Grinding Kinetics and Media Wear during Attrition Milling

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Effects of media size, density and hardness on attrition milling separately a grinding-resistant Bayer-process alumina powder and a much-less-resistant barium titanate powder were investigated. Milled powders were characterized in terms of the particle-size distribution, specific surface area (titanate) and media wear contamination.

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Introduction

Three types of mills commonly used for comminuting slurried powders to a micron size are ball mills, vibratory mills and planetary attrition mills. Ball milling is commonly used for high-capacity grinding and for the dispersion of agglomerates when a minimum of damage to particles or additives is required. Vibratory mills of low to medium capacity are widely used for grinding and dispersing particles in slurries for technical ceramics; grinding rates are faster than in ball milling because of the higher frequency and three-dimensional nature of the impacts[1]. The planetary attrition mill, also called an attritor or a stirred media mill, is also used for milling powder for advanced ceramics. It has been reported that the attritor produces the finest product for a fixed energy input[2]. Operated at a low rotor speed, its grinding action can imitate that of a ball mill, but at a higher rotor speed, the much higher power input per unit volume of media significantly increases the grinding kinetics[3].

Fine grinding generally produces more rapidly when the powder is a deflocculated slurry because chemical dispersion augments physical dispersion and grinding. The energy efficiency in dry grinding is commonly lower because mechanical forces must overcome surface forces that cause a cushioning of impacts. Slurry viscosity is also important because mobility of the particles on the media should not be high.

Grinding is one unit operation in powder processing that needs to be better understood and more carefully documented. Relatively little has been published about the operational parameters influencing the grinding kinetics and the media wear in attrition milling or the powder characteristics developed.

A laboratory stirred media attrition mill was used for this research. Objectives of this research were to (1) study particle size reduction rates and particle size distributions as a function of slurry and mill parameters when milling a grinding resistant alumina, (2) identify the parameters which control media wear in attrition milling and (3) discern differences when milling a less-grinding-resistant barium titanate powder and identify parameters enabling dispersion to a submicron size with minimal contamination.

The Attrition Mill

The stirred media attrition mill was developed over 40 years ago and is reported to be one of the most efficient fine-grinding and dispersing devices available today for ceramic materials[2]. A key to its efficiency is that the power input is used directly for agitating media for grinding and is not used for rotating or vibrating a large, heavy vessel in addition to the media charge. The material to be ground is placed in the stationary tank with the grinding media and the powder, and the media are agitated by a rotating central shaft with arms. The rotating arms exert sufficient stirring action to force the grinding media to move randomly through the entire tank. The rotating arms cause the irregular movement by exerting (1) impact action on neighboring media which collide with other media, (2) rotational (shear) forces on the media, and (3) impact forces on the media fall into the void left by the arms[5]. For efficient fine grinding both impact and shearing forces should be present.

The griding energy produced during milling is proportional to the product of the mass and the change in linear and rotational velocity of the media. The mass is larger when the media are of a larger size and/or density. The change in velocity depends on the differential velocity of the media produced by the action of the mill, directions of impacts and the elastic moduli of the media and particles in the impact zone. A higher slurry viscosity can reduce particle mobility, effectively holding particles in the impact zone, but can reduce the differential velocity and the effective modulus by a cushioning mechanism. For minimum wear, media should be harder than the particles being ground; microstructural parameters such as grain size, porosity, surface smoothness and toughening can be expected to influence wear.

Particle fractures are influenced by microscopic flaws and surface roughness, and, accordingly, particle characteristics have an important role in the grinding kinetics. Submicron particles have very small flaws and are relatively strong and grinding resistant, especially if they are single crystals. Size reduction by rubbing (attrition) may be relatively more important for aggregated materials. Whereas media size and/or density are increased in ball or vibratory milling to increase impact forces, in the attrition mill the rotor speed can be increased to increase both the impact force and the frequency of impacts. The frequency of impacts also depends directly on the media contacts/volume and, accordingly, varies inversely with the size of the media. In the attrition mill, the grinding energy and the frequency of impacts can be controlled somewhat independently because, when using smaller media, the rotational speed can be increased to maintain the grinding energy. The potential for using smaller media effectively is higher in attrition milling.

