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EFFECTS OF SURFACE-CHEMICAL REACTIONS DURING WET MILLING OF ALUMINA

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by

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Presented at
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13. ABSTRACT

Wet ball milling was studied as a method of reducing highly aggregated alumina powders to an ultimate particle condition. The particulate structures in powders milled by various methods were determined by electron microscope examination and correlated with changes in compaction behavior, sinterability and microstructural uniformity of sintered compacts. Denser aggregates were formed in the wet-milled aluminas. These powders showed improved compaction behavior but sinterability was reduced. Various experimental methods were used to wash the wet-milled powders. Optimum treatments yielded powders containing no dense aggregates and which showed improved processing behavior. These studies led to a better understanding of the mechanisms by which dense aggregates can be formed during wet milling of alumina. Apparently, gamma alumina particles react with water during milling to form aluminum monohydrate, and milling attrition aids the process by continually exposing unreacted surfaces. The reduced sinterability of powders milled in water appeared to be caused by microstructural disruptions during sintering.

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I. INTRODUCTION

During an investigation to optimize microstructural uniformity of sintered compacts, it was noted that powders milled in water had reduced sinterability and contained rather strong aggregates* with high surface areas. Analysis of powder-characterization data did not adequately predict the behavior of these powders relative to the unmilled powder or to dry-milled powder. Furthermore, the mechanism by which the strong aggregates formed during milling in water could not be explained. Therefore, an investigation was conducted to gain a better understanding of these phenomena. The objectives were

(1) To describe the significant characteristics of the starting material

(2) To show how the results of dry and wet milling differ

(3) To propose and substantiate a postulated mechanism for the surface-chemical reaction during milling of alumina in water

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* The following definitions, similar to those used by Stover(1)**, were adopted at the outset of this research program. An agglomerate is a particle composed of smaller particles which are held together by relatively weak attractive forces. An aggregate is a particle composed of grains held together by neck areas formed by diffusion.

** References are listed on page 19.

(4) To apply this information to meaningful characterization of ceramic powders

(5) To show why reactive alumina powders have poor sinterability after milling in water.

II. BACKGROUND

The average ultimate particle size of the as-received study powder is considerably smaller than the median particle size of commercial dry-milled reactive alumina powders,which are usually reported to be 0.6-0.7 micrometer. Therefore, normal problems of mill packing during dry ball milling were intensified during early dry milling trials. Special procedures developed to circumvent this problem were reported previously by the authors(2). The improvement in particulate condition by dry milling the study powder is indicated by comparison of Figures 1 and 2. The porous aggregates still present after 1 hour of milling (Figure 1) were completely broken down after 5 hours of milling. After 20 hours of dry milling, the chain-like aggregates were reduced to their ultimate particle condition (about 0.2-0.3 micrometer in size), and the 100-200 angstrom particles remaining from the porous aggregates appeared to be rather uniformly dispersed and attached to the surfaces of the coarser particles.

Considerably different results were obtained by wet milling. Electron micrographs similar to the one shown in Figure 3 indicated that the powders resulting from milling in isopropyl alcohol, carbon tetrachloride, or very dilute acids were composed of dense, strong-looking aggregates. After drying the alumina-water slurries at 200 F for a minimum of 64 hours, the dry cake was observed to be hard and brittle. Compaction behavior of powders resulting from pulverizing the dry cake in a mortar and pestle indicated, semi-quantitatively, the presence of strong aggregates in the powders.

Compaction behavior was improved by both dry milling and wet milling. Tap density was increased from 10.7 percent of theoretical to 20-33 percent of theoretical, and cold-pressed densities of 65-69 percent of theoretical density (at 100,000 psi) were achieved. The dry-milled powder had sinterability that was equivalent to that of as-received powder. However, the sinterability of powders milled in dilute acids of various types or in isopropyl alcohol was relatively poor.

III. MATERIALS

The reactive alumina powder studied was ceramic-grade Linde A alumina (Alumina I). Spectrographic chemical analysis indicated the powder was >99.98 percent aluminum oxide, and that the chief impurities were SiO_2 (0.004 percent) and Ga_2O_3 (0.004 percent). Thermogravimetric analysis indicated that the powder, which had been stored at constant conditions of 72 F and 45 percent relative humidity, contained 0.6 percent moisture. X-ray analysis revealed approximately 10 percent gamma alumina. The lot of powder used had a specific surface area of 14.6 m^2/g.

