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NASA Technical Memorandum 86974

Parametric Evaluation of Ball Milling of SiC in Water

(NASA-TM-86974) PARAMETRIC EVALUATION OF BALL MILLING OF SiC IN WATER (NASA) 17 p HC A02/MF A01 CSCL 11G
N85-21356
Unclas
G3/27 14534

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Prepared for the
Ninth Annual Conference on Composites and Advanced Ceramic Materials
sponsored by the American Ceramic Society
Cocoa Beach, Florida, January 20-23, 1985

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E-2399

SUMMARY

A statistically designed experiment was conducted to determine optimum conditions for ball milling α-SiC in water. The influence of pH adjustment, volume percent solids loading, and mill rotational speed on grinding effectiveness was examined. An equation defining the effect of those milling variables on specific surface area was obtained. The volume percent solids loading of the slurry had the greatest influence on the grinding effectiveness in terms of increase in specific surface area. As grinding effectiveness improved, mill and media wear also increased. Contamination was minimized by use of sintered α-SiC milling hardware.

INTRODUCTION

Silicon carbide (SiC) is being considered for various applications in high-temperature energy conversion systems, vehicular engines such as gas turbines, and industrial heat exchangers (refs. 1 to 4). Sintered SiC exhibits high flexural strengths from room temperature to above 1400 °C, excellent erosion, oxidation, and corrosion resistance, and good thermal stress resistance (refs. 1, 3, and 5). In addition, SiC has a lower density than superalloys which leads to lower inertia in moving parts such as turbine rotors (ref. 6).

Economical processing techniques are needed for the production of dense, high strength, complex SiC shapes (ref. 7). The pressureless sintering of SiC powder through the use of additives such as B, C, and Al is an inexpensive process that is applicable to the formation of such components. Pressureless sintering of α-SiC requires submicron-sized powder (refs. 8 to 10). Ball milling has been used to reduce the average particle size of Si_3N_4 powder to a submicron level with a minimum amount of property-degrading impurity pickup (ref. 11). Ball milling should be applicable to the problem of reducing the particle size of commercially available SiC. The increase in the impurity content of the milled powder resulting from mill and media wear would be minimized by using SiC grinding hardware.

The variables associated with ball milling have been reported by Quatinetz and are as follows (ref. 12):

(1) Type and amount of grinding (suspending) fluid

(2) Amount of powder charge

(3) Characteristics of the powder charge

(4) Grinding aids

(5) Type and amount of media

(6) Size, material, and construction of the grinding mill

(7) Rotational speed of the mill

(8) Grinding time

The type of suspending fluid, the liquid/powder charge ratio, the nature of the powder, and the modification of the grinding fluid through pH adjustment or the use of grinding aids will determine the rheological properties of the slurry. The amount of slurry, the slurry viscosity, the size and density of the milling media, the amount of media, the mill dimensions, and the rotational speed of the mill will affect the amount of energy imparted to the powder and therefore influence the grinding efficiency. Overall, it is expected that the particle size will decrease with increased milling time until an equilibrium situation is reached where the rate of particle breakage is equaled by the rate of reagglomeration (ref. 13).

SiC is conventionally cast from an aqueous slip (ref. 7). Therefore, milling SiC in water could eliminate the need to dry the milled powder prior to slip preparation. The purpose of this study was to determine optimum milling conditions through an examination of the influence of the liquid/powder charge ratio (volume percent solids loading), slurry pH, and mill speed on the grinding effectiveness of α-SiC ball milled in water using SiC milling hardware.

The authors wish to thank M. Millard for his technical assistance in planning the central composite design and statistically analyzing the data.

EXPERIMENTAL PROCEDURE

The α-SiC powder used in this study had the composition shown in table I. The "as-received" powder was riffled in order to eliminate any sample variation that might have occurred due to material segregation during shipment and storage.

Sintered SiC jar mills[1] and media[1] were used for ball milling. The average mill had a volume of 1.5 L and an 11.2 cm i.d. The milling media were 1.25 by 1.25 cm cylinders. Compositions of the mills and media are shown in table I. The ratio of media volume to the milling slurry volume was held constant with media filling 25 vol % of the mill and the slurry occupying 38 vol %.