The demand of the ceramics industry for materials of higher purity is increasing, and low impurity levels are now requisite for most high-performance ceramics. An advantage of the planetary attritor is that most of the grinding action occurs in a region extending to two-thirds of the radius; this permits the use of tank linings with polymer coatings and a relatively long service life. Wear of the rotor is much more severe, and the arms are commonly made from a very wear-resistant ceramic or a low-friction polymer material. It is reported that 90% of the powder contamination will come from wear of the grinding media, and selection of the media is most important[6]. For attrition milling to be cost effective, the optimum media size and composition must be established for each system. Media of the same composition as the particles may be used, but the possibility of particle-size contamination from the media wear must be recognized.

Experimental Procedure

Two laboratory stirred media mills (Union Process, Inc., Akron, OH) differing in power capacity were used in this research; the 750ml tank and rotor were interchangeable and were not varied. The shaft of the rotor was 17.8cm in length, 1.6cm in diameter (with a polyethylene coating), and the arms were 5.1cm in length and 0.71cm in diameter. Rotational speed could be varied up to a maximum of 1,000 rpm. The water-cooled tank was coated with ethylene tetrafluoroethylene copolymer with high abrasion and chemical resistance. Effects of media variables on the grinding of alumina were evaluated using the following media: 4.76- and 6.35mm regular zirconia (Zircoa, Inc., Solon, OH), 6.35- and 1.11mm toughened zirconia media (Zycron, Corning Inc., Corning, NY), 6.35mm alumina (Arleite, Ferro Corp., Cleveland, OH) and 6.35mm case-hardened steel (Union Process, Inc., Akron, OH).

The 250mL slurries containing 30, 40 or 50 vol% calcined alumina (A-14 Alumina, Alcoa, Inc., Bauxite, AK) were initially stirred into distilled water containing 4 wt% (powder basis) of ammonium polyacrylate deflocculant (821 A, R.T. Vanderbilt, Inc., Norwalk, CT). Each was milled at 200 (slow), 550 (medium) and 900 rpm (fast) rotor speed using untoughened zirconia media of 4.76mm diameter. The apparent viscosity was measured at 60 rpm using a rotating spindle viscometer (Model LV, Brookfield Labs, Inc., Stoughton, MA) and the pH was measured after 15, 30, 60, 120 and 240 min. The temperature of the slurry was monitored during milling.

Particle-size distributions were determined by centrifugal sedimentation analysis (CAPA 500. Horiba Instruments, Inc., Irvine, CA) using a portion of the sample withdrawn for viscosity testing. Each sample was analyzed three times to check for instrument precision and sampling error.

The amount of zirconium media wear contamination in the alumina powder was determined by standard wet chemical analysis. A dried 1g sample of milled powder was heated in concentrated sulfuric acid for several hours, diluted, and held at the boiling point for 1 hour. An excess of ammonium hydrogen phosphate was added to a filtered solution, and the zirconia content was determined gravimetrically from the zirconium phosphate precipitate.

The comparative effects using other media were determined by milling only slurries containing 50 vol% alumina. All analyses were performed as described above except that the media wear was determined by weighing the media charge before and after each milling time. The surfaces of the media before and after milling for 240 min were examined using standard scanning electron microscopy (SEM) techniques.

A high purity, calcined barium titanate powder (Transelco Division, Ferro Corp., Penn Yan, NY) for electronic applications was also attrition milled to discern differences when milling a powder of much lower hardness than alumina. Media used were either 6.35 or 1.11mm toughened zirconia. The target specification for the milled titanate was a mean particle size of 0.5 to 0.6mm, a specific surface area of approximately 3.5 m2/g and ≤0.2% zirconia media contamination, with no chemical deflocculant present. The 250mL slurries containing 20 and 30 vol% titanic powder were milled without deflocculant at 600 rpm. Also, slurries containing 30 and 45 vol% powders were milled with 2 wt% polyacrylate deflocculant at 600 rpm to discern chemical dispersion effects (the appropriate deflocculant level was determined from preliminary viscosity measurements). The particle-size distribution and zirconia contamination were determined as described above. Specific surface area was determined by standard cryogenic nitrogen adsorption. Phases present in the as-received and milled titanate powder were determined by automated X-ray diffractometry (XRD) using CuKa radiation. The analysis was performed from 10° to 70° 20 at a step width of 0.05° with 2 s/step. Computer analysis was used to locate and analyze diffraction peaks for barium titanate.

Results and Discussion

Alumina Powder

Size analysis of the as-received alumina powder indicated a lognormal size distribution with geometric mean size (50% size) of 6.2µm and a geometric standard deviation of 1.6. Size results for milled powders indicated that a lognormal size distribution was maintained and that the geometric standard deviation was changed only slightly.

