Demonstration of a Silicon Nitride Attrition Mill for Production of Fine Pure Si and Si_3N_4 Powders

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To avoid metallic impurities normally introduced by milling ceramic powders in conventional steel hardware, an attrition mill (high-energy stirred ball mill) was constructed with the wearing parts (mill body, stirring arms, and media) made from silicon nitride. Commercial silicon and Si_3N_4 powders were milled to fine uniform particles with only minimal contamination—primarily from wear of the sintered Si_3N_4 media.

Ball milling of commercial silicon and silicon nitride (Si_3N_4) powders has been applied as a means of improving the slip casting and injection molding characteristics and of increasing the microstructural homogeneity and strength of reaction-bonded Si_3N_4 and sintered Si_3N_4.[1–5] Wet milling of silicon in a conventional 4-L capacity steel attrition mill results in the pickup of considerable (e.g., 0.25 wt% in 7 h) Fe contamination.[5] And the wet milling of Si_3N_4 in a small steel attrition mill yielded a powder with more than 10 wt% Fe after only 2 h.[6] An example of the uniform structure of RBSN made from wet milled (steel attrition mill) powder is shown in Fig. 1, Part C, taken from Ref. 7.

Dry milling, while avoiding metallic contamination problems has not been effective in uniformly reducing the particle size of commercial silicon powder. Large silicon particles are retained (Fig. 1), apparently within strong agglomerates, even after 16 h of milling.[7] Due to its highly abrasive nature, the dry milling of Si_3N_4 in a metallic mill has not been attempted.

To obtain the uniform fine particle size potentially inherent in wet milling while avoiding uncontrolled metallic contamination, a mill was constructed having wearing parts of Si_3N_4. The container of this mill shown schematically in Fig. 2 was patterned after a commercial model* high energy stirred ball mill. In an attrition mill of this type the milling media are continuously activated by arms protruding from a rotating shaft. Since the maximum kinetic energy of colliding media is not limited by the distance fallen as in a ball mill, comminution can proceed more rapidly.

The wearing parts of an attrition mill include the stirrer arms, the media, and the mill body itself. The central shaft, while also in contact with the media and powder, typically experiences little wear. The cylindrical stirrer arms, ground from hot-pressed Si_3N_4,† were mounted in the metal drive shaft by shrink fitting. The media were 6.3 mm diam. high density cold-pressed and sintered Si_3N_4 balls containing 6 wt% Y_2O_3+2 wt% Al_2O_3.‡ Lower-density reaction-bonded Si_3N_4 media were tried but proved to be too friable. The mill body was slip-cast reaction-bonded Si_3N_4§ of four liter capacity. Impurity analysis of the three ceramic components is shown in Table I. The cylindrical chamber was resiliently

Table I. Impurity Analysis of Ceramics Attrition Mill

Mill component	Component (wt%) Al	Fe	Mg	Y
Stirrer arms; hot-pressed Si_3N_4*	0.17	0.55	0.84	
Mill body; reaction-bonded Si_3N_4†	0.24	1.6	0.03	0.20
Milling media; sintered Si_3N_4‡	1.4	<0.001	<0.0001	9.7

*NC132. Norton Co., Worchester, MA. †Ceramic Systems, Inc., Detroit, MI. ‡Wesgo Division, GTE Products Corp., Belmont, CA.

*Member, the American Ceramic Society.
*I-S Atritor, Union Process Co., Akron, OH.
†NC132, Norton Co., Worchester, MA.
‡Wesgo Div. of GTE Products Corp., Belmont, CA.
§Ceramics Systems, Inc., Detroit, MI.
¶Kawecki Berylco Industries, Reading, PA.
**AME CP85, Kawecki Berylco.