A central composite design (ref. 14), as shown in figure 1, was used to examine the influence of mill speed, solids (powder) loading, and pH adjustment on grinding effectiveness. The experiments that were performed are given in table II. The order in which tests were performed was randomized. Mill rotational speed, ω, was varied from 68 to 92 rpm, which is 54 to 73 percent critical speed. The critical speed, ω_{crit}, is the rotational speed at which the media would begin to centrifuge in the absence of a milling slurry. This rotational speed (in rpm) is related to the inner mill radius, r (in cm), as shown in equation (1) (ref. 15).

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[1] The Carborundum Company, Niagara Falls, NY.

$$\omega_{crit} = \frac{299}{\sqrt{r}} \quad (1)$$

The solids loading of the slurries ranged from 10 to 30 vol %. Initial slurry pH ranged from 8.0 to 11.4. All slurries were milled for 144 hr.

SLURRY PREPARATION

Alpha-SiC powder was dried, weighed, and mixed with distilled water in a polyethylene bottle containing ten pieces of SiC media. The pH of the slurry was increased with ammonium hydroxide and the slurry was tumbled for 20 hr at 80 rpm. Additional pH adjustments were made with ammonium hydroxide or nitric acid and the slurry was tumbled until the pH equilibrated. The slurry was then combined with milling media in a jar mill and the mill was sealed with a neoprene rubber cap.

ANALYSIS

Samples of the slurry containing 6 g of powder were removed from the stopped mill with a glass syringe at 24, 72, and 144 hr and the pH of the slurry was measured. The samples were air-dried in glass Petri dishes and crushed in an agate mortar.

Dilute samples of powder optimally-dispersed in water were analyzed for particle size distribution and specific surface area, S, was calculated using the Microtrac Small Particle Analyzer.[1] TEM was used to examine the particle shape of milled and as-received SiC powder.

Trace impurities present in the starting powder were quantified at an accuracy of ±10 percent by the Inductively Coupled Plasma (ICP) Atomic Absorption Emission Spectrometer. Milling hardware impurity levels were furnished by the supplier. Oxygen and nitrogen content of the milling hardware and SiC powder were determined by fusing the sample, converting the O to CO_2, separating the CO_2 and N_2 on a chromatographic column, and measuring the amount of CO_2 and N_2 with a thermal conductivity detector. Free carbon content was determined by heating the sample in a resistance tube furnace and measuring the evolved CO_2. Values are reported at an accuracy of ±5 percent for oxygen, nitrogen, and free carbon content.

RESULTS AND DISCUSSION

Selection of Milling Conditions

Preliminary experiments indicated that slurries containing more than 30 vol % solids did not mill effectively, i.e., the observed rate of increase in specific surface area was very low. The lower limit of solids loading (10 vol %) was chosen in order to avoid large amounts of contamination from excessive mill and media wear. The range of pH conditions was chosen because

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[1] Leeds and Northrup, St. Petersburg, Florida.

a viscosity minimum exists for the SiC and water system between pH 9.0 and 11.5. Mill speeds were chosen in the range 54 to 73 percent critical speed where it was anticipated that optimum grinding effectiveness would be achieved.

Data Analysis

The influence of solids (powder) loading, slurry pH, and mill speed on the grinding effectiveness of α-SiC ball milled in water was determined from the examination of samples obtained using the central composite design. In this design six duplicate test runs were performed under milling conditions of pH = 9.7, 80 rpm, and 20 vol % solids loading. The average specific surface area of powders milled under these conditions for 144 hr was 9.4 m^2/g with a standard deviation of 0.1 m^2/g. This indicates that the grinding experiments and particle size analyses were very reproducible. The specific surface area values of powders that had been milled for 144 hr ($\overline{S}_{144h}$) were combined with the appropriate milling experiment variables (see table II) and analyzed using a MINITAB[1] least squares regression analysis program. An equation defining the influence of initial slurry pH (pH_i), mill speed (ω), and volume percent solids loading (L) on $\overline{S}_{144h}$ was obtained (eq. (2)).

$$\overline{S}_{144h} = 21.1 - 0.953(pH_i) - 0.798(L) + 0.06(pH_i \times L) + 0.0025(pH_i \times \omega) \quad (2)$$

For this equation all of the variables were significant, $R^2 = 0.96$, and the standard deviation of $\overline{S}$ about the regression line was low (s = 0.2428).