Figure 1 is an example of the decrease of the decrease in mean size with milling time for 900rpm. Milling at a high speed significantly increased the grinding rate and concentration of submicron particles, but submicron mean size was not achieved after 4 h because of the extreme resistance to grinding. Milling at 200rpm at this high solids loading reduced the mean particle size only perceptively after the initial particle aggregates were dispersed (30 min); milling at this speed was comparable to ball milling.3 Clearly the milling rate depends on the microstructure as well as the phase hardness of the particles.

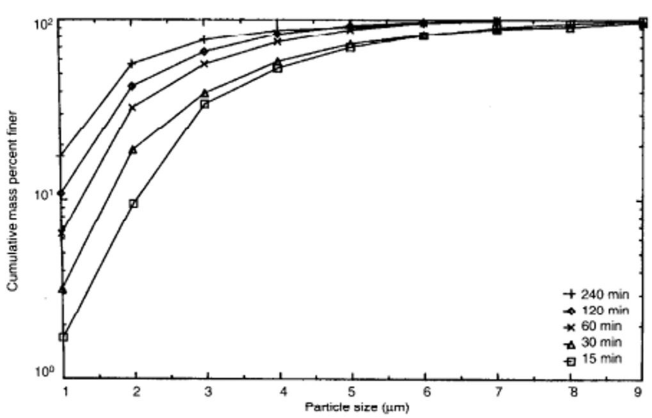

Figure 1

Particle-size distributions for the 50 vol% alumina milled using 4.76 mm zirconia media at 900 rpm.

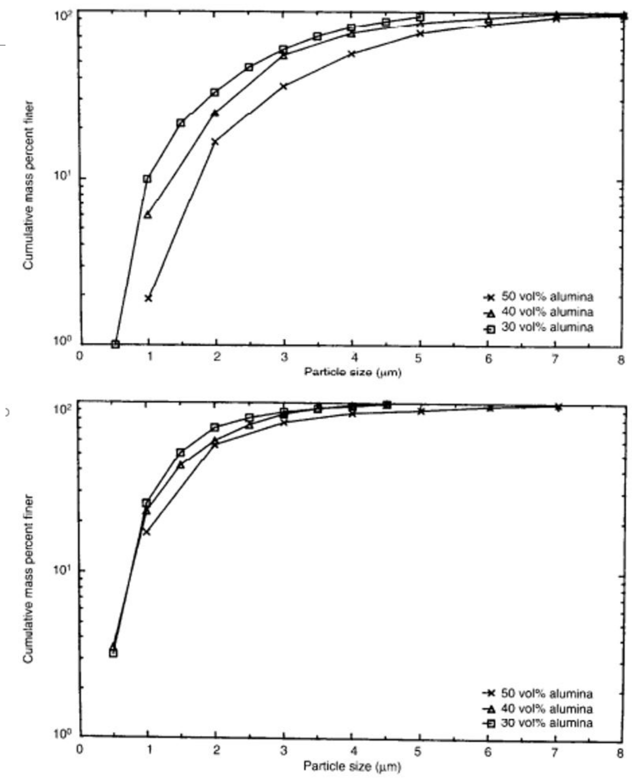

Figure 2

Dependence of size distribution on powder loading in alumnia slurry after milling 4 h: (A) 200 and (B) 900 rpm.

Powder solids loading is also an important variable (**Figure 2**). Compared to the lowest solids loading of 30 vol.%, milling for 4 h at 900rpm at the highest loading size of 50 vol% produced a mean size that was about 17% larger. The average geometric standard deviation was 1.6 after milling at 200 and 550rpm and 1.7 after milling at 900rpm, which indicates that the size dispersion changed only slightly when the milling conditions were altered. As indicated in **Figure 2** (B), the upper size limit was significantly reduced, but all distributions appeared to approach a lower size limit of approximately 0.4µm.

Because water circulated through the tank, the slurry temperatures remained very constant during milling. The apparent viscosity (~ 150 mPa-s at a shear rate of 79 s-1) first decreased for all then increased with milling time. Possible causes for the increase at the higher rotor speeds are the degradation of the deflocculant and a chemical change at the surface of the alumina particles. The pH of 8 of the slurries increased with time to <9 and at a greater rate when a faster rotor speed was used. The increasing pH most likely indicates an exchange of II* for Na+ leached from the fracture surfaces.[7] Attrition milling effectively "scrubs" particle surfaces.[8] The decrease in viscosity during the first 30 min of milling is probably a consequence of dispersing aggregates in the initial powder.