The characteristic aggregate structure of the as-received powder is illustrated by Figure 4. This electron micrograph shows that the powder is composed of two distinct types of aggregates. At the top, chain-like aggregates are composed of ultimate particles of about 0.2-0.3 micrometer in diameter and are joined at necks of size similar to that of the ultimate particles. These are thought to be alpha alumina. The other type of aggregate in the as-received study powder is composed of much smaller ultimate particles, about

100-200 angstroms in size, clustered into large porous aggregates as illustrated in the lower portion of Figure 4. The particles in these porous aggregates are thought to be the gamma alumina which comprises about 10 weight percent of the study material. The median size of the aggregates in Alumina I has been measured to be 9-20 micrometers by MSA and Coulter Counter analysis techniques.

Use of this calcined but unmilled powder to fabricate alumina bodies results in poor processing behavior and in microstructures which are typically inhomogeneous, as discussed previously.(2) Figure 17 shows a typical fracture surface of a compact fabricated from Alumina I by isostatic pressing and sintering to 95 percent of theoretical density. The microstructure is characterized by regions of different densities in which porous pockets of small grains are scattered among a relatively dense matrix composed of considerably larger grains. These porous areas have been traced to the porous aggregates in the Alumina I powder from which the compact was fabricated.

IV. EXPERIMENTAL PROCEDURES

All milling experiments were performed using a 1-liter Degussit ball mill composed of 99.5 percent alumina. The mill speed used was 75 rpm, or 60 percent of critical for this size mill. Eight hundred and fourteen grams of Degussit 99.5 percent alumina milling pieces (initial diameter = 1/2 inch) and 25.4 grams of alumina powder charge were used for all experiments.

The principal sampling method used in this study was to draw samples at incremental milling times. Although recognizing that depletion of mill contents would probably affect milling efficiency, it was anticipated that all experiments would be affected equivalently, making comparisons valid. The wet-milled slurry samples were dried in air at 200 F for a minimum of 64 hours. The dry cakes were then pulverized by mortar and pestle.

During dry milling, one-quarter weight percent additions of naphthenic acid (Eastman Kodak Company) were made initially and after 1, 8, and 15 hours to reduce mill packing, as reported previously.(2)

Wet-milling experiments usually incorporated 26 milliliters of liquid media. Milling in this amount of water without addition of a dispersing aid was found to be an impossibility during preliminary studies. Small additions of acid were used as dispersants, since it has been shown(3) that alumina-water slurries experience viscosity minima in the range where pH equals 3-4, depending on specific gravity. The types of liquid milling media studied are listed in Table 1.

Special powders for study of the role of milling attrition in surface-chemical reactions were prepared by using carbon tetrachloride and isopropyl alcohol (IPA) to wash the naphthenic acid from dry-milled alumina powders. Although slower, IPA washing was preferred because IPA is compatible with water. Thus, preparation of additional powders to study the effect of aging exposures in water and acid milling media was possible without drying the alumina as an intermediate step. In these washing experiments, evaporation was used in preference to decantation to remove the naphthenic acid-isopropyl alcohol solution in order to preclude the removal of any alumina material. Three evaporation cycles were used, and the 10-gram alumina samples were washed with 900 millimeters of liquid during each cycle. Magnetic stirrers were used to prevent the material from settling prior to the evaporation portion of the cycles, thus promoting maximum potential for reaction of the washing media with the dispersed alumina. Evidence that the washing technique was successful in removing naphthenic acid was furnished by the fact that the washed powder was "wet" during subsequent exposures to water and dilute acids. Exposures to water and dilute acids were also performed on an evaporation-cycle basis to insure removal of alcohol while precluding removal of alumina or potential alumina-water reaction products. The various washing-exposure combinations studied and the corresponding exposure times are listed in Table 2.

A second type of washing experiment was used to study the effect of hydrated alumina mill products on powder character and processing behavior. The objective of this type of washing was to remove the colloidal and/or hydrated alumina. Therefore, powders resulting from milling alumina in the presence of water were washed in acids to try to dissolve any hydrated alumina which might be present. Approximately 10-gram powder samples were stirred into 900 millimeters of acids of various strengths for periods of several hours. Then, the solids were permitted to settle until decantation was possible. After decantation the wash cycle was repeated for a total of three times. Then, the washed solids were dried at 200 F as usual. The effectiveness of this washing treatment is indicated by comparison of Figures 9, 10, and 11. Comparison showed that washing in acid with a pH of 1 was much more effective than when a pH of 3 or 5 was utilized. The effectiveness of acidic washing indicates that hydrated alumina or alumina gels were present in the milled powder and that they were dissolved by acidic washing.

