both room temperature and 1400° C that are higher than for specimens prepared from as-received silicon powder
4. The retention of some unreacted large silicon particles and agglomerates of fine silicon particles in the product RBSN

*A jet mill is an apparatus in which comminution is effected by the collision of powder particles entrained in opposing jets of gas. In a pin or stud mill particles are broken by impact with rapidly moving pins or studs. In either mill the powder is carried by a gas stream facilitating size fractionation as for example by centrifugal (conical) separators.

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TABLE I. - TRACE IMPURITY ANALYSIS
OF STARTING SILICON POWDER

Element	Amount, ppm
Aluminum	670
Calcium	380
Chromium	170
Iron	6200
Magnesium	80
Manganese	850
Nickel	90
Titanium	130
Vanadium	90

TABLE II. - CHEMICAL ANALYSIS AND SURFACE AREA OF
SILICON POWDERS^a

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
Milled 1 hr	2.29	.04	.017	.59	11.5
Milled 4 hr	2.57	.04	.028	.58	14.5
Milled 18 hr	3.67	.04	.037	.55	23.3

^aAfter exposure to air.

TABLE III. - DENSITY AND WEIGHT GAIN OF SILICON BARS

Material	Sintered ^a density, g/cm ³	Nitrided density, g/cm ³	Weight gain on nitriding, %
As-received	1.71	1.96	17
Milled 1 hr	1.75	2.57	47
Milled 4 hr	1.72	2.58	50
Milled 18 hr	1.60	2.51	57

^a4 hr, 1200° C, helium.

TABLE IV. - RELATIVE AMOUNTS OF PHASES PRESENT

IN NITRIDED SILICON BARS

Material	Amount of phase present, percent			
	Residual silicon	α Si ₃ N ₄	β Si ₃ N ₄	α/β ratio
As-received	53	47	0	---
Milled 1 hr	14	70	16	4.4
Milled 4 hr	10	75	15	5.0
Milled 18 hr	1.4	86	13	6.6

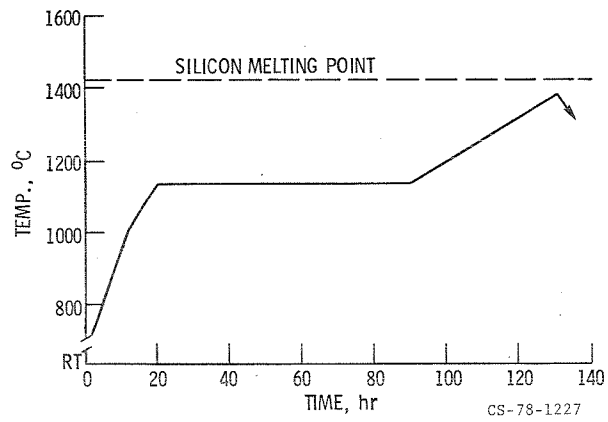
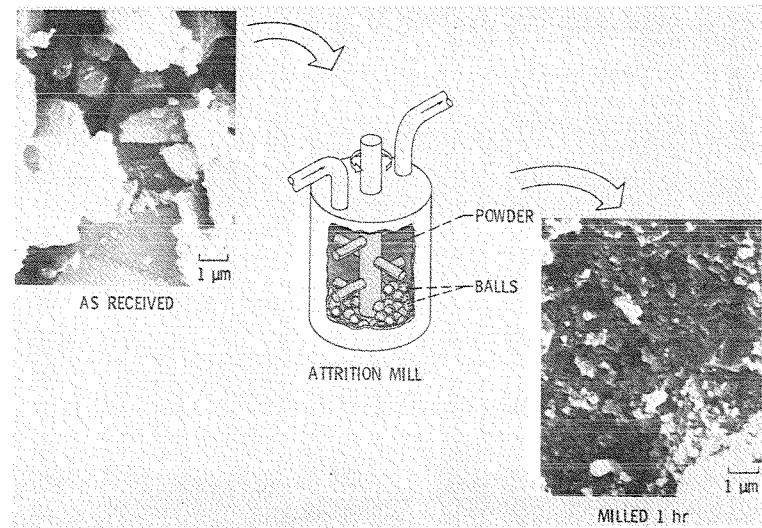


Figure 1. - Nitriding schedule.



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Figure 2. - As received and attrition milled silicon powder, (SEM).