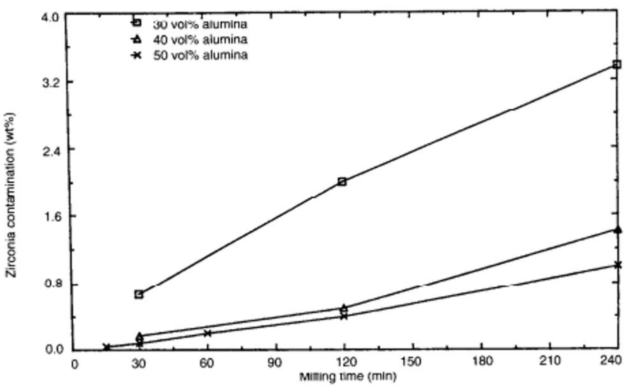

Figure 3

Dependence of media wear on milling time for different powder loading (4.76 mm media, 900 rpm)

As expected, media wear increased with milling time and milling speed. Increased slurry solids content reduced the media wear rate. Figure 3 shows that an increase in solids from 30 to 50 vol% reduced the media wear product by about 70%. At the higher powder loading, media were more completely covered with particles, and media-media grinding was reduced. The amount of zirconia impurity as a function of the mean particle size was lowest when milling a slurry containing 50 vol% powder using a rotor speed of 900rpm. This difference is probably due to a difference in the motions of media and the grinding action at the higher rotor speed.

Table I. Mean Size after 4-h Milling*

Zirconia media	$\bar{a}_g$ (µm) 550 rpm	900 rpm
4.76-mm regular zirconia	2.2	1.8
6.35-mm regular zirconia	2.6	2.2
6.35-mm toughened zirconia	2.7	2.3
1.11-mm zirbeads	4.2	3.4

*50 vol% powder in slurry.

The grinding action in the attrition mill was also dependent on the size and hardness of the media. With the exception of the 1.11mm media (zirbeads), the mean particle size of the alumina slurries decreased with increased milling time in a similar fashion. Size distributions were lognormal and the average geometric standard deviation for each mill run was in the range 1.6 to 1.7. Table 1 presents mean particle sizes after milling for 4 hours using zirconia media. At the highest rotor speed, the 4.76mm media produced a smaller particle size than when using 6.35mm media or the zirbeads. These results suggest that there is an optimum media diameter for a particular slurry and powder type. It has been reported that, when using media with a diameter in the range 0.3 to 10mm, the smaller medial will produce faster grinding.[9] The explanation is that the smaller media produce more impact zones per unit mill volume. This observation was substained here in that the grinding rate was greater using 4.76mm rather than 6.35mm media. The zirbeads were ineffective for grinding this alumina; apparently, they were too small in mass for effective grinding after aggregates had been dispersed. Interestingly, milling with the toughened zirconia media of the same diameter and density as regular media produces a slightly larger mean particle size. SEM results discussed below indicated that, after "breaking in" the surface of the toughened media was much smoother, which indicated that the surface effects played some role in the grinding mechanics.