The powder-characterization methods used to provide data for comparing the powders prepared by various experimental procedures were

(1) Examination by transmission electron microscopy of dry particles on a carbon film supported by a copper grid

(2) Measurement of surface area with a Strohlein areameter

(3) Analysis of compaction behavior

(4) Analysis of sinterability.

The development of a procedure useful for the detection and determination of comparative strength of aggregates in powders has been previously reported.(4) It was shown that the pressure versus density data resulting from compacting a powder by externally applied pressure resulted in curves composed of linear segments when percent relative density was plotted as a function of the logarithm of pressure in the manner shown in Figure 13. Using the curve for as-received material as an example, the pressure breakpoint (or intersection point) was shown to be a function of aggregate, or agglomerate, strength. The absence of a breakpoint was shown to correspond to the absence of aggregate particles, except in cases where particle-particle binding in aggregates was equivalent to ultimate particle strength.

Research compacts were fabricated by pressing powders isostatically at 25,000-100,000 psi, then sintering in air in an electrically heated tube furnace with a working chamber of 99.5 percent alumina. Dew point of the air atmosphere was maintained at less than -30 F. Microstructures were evaluated by examining fracture surfaces of sintered compacts, using a scanning electron microscope (SEM). Sample chips were coated with a thin (few Å) gold coating to permit charge bleed-off during scanning electron microscopy.

V. RESULTS AND DISCUSSION

Surface-Reaction Mechanism

A hypothesis for the surface-chemical reaction of alumina particles during wet milling in the presence of water is schematically represented in

Figure 5. The left-hand view depicts a water-solvated alumina particle, with hydrogen ions preferentially adsorbed on the surface in a double layer effect. The proposed surface reaction is modeled in the right-hand view, which depicts a fresh fracture surface exposed by mill attrition.

Exchange of hydrogen ions for aluminum ions permits the reaction to penetrate below the outer surface of the particle. The aluminum ions, in conjunction with hydroxyl ions in the liquid media, apparently form an aluminum monohydrate layer on the surface of the particles. The depth of this reaction is very limited during typical milling times, but attrition continually removes the monohydrate products from the particle surfaces and continually presents fresh surface so that the extent of reaction during the milling period is greatly increased. Although the formation of $Al(OH)_3$ is thermodynamically favored, experimental data indicate that the particular circumstances of these milling experiments resulted chiefly in formation of aluminum monohydrate. Another possible reaction would be continual solution of a hydrated surface layer, followed by precipitation as pH increases during milling or as concentration is increased during drying. Our data support the hydroxylation reaction rather than the solution-precipitation reaction. However, the increase in pH during milling indicates that some solution apparently takes place. Therefore, some aluminum hydroxide gel ($Al(OH)_3 \cdot xH_2O$) probably forms when the milled powder is dried. This material was not detected in characterization of the powders.

Characterization of the Milled Powder

Various analytical methods were utilized in an attempt to characterize the product of the surface-chemical reaction during milling of alumina in water.

X-ray analysis, infrared absorption spectroscopy, and differential thermal analysis were not successful in revealing the presence of suspected aluminum hydroxide phases. This lack of detection might have been caused by the presence of an inadequate concentration of the reaction product or by the effects of extremely small particle size.

Thermogravimetric analysis (TGA) was more revealing than other analytical techniques. Differential-weight-loss curves are shown in Figure 6 for a typical experimental powder which was milled for 1, 5, and 20 hours in dilute citric acid, as compared to the powder in the as-received condition. The curve for the as-received powder exhibits a single peak at about 100 C, corresponding to the loss of 0.6 percent surface-adsorbed water. The curve for powder milled 1 hour also shows only one distinct peak at 100 C, but also signs of emerging peaks, possibly signifying the early formation of reaction products. After 5 hours and after 20 hours of milling, three distinct peaks in the thermograms are indicated at about 100, 250, and 450 C. The peak at 100 C is attributed to loss of surface-adsorbed water. The peak at 250 C reportedly corresponds to conversion of aluminum monohydrate to chi alumina, and the peak at 450 C corresponds to transformation of chi alumina to delta alumina.(5,6) The presence of alumina trihydrate should have been indicated by a peak at 175 C. Since no such peak was indicated by the differential-weight-loss curves, it was concluded that the reaction had not proceeded sufficiently for formation of a detectable amount of aluminum trihydrate, or that the corresponding weight loss might have been blended into the peak attributed to loss of surface-adsorbed water.