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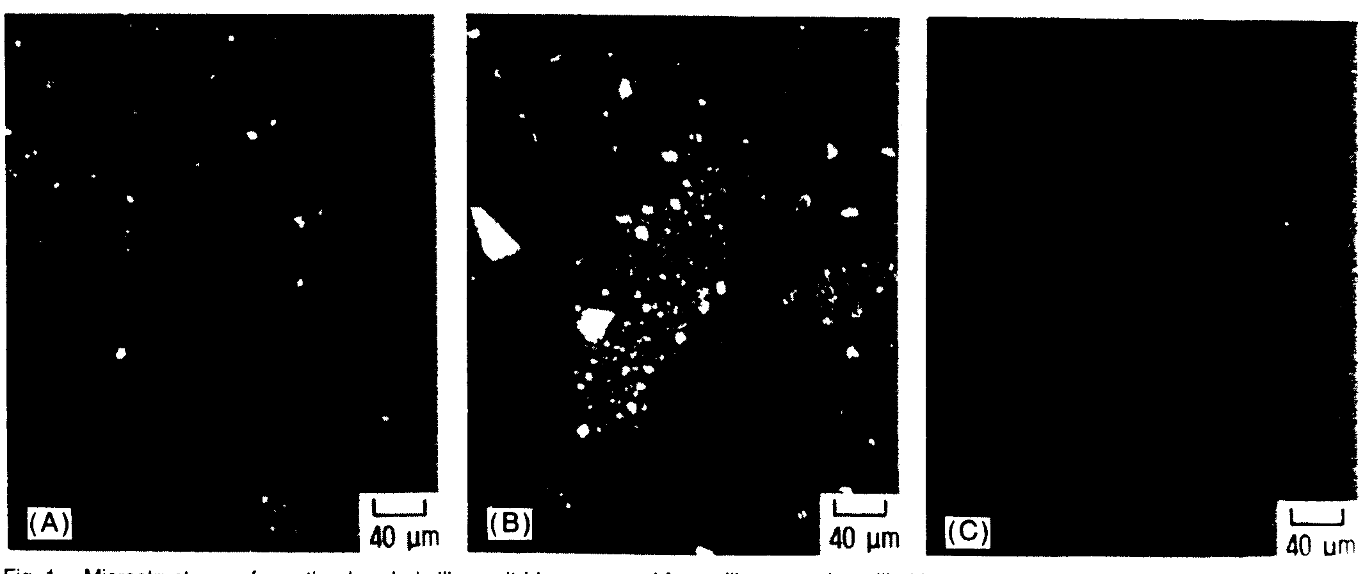


Fig. 1. Microstructures of reaction-bonded silicon nitrides prepared from silicon powder milled in a steel attrition mill (Ref. 7). (A) Typical area of sample dry-milled for 18 h; (B) same sample as in (A), showing retained silicon and pores; (C) sample wet-milled for 8 h.

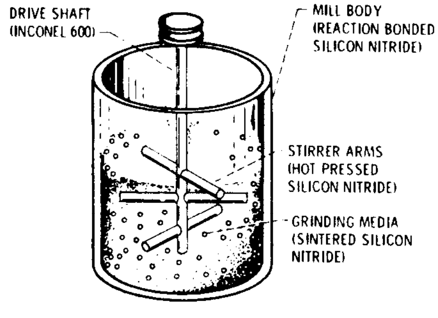


Fig. 2. Silicon nitride attrition mill (schematic).

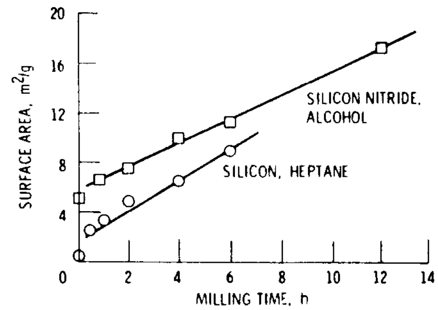


Fig. 3. Surface area as a function of time of wet-milling in Si_3N_4 mill.

mounted, using sections of soft plastic tubing, within a water-cooled sheet metal cylinder. The annular space between the ceramic and metal cylinders was filled with a heat transfer fluid, generally the same composition as the milling fluid.

The stirring arms extend 6.5 cm from the 2.6-cm diam. central shaft leaving an approximately 3½-ball diameter clearance between the arm ends and the mill inside diameter (20 cm). The clearance between the lowest stirrer and the bottom of the mill was about 3 ball diameters.

Experimental

In a trial run with silicon, the mill was loaded with 6160 g of balls, 1850 mL of *n*-heptane, and 400 g of metallurgical grade Si powder.[†] Total milling time was 6 h at a shaft speed of 164 rpm. Samples of the milled powder were extracted at 0.5, 1, 2, 4, and 6 h. Silicon powder was recovered by vacuum evaporation of the heptane. In the case of Si_3N_4 the mill was loaded with 6160 g of balls, 2000 mL of 200 proof ethyl alcohol, and 400 g of controlled phase grade Si_3N_4 powder.** Total milling time was 12 h at a shaft speed of 100 rpm. Powder samples were extracted at 1, 2, 4, 6, and 12 h. Powder recovery was accomplished by evaporation in a high velocity hood.

Selection of milling fluid for the trial runs was based on previous qualitative observations that the silicon powder appears to disperse better in *n*-heptane while the Si_3N_4 powder appears to disperse better in ethyl alcohol. Choice of shaft speed was arbitrary; however, in both cases it was within the range of speeds that yield good visual stirring without spattering of the powder slurry on the walls of the mill body. Finally, although no further grinding of silicon has been attempted, numerous Si_3N_4 grinds have been performed over a range of shaft speeds with results that are consistent with those reported here.