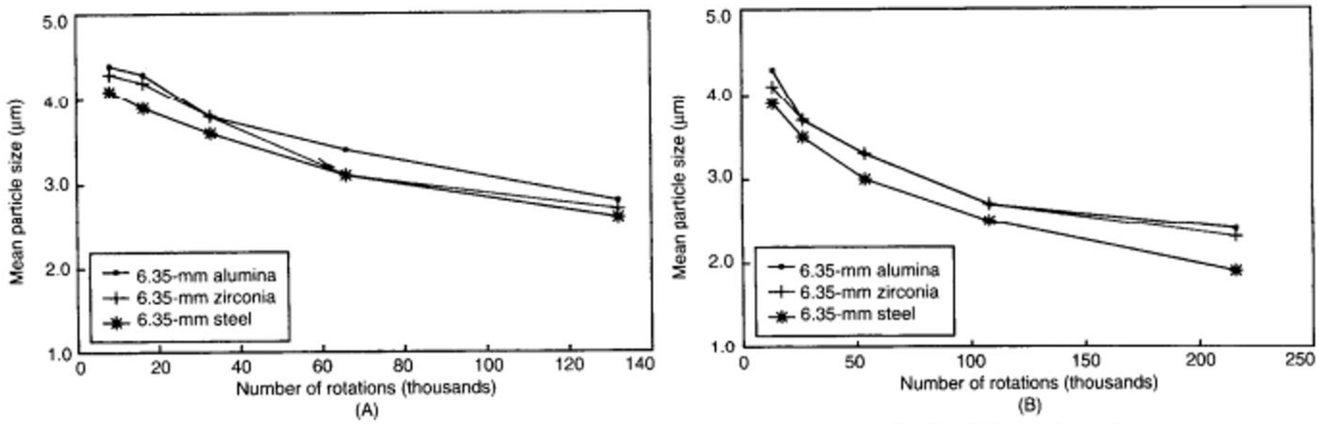

Figure 4

Dependence of mean particle size on number of mill rotations for different media (A) 550 and (B) 900 rpm.

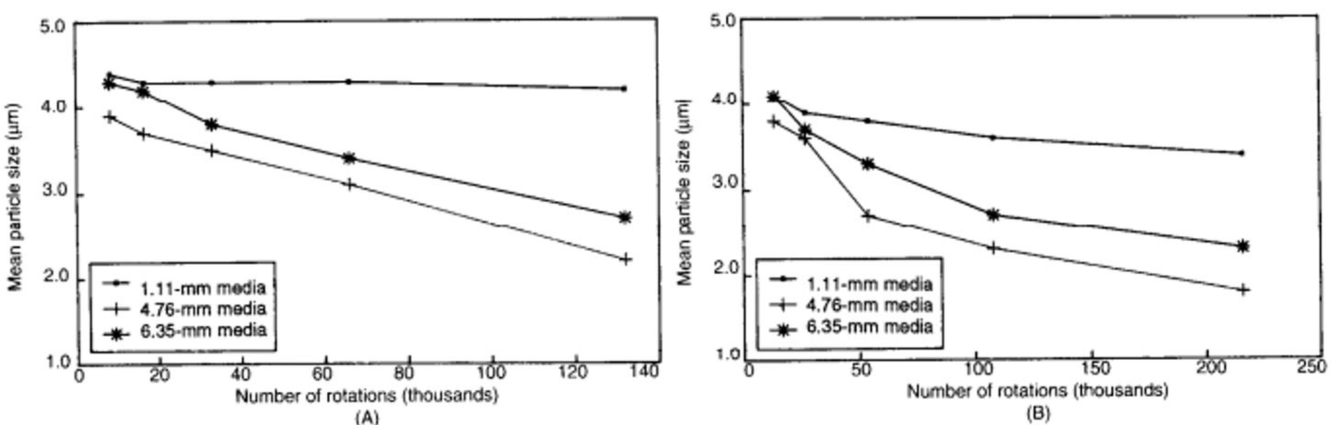

Figure 5

Dependence of mean particle size on number of mill rotations when using zirconia media of different size: (A) 550 and (B) 900 rpm.

Figures 4 & 5 present the decrease in mean particle size with cumulative rotor rotations for different rotor speeds, media densities and sizes. When the results using 6.35mm media were compared, the most dense carbon steel (7.8 Mg/m^3) produced a smaller mean size than zirconia (5.4 Mg/m^3) or alumina (3.6 Mg/m^3), especially at 900rpm. However, grinding with alumina media at 900prm is superior to grinding with steel at 550 rpm in terms of efficiency on a cumulative rotation basis; i.e., increased speed can compensate for the reduced momentum due to a lower media density when using media of the same size. These data do suggest that an onset of greater grinding efficiency may occur at 900rpm using the highest-density media. For the resistant alumina, the size reduction depends on the local grinding energy produced. Since electrical power was not measured, it is not clear if agitation at a higher speed is more energy efficient. The cost of the media and their wear resistance must also be considered to determine the most efficient configuration. Figure 5 shows a significant media size effect on the grinding efficiency. The form of this curve is quite different for the 1.11mm zirbeads, even at 900rpm. This difference is apparently due to the reduced grinding energy effect of these media of low mass, as discussed above. When the 6.35 and 4.76mm zirconia media were used, the efficiency was slightly dependent on the milling speed, but the grinding efficiency was distinctly superior using the 4.76mm media.

An equation that has been proposed to correlate the effect of milling time and rotor speed for a particular configuration is [9]**(time)(speed)$^{1/2}$ = constant (1)**

However, for the grinding of the calcined alumina in this study, the exponent for the rotor speed term is 0.9 to 1.0. The constant on the right side of **Equation 1** depends to a great extent on the media size and to a lesser extent on the media density. For a lognormal size distribution, and an invariant geometric standard deviation, the exponent of 1.0 indicates that the specific surface area increases linearly with milling time if the particle shape remains constant.