The total weight loss by the powder milled for 20 hours was 1.5 percent. The 0.9 percent in excess of the 0.6 percent loss attributed to surface-adsorbed water for the as-received powder amounts to 5 percent of the weight gain corresponding to complete conversion of alumina (102 gram/mole) to aluminum monohydrate (120 gram/mole). This corresponds qualitatively with the amount of gamma alumina present in the as-received alumina. This fact, coupled with higher expected activity because of the much smaller ultimate particle size of the gamma-alumina phase, leads to the conclusion that the small,gamma-alumina particles are primarily involved in the surface-chemical reaction during milling of alumina in the presence of water.

Milling Observations

The milling relationships plotted in Figures 7 and 8 provided some of the earliest indications that unexplainable phenomena were occurring during wet milling in dilute acids. However, they fit well into the proposed reaction mechanism and correlate with other powder-characterization data. In Figure 7, pH of the alumina-water slurries is seen to increase with increased milling time, indicating that the mill contents became progressively more basic as milling continued. The reason for the indicated differences in rate of increase in pH value for milling during the various experiments has not been learned. The pH values of the alumina-water slurries were initially adjusted to three in order to maximize particulate dispersion and minimize slurry viscosity, according to the relationships reported by Hauth(3).

Surface-Area Relationships

In Figure 8, the relationship of surface area to milling time is shown for some of the experimental powders milled in dilute acids. The indicated phenomena were observed in all milling experiments where water was present in the mill. The surface-area values minimized after 5-10 hours milling, then rose to values as high as 23 m^2/g after 20 hours' milling. Most experiments were terminated after 20 hours because mill contents often became too viscous to permit further milling. It is interesting to note that those slurries which had become more basic after 20 hours of milling, indicating more extensive reaction in the mill, also exhibited correspondingly higher surface area for the dried mill products. The increased surface area is attributed to formation of an aluminum monohydroxide phase, which would be expected to have a surface area of 300-400 m^2/g.(6,7) This condition is often accompanied by the presence of material resembling the skeletal-dried residue of colloidal sol-gel products(8) noticeable during electron-microscope examination of powders after drying. This material apparently has a high specific surface and, typically, is observed to have become concentrated at particle-particle contacts and aggregate interstices, as shown in Figures 9 and 10. In an extreme condition, as shown in Figure 9, the colloidal material has actually been observed to encapsulate the aggregated particles. The surface-area increase of 9 m^2/g caused by milling in citric acid may be compared with an increase of about 300 m^2/g which would be expected if complete conversion of alumina to aluminum monohydroxide occurred, to show that about 3 percent of the milled material was converted to the higher surface area product. This compares favorably in a qualitative way with the 5 percent conversion indicated by TGA data, and again suggests that the small, gamma-alumina particles which represent about 10 percent of the as-received alumina are principally involved in the indicated reaction with water during milling.

The initial lowering of surface area during the first 5-10 hours of milling is not well understood but may correspond to solution of a portion of the fine gamma alumina in the powder. It is only during later stages of milling that the extensive formation of high-surface-area hydroxyl products outweighs the effects of this phenomenon which dominates during earlier milling stages. As will be shown, however, the strong, dense aggregates are not eliminated during later milling and their formation seems to continue.

Thus, surface-area data, which are usually assumed to be a reliable indicator of particle-size reduction as a result of milling, were seen to be misleading in the case of powders milled in the presence of water. A more complete set of powder-characterization procedures is required to adequately describe the changing character of the powder during milling.

Study of Washed Powders

Several of the foregoing points are supported by the results of experiments in which dilute hydrochloric acid was used to wash powders milled in the presence of water. Similar results were obtained using centrifuging or shelf sedimentation to separate the washed particles prior to decantation of the washing liquid. The results are indicated by comparison of the electron micrographs shown in Figures 10 and 11.