Equation (2) can only be used to predict $\overline{S}_{144h}$ for this specific powder. The equation is only valid within the range of milling conditions that are bounded by a sphere which has axes that are defined as follows: pH = 8 to 11.4, rpm = 68 to 92, and loading = 10 to 30 vol %. However, an examination of the coefficients and variables of equation (2) provides information that should be applicable to the milling of other types of SiC under different milling conditions.

Effect of Initial Slurry pH, Mill Speed, Volume Percent Solids Loading, and Milling Time

Equation (2) indicates that $\overline{S}_{144h}$ increases, and thus, grinding effectiveness improves, as volume percent solids loading is decreased and mill speed is increased. In addition, there are interaction effects between slurry pH and solids loading, and between slurry pH and mill speed. The first interactive effect is probably due to the combined influence of pH and loading on slurry viscosity and particle dispersion. At high volume percent solids loading (~26 vol %), increasing the pH from 8.7 to 10.7 significantly improves the grinding effectiveness as shown in table III. At lower volume percent solids loading (≤14 vol %) a similar increase in pH has little or no influence on grinding effectiveness. This phenomenon is attributed to the decrease in the effect of pH on viscosity as solids loading decreases. The interactive effect between pH and mill speed is probably the result of an interaction between slurry viscosity and mill speed. This influences the cataracting and

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[1] Statistics Department, Pennsylvania State University

cascading motion of the media within the milling jar. Overall, the effect of volume percent solids loading of the slurry has the greatest influence on the grinding effectiveness and milling speed has the least influence.

The greatest amount of particle size reduction occurred at pH = 9.7, mill speed = 80 rpm, 10 vol % solids loading, and 144 hr milling time (see table II). This grinding effectiveness resulted from a combination of low solids loading and good dispersion providing a low viscosity milling slurry. As the volume percent solids loading of the slurries was increased (with pH = 9.7 and mill speed = 80 rpm) the viscosity of the slurries increased and the grinding effectiveness decreased as indicated in figure 2. Powders milled in slurries consisting of 10, 20, and 30 vol % solids loadings had final specific surface areas ($\overline{S}_{144h}$) of 11.6, 9.5, and 7.0 m^2/g, respectively. The grinding rate (change in $\overline{S}$ with time) of the 10 and 20 vol % solids loading slurries diminished noticeably after 72 hr of milling and the average particle size approached a constant value (fig. 3). This indicates that there is a practical grinding limit for the ball milling of α-SiC in water. Similar decreases in grinding rate were observed in every test run except those exhibiting very low grinding effectiveness (e.g., the 30 vol % solids loading slurry).

Differential particle size distribution analyses of the as-received α-SiC powder and powder milled for 24, 72, and 144 hr under conditions of pH = 9.7, 80 rpm, and 10 vol % solids loading are shown in figure 4. The starting powder exhibited a broad particle size distribution having a 90 to 10 percentile range of 5.4 to 0.4 µm, a specific surface area of 6.2 m^2/g, and an average particle diameter of 2.3 µm. The particle size distributions became narrower and the amount of particles having a diameter ≤ 1.0 µm increased with milling time. The powder that had been milled for 144 hr had a 90 to 10 percentile range of 1.3 to 0.3 µm, a specific surface area of 11.6 m^2/g, and an average particle diameter of 0.7 µm. The particle size and shape of the as-received α-SiC powder and the powder milled to a specific surface area of 11.6 m^2/g are shown in figure 5. The as-received powder consisted of angular, blocky flakes of α-SiC. Particle size as observed by transmission electron microscopy (TEM) ranged from 0.03 µm to over 25 µm. The milled powder, which had a similar morphology, consisted of particles that ranged in size from 0.02 to 3.0 µm.