Powder contamination from the wear of the media was also of interest for both expense and purity considerations. Powder contamination was largest when grinding with steel media and lowest when grinding with the zirbeads (ineffective). Wear of the alumina media was less than one-half of that of the untoughened zirconia media but slightly higher than that of the toughened zirconia. Media weight loss plotted against media hardness indicated a decreasing trend, as was reported in another study.[10] SEM analysis of as-received and worn media provided information about microstructural factors influencing wear resistance. Dispersed surface pits of =10 µm were observed on as-received alumina media, but after milling the pit population was greatly reduced (surface was much smoother). The surface of the regular zirconia media was much more pitted and rougher, and after milling the surface remained rough with many apparent grain pullouts and relatively few smooth regions. The surface of the toughened media was much smoother as-received with only scattered pits and roughness; after use the surface remained smooth and quite uniform. The surface of the steel media was also very smooth before grinding but appeared to be less smooth after grinding; this change was in contrast to the behavior of the ceramic media. The surface of the zirbeads was very smooth and grain boundaries were evident; after milling the surface was smooth and similar to that for the larger toughened zirconia media. These SEM micrographs show that a wear mode that propagates surface pits and grain pullouts, due to microstructural heterogenicity, significantly shortens media life.

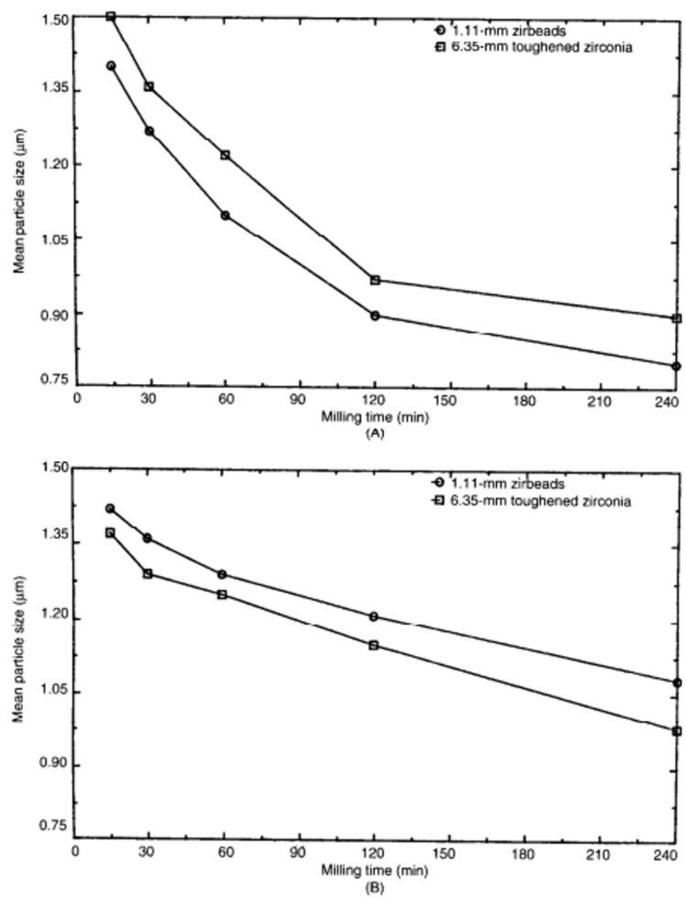

Figure 6

Dependence of mean particle size of barium titanate powder with time and media size: (A) 30 vol% powder, undeflocculated and (B) 45 vol% powder, deflocculated.

Barium Titanate Powder

The mean particle size and specific surface area of the starting powder were 1.7µm and 1.4 m2/g, respectively. Slurries containing different amounts of barium titanate were milled at 600rpm using 6.35 or 1.11mm toughened zirconia media. First, slurries containing 20 and 30 vol% titanate powder were milled without a deflocculant. As first shown in Fig. 6, at this solids loading and the low viscosity of <50 mPa-s, better results were obtained using the zirbeads. SEM analysis showed the titanate particle to be porous, rough aggregates in contrast to the dense alumina particles (Fig. 7). Milling at 20 vol% solids resulted in a smaller mean size than when milling at 30 vol% solids as would be expected.