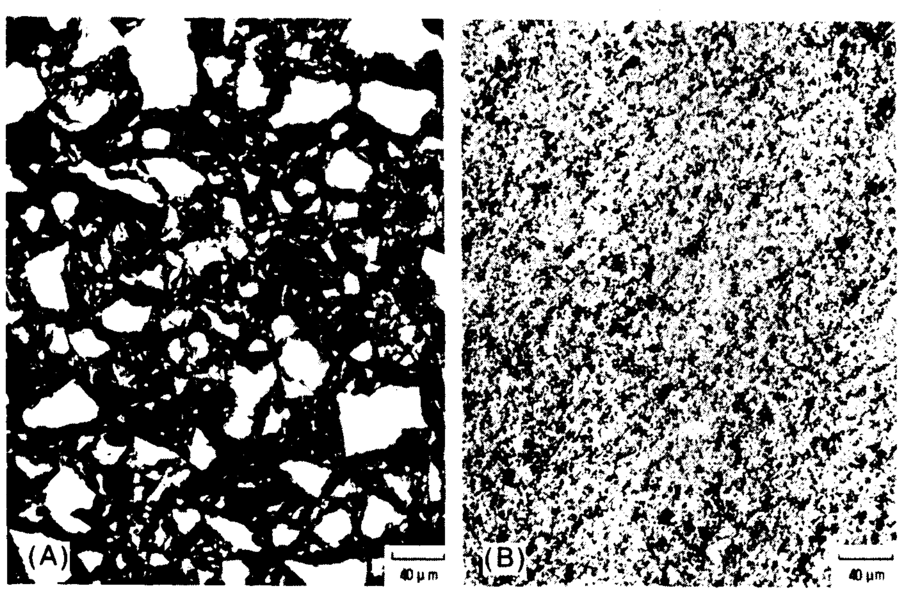
Table II. Chemical Analysis and Surface Area of As-Received and Milled Silicon and Silicon Nitride Powder

Sample	Chemical analysis (wt%)					Surface area (m²/g)
	Fe	C	O	Y	N	
As-received Si	0.38	0.07	0.13	*	*	0.5
Si milled for 6 h	0.36	0.27	1.46	0.01	0.12	8.9
As-received Si_3N_4	0.47	0.27	1.7	0.005		5.1
Si_3N_4 milled for 6 h	0.51	0.90	2.3	0.147[†]		11.2

*Not detected. †Correlates with weight loss of media.

Results

A comparison of the composition of the Si and Si_3N_4 powders before and after milling for 6 h is given in Table II. Figure 3 shows the effect of milling time on the surface area. The data indicates a linear increase with time for the range of milling times studied. For silicon the major changes in composition are in oxygen, carbon, and nitrogen. The oxygen increase is related to the increase in Si surface area (S) and to a much smaller extent to wear of the sintered Si_3N_4 media. The very small increase in Y content indicates that media wear was slight. Carbon results from reaction with the *n*-heptane milling fluid. The nitrogen content is a good indicator of wear of the mill and its media and corresponds to an addition of approximately 0.3 wt% Si_3N_4 to the Si. The effect, if



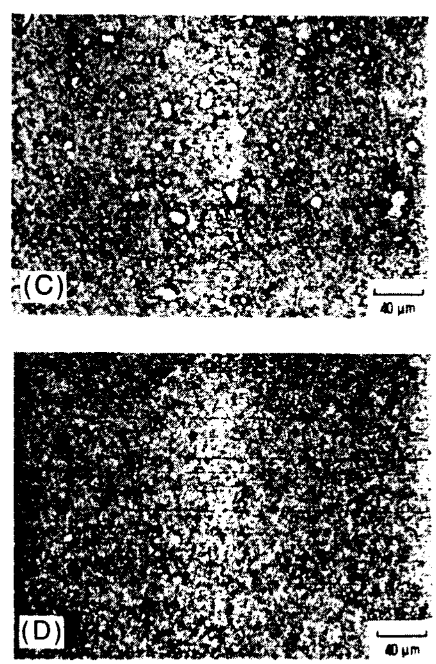


Fig. 4. Structure of (A) as-received silicon powder, (B) silicon powder wet-milled in ceramic attrition mill, (C) as-received silicon nitride, and (D) silicon nitride milled for 6 h.

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any, of this addition on the properties of RBSN is not known. As expected, no change in iron content was observed.

With silicon nitride, the carbon, oxygen, and yttrium content increased significantly. As with Si powder the oxygen and carbon pickup relate to increased surface area and reaction with the milling fluid (ethyl alcohol in this case). The appreciable yttrium content in the Si_3N_4 powder indicates that wear of the media was much higher than with the milling of Si powder. This result is not unexpected since Si_3N_4 powder is considerably harder and more abrasive than Si powder. The Y content correlates with the weight loss observed for the milling media and represents a Y_2O_3 content of approximately 0.2 wt% in the milled powder.

Figure 4 shows the fine Si and Si_3N_4 powders produced after 6 h of milling time. Surface area measurements indicate an average equivalent spherical particle diam. of 0.28 and 0.17 micrometer, respectively, for the Si and Si_3N_4 powders. It is believed that these powders have potential for use in the preparation of reaction-bonded Si_3N_4 and sintered Si_3N_4. Ceramic attrition mill grinding represents an improved method of rapidly preparing fine pure powders for use by the ceramic industry.

Acknowledgment

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