Change in Slurry pH During Milling

Prior to milling, the pH of each slurry was adjusted until the pH equilibrated. The slurry pH was monitored during milling, but no further adjustments were made. As shown in figure 6, the pH varied differently with time depending upon the initial slurry pH (pH_i). When pH_i was ≥ 9.7, the decrease in pH during milling was slight and these slurries remained fluid. A more pronounced decrease was noted when pH_i was ≤ 8.7. The viscosities of high solids loading (25.9 vol % solids) slurries adjusted to pHi = 8.7 increased noticeably during the 144 hr of milling. This presumably caused a decrease in grinding effectiveness. The observed change in pH was independent of solids loading.

The decrease in slurry pH during grinding was the result of hydrolysis of the SiC powder which can occur by the following reaction (ref. 16)

$$SiC(s) + 4H_2O(\ell) \rightarrow Si(OH)_4(\ell) + CH_4(g) \qquad (3)$$

The formation of silicic acid ($Si(OH_4)$ causes the slurry to become more acidic. High pH slurries ($pH \geq 9.7$) were affected to a lesser extent than low pH slurries ($pH \leq 8.7$).[1]

Impurity Pickup

Slurries containing an average of 350 g of α-SiC powder dispersed in water were milled for 144 hr. The average mill weight loss was 2.9 g and the average media weight loss was 6.5 g. Milling conditions that provided the most effective grinding were accompanied by high amounts of mill and media wear, whereas low amounts of milling hardware degradation occurred under poor milling conditions.

The milling of four slurries having 14.1 vol % solids loadings led to average mill and media weight losses of 4 and 11.3 g, respectively. Conversely, the grinding of four slurries having 25.9 vol % solids loadings resulted in mill and media weight losses of 2.5 and 3.3 g, respectively. The viscosities of the slurries increased with increasing volume percent solids content and grinding effectiveness and mill and media wear decreased. These observations are consistent with conventional milling theory which predicts that high viscosity slurries will give rise to low grinding rates and that slurries exhibiting high fluidity will lead to high levels of contamination from milling hardware degradation (ref. 15).

The free carbon content of the powders increased linearly from 1.9 wt % to a maximum of 2.5 wt % as grinding effectiveness improved. This increase is attributed to the degradation of the neoprene rubber mill cap.

The nitrogen content of powders milled for 144 hr ranged from 0.16 to 0.94 wt %. The majority had nitrogen contents less than 0.25 wt %. Nitrogen content levels apparently increased due to the formation of ammonium nitrate from a reaction between the NH_4OH which was used to increase the initial slurry pH and HNO_3 which was used only when the slurry pH exceeded the desired level.

The oxygen content of the milled powders depended on specific surface area and the amount of nitric acid added during the pH adjustment. In the absence of HNO_3 addition, the oxygen content of the milled powder increased linearly from 0.6 to 1.2 wt % as specific surface area increased from 6.2 to 11.6 m^2/g. When HNO_3 was added, oxygen and nitrogen levels increased which further indicated the presence of ammonium nitrate.

The formation of ammonium nitrate during slurry pH adjustment and milling could be avoided by gradually increasing the pH to the desired level through small additions of NH_4OH. This would eliminate the need for introducing an acid into the slurry.

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[1] A solution of pH = 11 has a hydroxide ion concentration 1000 times that of a solution of pH = 8, and thus, would be affected to a lesser extent by the addition of a given amount of acid.

CONCLUDING REMARKS

An examination of the information obtained from the central composite design indicates that the practical optimum milling conditions (10 vol % solids loading, pH_i = 9.7, and mill speed = 80 rpm) which will provide the maximum increase in specific surface area from 144 hr of ball milling were determined in this study. Equation (2), which relates S_{144} (specific surface area after 144 hr of milling) to the variables mill speed, solids loading, and initial slurry pH, indicates that grinding effectiveness improves as solids loading decreases. It is probable that slurries consisting of less than 10 vol % solids would provide more effective grinding. However, this limits the amount of powder that can be milled in a given time interval and it is probable that increased milling hardware degradation would occur. Further, the equation predicts that when ball milling slurries which contain approximately 10 vol % solids, the initial slurry pH has little effect (within the range pH 9 to 11) on $\overline{S}_{144}$. Finally, since equation (2) predicts that a large increase in mill speed would only slightly increase $\overline{S}_{144}$, a practical optimum mill speed from an energy efficiency point of view was reached near 80 rpm.