Next, slurries containing 30 and 45 vol% powder and the deflocculant were milled at 600rpm. When higher powder loading and viscosity were used, significantly better results were obtained with the 6.35mm media. The viscosity was initially below 300 mPa-s and remained at this level when the zirbeads were used; the viscosity rose to over 1,000 mPa-s after 1 hour of milling when the larger media were used. Milling at the 45 vol% level resulted in a mean particle size larger than 1µm after 4 h of milling. These results indicated the importance of coordinating the media size, powder loading and slurry viscosity to maximize grinding efficiency.

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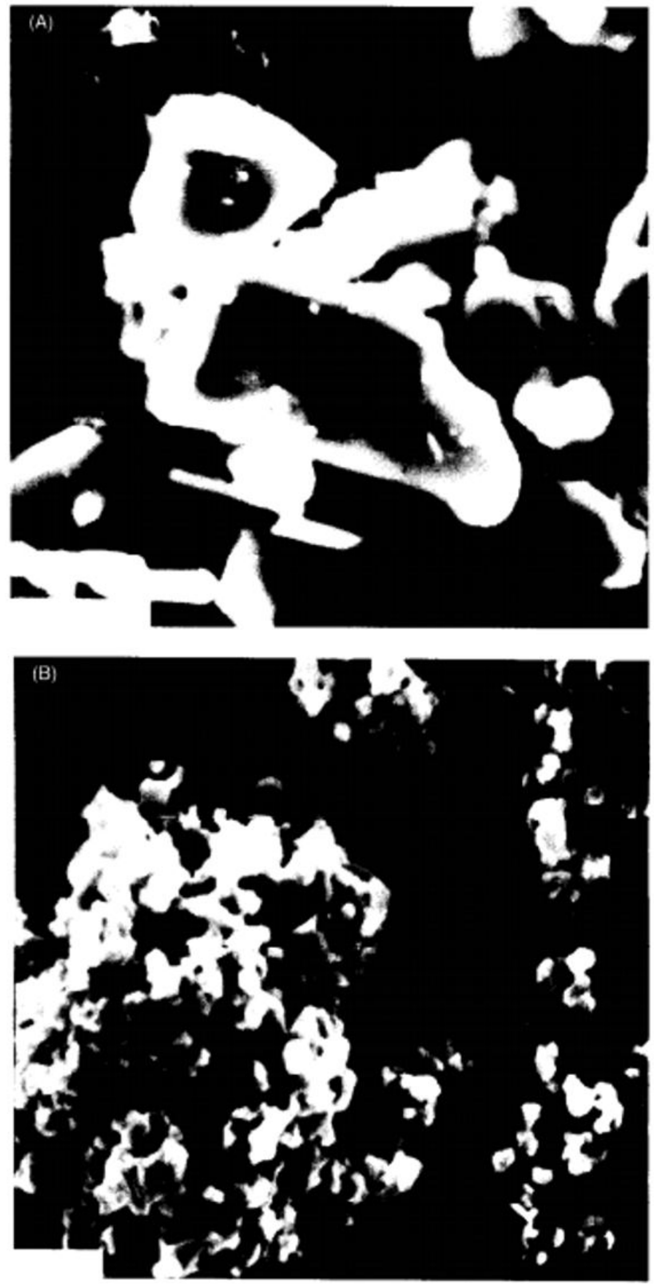

Figure 7

SEM of as-received powders: (A) alumina and (B) titanate (bar=2.5 µm).

An insight into differences in the grinding behavior of the alumina and barium titanate powders can be realized by correlating the dependence of the mean size (ã) with the grinding time (t) using the Charles equation.[3,4,11] Data were plotted in the form

$$\left(\frac{1}{\bar{a}^m}-\frac{1}{\bar{a}_0^m}\right) \text{ vs } t$$

and the value of m that gave a linear relationship was determined. When the toughened 6.35mm media was used, the m value was in the range of 2 to 3 for the barium titanate. The much higher m value for the barium titanate is expected for grinding particles that are porous aggregates.[4]

The increase in specific surface area paralleled the reduction in mean particle size, as expected. The greatest increase occurred for the slurry containing 20 vol% powder milled using zirbeads; the specific surface area of 6.6 m^2/g exceeded the target of 3.5 m^2/g, as did that of all slurries milled at 20 and 30 vol% solids. The temperature remained constant to ± 2° C during the milling. The pH of the slurries without deflocculant was about 11.9 and increased slightly to 12.2 with time; this is explained by the leaching of Ba2+ and the exchange with II+ from the aqueous phase. When ammonium polyacrylate deflocculant was added, the pH was initially 9.9 and increased to 11.7; the lower pH was produced by the polyelectrolyte which had a pH of 7.0.