The material of relatively small ultimate particle size, thought to be a product of the gamma alumina in the as-received alumina powder, is observed to be preferentially located at particle-particle contacts in the aggregates formed during milling and subsequent drying, shown by the typical electron micrograph of Figure 10. The hydrated alumina has apparently been dissolved by the hydrochloric acid and washed out by the cyclic decantations from the material shown in the electron micrograph of Figure 11. As a result, the surface area of the washed powder shown in Figure 11 was lowered to 6.5 m^2/g from the value of 23 m^2/g determined for the as-milled and dried material shown in Figure 10. This corresponds to the removal of about 4.8 percent of 350 m^2/g material, roughly in agreement with the starting portion of gamma alumina.

If, as postulated by the proposed hypothesis stated earlier, the deposition and/or precipitation of hydrated alumina at particle-particle interstices produce a cementing effect on the resulting aggregates, then this washing treatment would be expected to remove the "cementing" material and no strong aggregates should be detectable in the "washed" powder. Also, the strength of the "cemented" aggregates should be comparable to that of dried, colloidal gel products of similar nature. Both of these expectations were investigated by compaction analysis techniques.

Strength of Powder Aggregates

The effect of various powder-processing procedures and the resulting particle structures on powder compaction are indicated by Figure 13. Tap densities are shown at 1 psi, but obviously correspond in every case to lower pressure values. The pressure break at about 300 psi in the curve for as-received material corresponds to the strength of the porous gamma-alumina aggregates depicted at the bottom of Figure 4. There is no pressure break corresponding to the strength of the chain-like aggregates depicted at the top of Figure 4. Because the size of the particle-particle necks approximate the ultimate particle diameter, these aggregates apparently are equivalent in strength to ultimate particles. The tap density of the as-received powder is only about 11 percent of the theoretical value. This low-density value is attributed to the effect of the porous gamma-alumina aggregates.

In contrast, the dry-milled powder, which was previously shown by electron micrographs (Figure 2) to be in the ultimate particle condition, had a tap density of about 30 percent of theoretical, and no curve breaks were observed between 1.5 and 100,000 psi. The curve for a typical powder milled in the presence of water had a high-pressure breakpoint at about 3,000 psi, indicating that the aggregates which were observed in electron micrographs such as those in Figures 3, 9, and 10 were indeed quite strong. Tap density was raised to above 25 percent, indicating that porous aggregates had been eliminated from the material during milling. This conclusion was also verified by electron microscopy.

After optimum washing treatment to eliminate colloidal products formed by milling in the presence of water, as demonstrated by Figure 11, the compaction curve was observed to be linear. This was attributed to removal of the cementing hydrated alumina phase from the aggregates. Tap density was raised to about 30 percent of theoretical, perhaps because of elimination of bridging effects or elimination of the low-density hydrate phase. The curve for the dried alumina gel represents a study powder which was prepared by precipitation of aluminum hydroxide from an aluminum sulfate solution through ammonium hydroxide addition. This curve shows a high-pressure breakpoint at 3000 psi which is similar to the breakpoint for the powders milled in water. This similarity supports the hypothesis that the aggregates in this powder are held together by an aluminum hydrate, which determines the strength of the aggregates.

Role of Attrition

The proposed mechanism for surface-chemical reaction of alumina with water during milling includes the stipulation that attrition by milling action continually exposes fresh alumina surface for the reaction, thus maintaining reaction continuity. The most likely alternative to this proposal is that the reaction would be merely an aging phenomenon. To test this possibility, powders which had been dry milled to break down porous aggregates were exposed (aged) to the various milling media for time periods much longer than those utilized for wet milling and drying combined. During the experimental aging studies, the slurries were quite dilute (10 grams alumina in 900 cc of liquid). As a preliminary step, the dry-milled powders were washed with isopropyl alcohol (IPA) to remove the hydrophobic naphthenic acid grinding aid so the powders could be "wet" by water. Twenty-one days were used in washing the powders with IPA. Times of the experimental exposures to IPA, carbon tetrachloride, water, and various dilute acids are listed in Table 2.

Also shown in Table 2 are surface-area data for these experimentally washed powders compared to the measured value of 17.7 m^2/g for the dry-milled, unwashed powder. The indicated differences are not considered to be significant, but these values alone would not indicate whether dense, hard aggregates were formed during the exposures. Compaction data analysis results are also listed in Table 2, however, and the low breakpoint pressure values shown indicate that no strong aggregates were formed during any of the exposures. Electron microscopy also indicated that dense aggregates were not formed during the process, as illustrated by the typical electron micrograph in Figure 12. Thus, the evidence resulting from compaction analysis and electron microscopy, which have been found to be more conclusive than surface-area data, indicates that the milling-attrition process does, indeed, seem to be a requisite factor in the mechanism for formation of dense, strong aggregates during milling of reactive alumina powder in the presence of water.