The effect of reduced particle size on the sinterability of α-SiC and the feasibility of forming specimens using slurries directly from the mill are currently being examined.

SUMMARY

This study of the ball milling of α-SiC in water yielded the following results:

1. The average particle size of SiC powder was decreased from 2.3 to <1 μm in 144 hr.

2. An equation relating powder loading, initial pH, and mill speed to specific surface area after 144 hr of grinding was obtained using a central composite design.

3. Grinding effectiveness improved as the solids content decreased from 30 to 10 vol % solids loading and the mill speed increased from 54 to 73 percent critical speed.

4. The influence of slurry pH on grinding effectiveness depended on both mill speed and volume percent solids loading.

5. Lower volume percent solids content resulted in greater mill and media degradation.

6. A practical grinding limit for ball milling SiC in water was indicated.

7. The slurry pH decreased with milling time.

8. In general, oxygen content of the milled powder was proportional to specific surface area.

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TABLE I. - CHEMICAL ANALYSIS OF STARTING SiC POWDER AND MILLING HARDWARE (wt %)

	Free C	O	N	Al	B	Ca	Cr	Fe	Mg	Ti	V
Powder[a,b]	1.9	0.6	0.15	0.015	- -	<0.001	0.004	0.025	<0.001	0.016	0.018
Milling jars and media[c]	1.0	.03	.04	.1	0.6	.01	.04	<1.0	.01	.04	.006

[a] Hermann C. Starck, Berlin - Type I α-SiC.
[b] Specific surface area of 6.2 m^2/g.
[c] The Carborundum Company, Niagara Falls, NY. Trace impurity analysis furnished by supplier.

TABLE II. - CENTRAL COMPOSITE DESIGN AND SPECIFIC SURFACE AREA OF SiC POWDER MILLED FOR 144 HR ($\bar{S}_{144h}$)

X_1	X_2	X_3	Initial slurry pH X_1	Mill speed, rpm, X_2	Volume percent solids loading, X_3	$\bar{S}_{144h}$,[a] m^2/g
-1	-1	-1	8.7	73	14.1	10.4
-1	-1	1	↓	73	25.9	7.6
-1	1	-1	↓	87	14.1	10.7
-1	1	1	↓	87	25.9	7.3
1	-1	-1	10.7	73	14.1	10.6
1	-1	1	↓	73	25.9	8.8
1	1	-1	↓	87	14.1	10.9
1	1	1	↓	87	25.9	9.2
-1.682	0	0	8.0	80	20	8.6
1.682	0	↓	11.4	80	↓	10.2
0	-1.682	↓	9.7	68	↓	9.4
0	1.682	↓	↓	92	↓	10.3
0	0	-1.682	↓	80	10	11.6
0	0	1.682	↓	80	30	7.0
[b]0	0	0	[b]9.7	80	20	[c]9.4

[a] Specific surface area of starting powder = 6.2 m^2/g.
[b] Six replications performed under these conditions.
[c] Average of six duplicate runs.

TABLE III. - PREDICTED[a] EFFECT OF VOLUME PERCENT SOLIDS LOADING, MILL SPEED, AND INITIAL pH (pH_i) ON SPECIFIC SURFACE AREA OF SiC POWDER MILLED FOR 144 HR ($\bar{S}_{144h}$)

Volume percent solids loading	Mill speed, rpm	$\bar{S}_{144h}$ (m^2/g), when pH_i = 8.7	$\bar{S}_{144h}$ (m^2/g), when pH_i = 9.7	$\bar{S}_{144h}$ (m^2/g), when pH_i = 10.7
14.1	73	10.5	10.6	10.7
14.1	87	10.8	10.9	11.0
20	73	8.9	9.3	9.7
20	87	9.2	9.7	10.1
25.9	73	7.3	8.0	8.8
25.9	87	7.6	8.4	9.2

[a] Values calculated using Eq. (2).