Figure 8 shows that a higher solids loading significantly reduced media wear contamination when using either size of media. But the wear rate of the 1.11mm media was only about one-tenth of that using the 6.35mm media. Note that this differential was considerably greater than that for the milling of alumina powder and that the zirbeads were very effective in grinding the titanate powder. This difference must have been related to a difference in the collective movements of the smaller media which produce a greater frequency of grinding events but a lower grinding energy. For the weaker porous titanate particles, the rubbing frequency was apparently more effective for grinding, and the lower rate of media wear was a concomitant benefit. XRD results indicated that milling with either size media did not produce a change of phase in the barium titanate lattice.

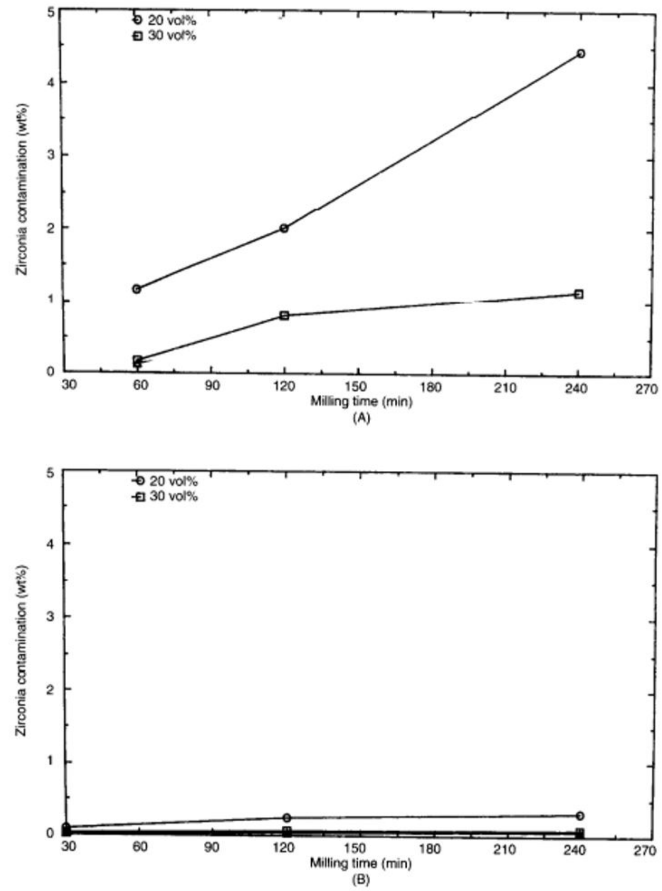

Figure 8

Variation of media wear product with milling time for different powder loadings in slurry: (A) 6.35 mm media, no deflocculent at 20 and 30 vol% and (B) 1.11-mm media, no deflocculent at 20 and 30 vol %

Grinding kinetics for the alumina, indicated by the change in mean size with time, were improved by using a higher milling speed and media of an intermediate size; media density and powder loading had a lesser effect. Grinding efficiency, indicated by the change of mean size with cumulative agitator rotations, indicated that an intermediate media size and higher rotor speed were optimum. Particle-size distribution remained lognormal during milling. Media wear resistance scaled directly with the media hardness/particle hardness and inversely with media size and was also dependent on the surface microstructure and, for zirconia media, transformation toughening. Increased powder loading from 30 to 50 vol% had the effect of reduced media wear by about 70% but reduced the grinding rate by only 17%. Aggregates in the as-received alumina were comminuted at a faster rate than second-generation particles.

The porous titanate powder aggregates were observed to be much less grinding resistant. When the titanate powder was milled, grinding it at a low to medium powder loading in a slurry of relatively low slurry viscosity using 1.11mm media produced the best grinding kinetics with a minimum of contamination from media wear.

Summary and Conclusions

A high-temperature calcined alumina and a lower-temperature, solid-state reacted barium titanate powder were ground in a planetary stirred media attrition mill at slow, medium and fast speeds using aqueous slurries containing different powder loadings. Media of different composition and varying in size, density, hardness and microstructure were evaluated and the viscosity, pH and temperature of the slurries were monitored during the course of milling. Samples were withdrawn during milling to determine the change in particle-size distribution and the effects of changing the milling speed and the slurry and media parameters.

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