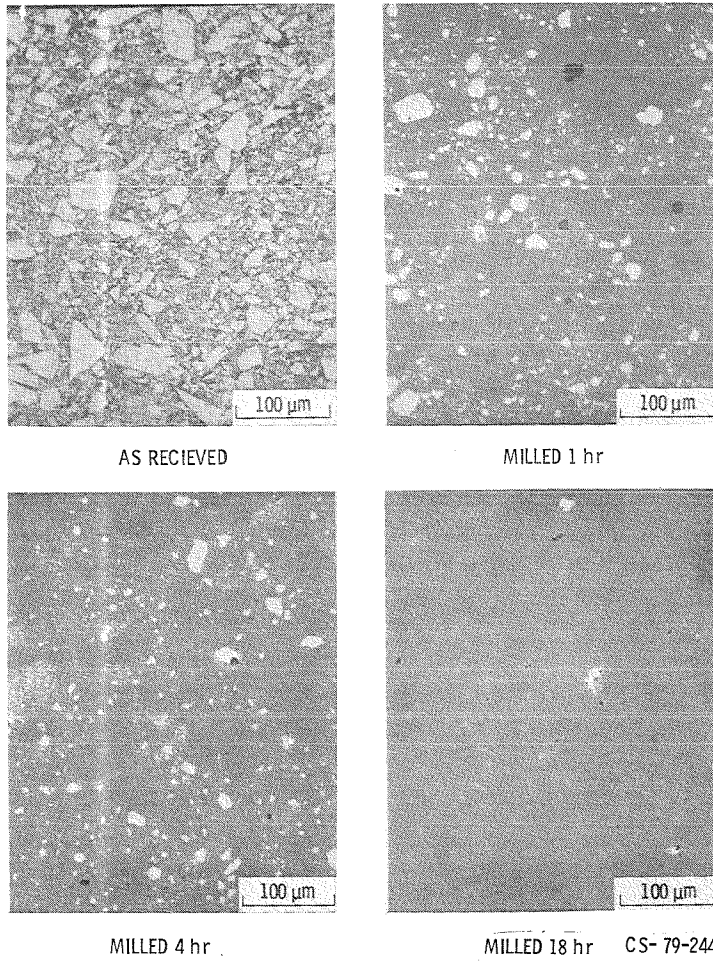


Figure 3. - Microstructure of nitrided bars prepared from "as received" and from attrition milled power.

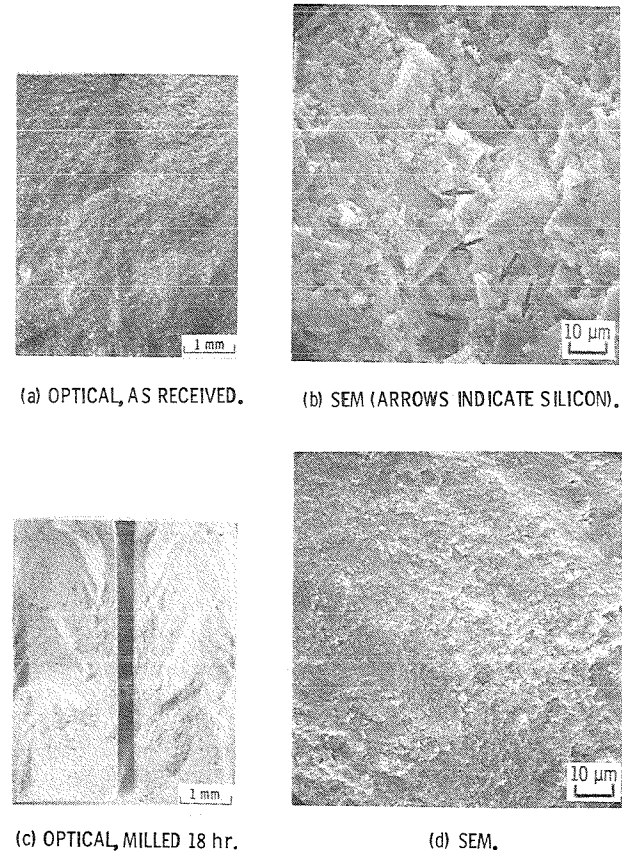


Figure 4. - Room temperature fracture surfaces of bars prepared from "as received" and from power milled 18 hours.

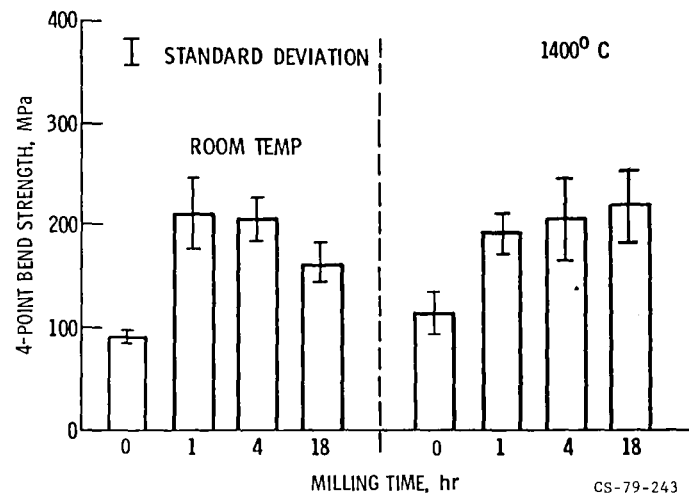


Figure 5. - Strength of nitrided bars as function of milling time.

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