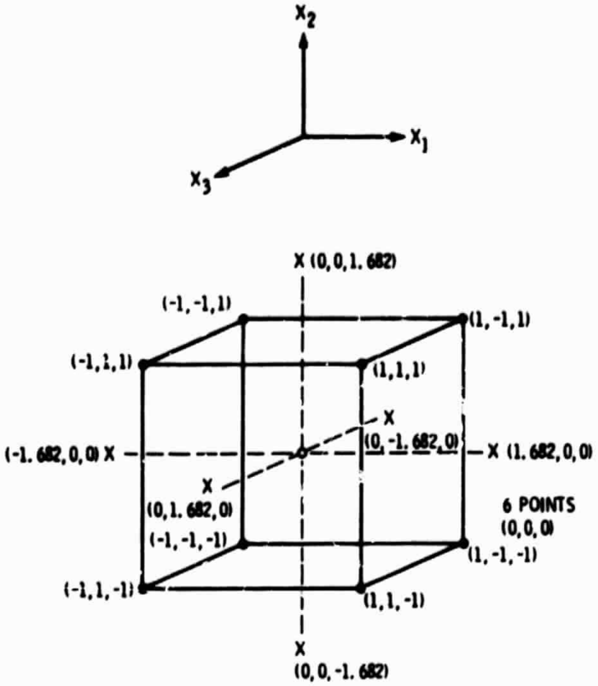

Figure 1. - Representation of central composite design where X_1 = initial slurry pH, X_2 = mill speed, and X_3 = volume percent solids loading.

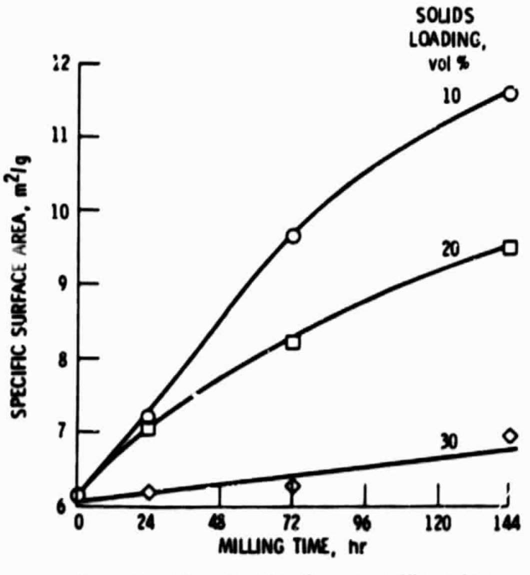

Figure 2. - Effect of milling time on specific surface area of SiC for various solids loadings (pH of 9.7, mill speed = 80 rpm).

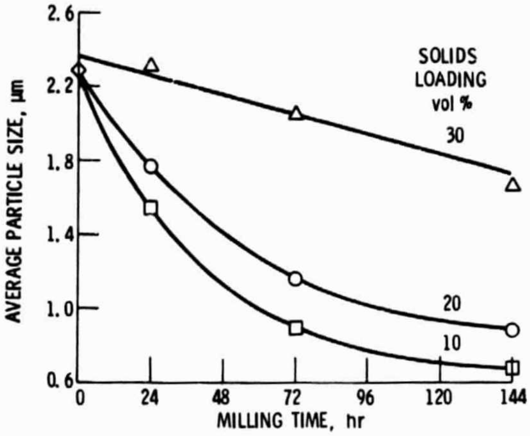

Figure 3. - Effect of milling time on average particle size of SiC for various solids loadings (pH of 9.7, mill speed = 80 rpm).

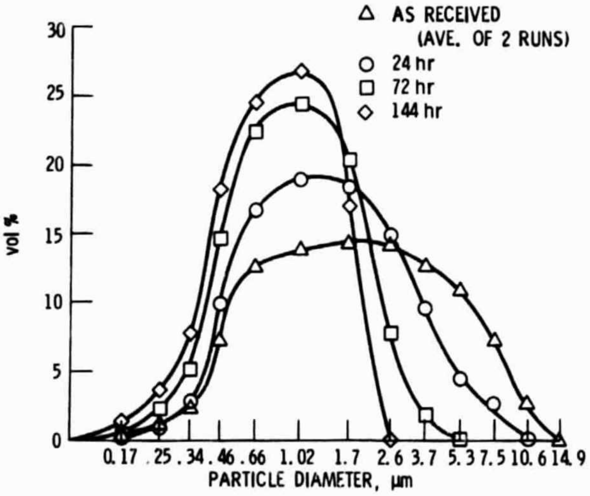

Figure 4. - Differential particle size distributions of the starting α-SiC powder, and powder milled for 24, 72, and 144 hr under grinding conditions of pH = 9.7, mill speed = 80 rpm, and 10 vol % solids loading.

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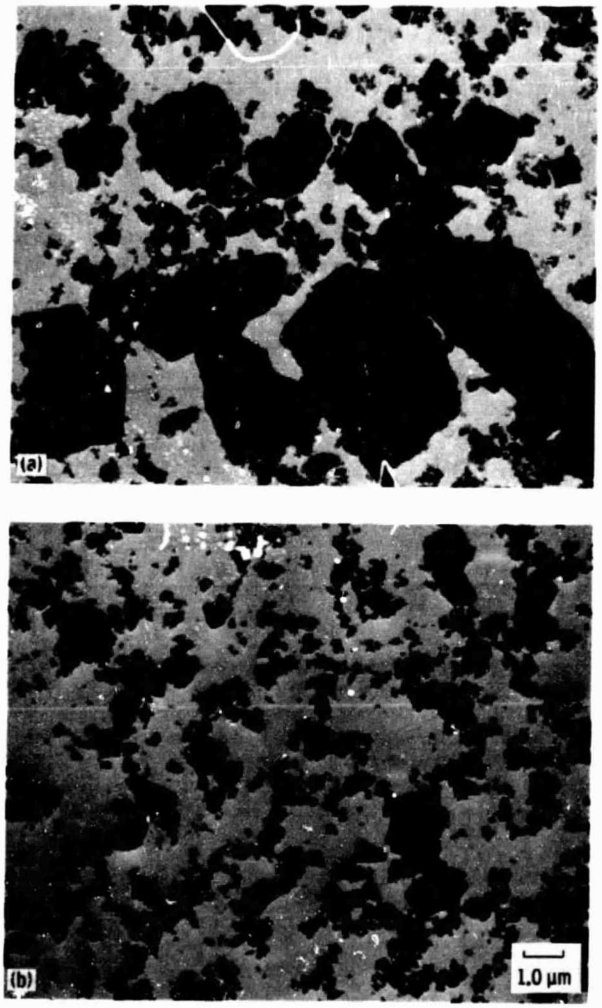

Figure 5. - Transmission electron micrographs of (a) starting α-SiC powder and (b) powder milled to a specific surface area of 11.6 m^2/g under grinding conditions of pH = 9.7, mill speed = 80 rpm, 10 vol % solids loading, and time = 144 hr.

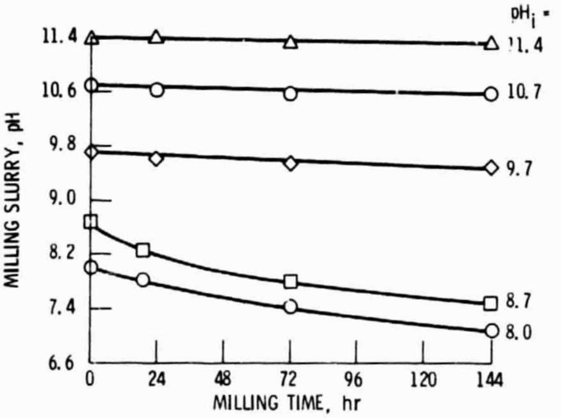

Figure 6. - Effect of milling time on slurry pH for various initial pH (pH_i) values. The pH values shown represent an average slurry pH, which was calculated using the pH data from all of the tests performed at a specific pH_i.