Sinterability

Sinterability of the ball-milled alumina powders was examined using data such as that listed in Table 1. The data-presentation format was intended to take into account the effect of green density of a compact on the sintered density obtainable using a particular set of sintering conditions. Thus, the data column at the extreme right of Table 1, which shows the increase in relative density of the compact during sintering, is considered indicative of the relative sinterabilities of the powders prepared as described at the extreme left.

The dry-milled powder, when sintered under identical conditions, had the same sinterability value as the as-received powder. It is interesting to note that if only the sintered density had been compared, as is often reported, the influence of improved compaction behavior of the dry-milled powder in raising both the pressed density and the subsequent sintered density would have been mistaken for improved sinterability.

The sinterability values of powders milled in dilute acids of various types or in isopropyl alcohol were 11-14.2, compared to the values of 29.8-29.9 percent sintering densification obtained for dry-milled and as-received powders.

The reason for the poor sinterability of alumina powders milled in the presence of water might be explainable on the basis of typical electron micrographs as shown in Figures 14 and 15. These typical views indicate that microstructural disruption has caused poor particle-particle contact. The microstructural disruption is attributed to shrinkage in the transition aluminas and aluminum hydrates, which causes particle-particle contacts to be broken.

This behavior of alumina powders milled in the presence of water is in sharp contrast to that of dry-milled powders. The electron micrograph of Figure 16 indicates the uniform microstructural development in a compact fabricated from dry-milled powder. In contrast, a very nonuniform microstructure results from use of the as-received powder, as shown in Figure 17. It is also significant that equivalent densification of the compact fabricated from dry-milled powder could be obtained using a sintering temperature that was about 200 F lower than for the compact made from as-received powder.

VI. SUMMARY AND CONCLUSIONS

The formation of dense, strong aggregates during milling of a reactive alumina in the presence of water seems to result from a surface-chemical reaction which is perpetuated by milling attrition. Apparently, very small gamma-alumina particles are hydroxylated to form aluminum monohydrate which, upon drying, acts as a bonding or cementing constituent in powder aggregates. Milling attrition appears instrumental in maintaining the reaction by continually exposing fresh alumina surface for reaction. Poor sinterability of reactive aluminas milled in the presence of water is apparently due to microstructural disruption during sintering. This effect is attributed to shrinkage of surface-chemical reaction products as a result of sintering and phase transformation.

Surface-area data appear to be inadequate to unambiguously characterize the effects of ball milling a reactive alumina powder. Additional characterization must be undertaken to account for possible hydrated reaction products.

The eventual solution to the problem of how to wet mill a reactive alumina seems to require (1) the selection of a liquid milling media which will not react to a significant degree with the particulate alumina during the milling period or (2) use of a powder that does not contain aggregates with surface areas above about 20 m^2/g. Such an investigation is currently being conducted.

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TABLE 1. SINTERABILITY(a) OF BALL-MILLED ALUMINA I

Milling Media	Milling Time, hours	Percent of Theoretical Density			Percent Density Increase	
		Tap	Pressed	Sintered	T→P	P→S
Hydrochloric Acid(b)	20	29.8	65.2	76.2	35.4	11.0
Citric Acid(b)	20	26.8	65.9	80.1	39.1	14.2
Acetic Acid(b)	20	32.9	64.6	78.4	31.7	13.8
Isopropyl Alcohol	20	18.4	68.7	79.8	50.3	11.1
Dry	20	29.6	63.8	93.6	34.2	29.8
Dry	5	28.7	60.5	89.5	31.8	29.0
As-Received	--	10.7	54.3	84.2	43.6	29.9

(a) Pressed isostatically at 100,000 psi. Sintered in air at 2555 F for 1 hour.

(b) Initial slurry pH was 3.

TABLE 2. EFFECT OF WASHING DRY-MILLED ALUMINA I ON SURFACE AREA AND COMPACTION CHARACTER

Washing Treatment	Exposure Time, days	Specific Surface, m^2/g	Compaction Curve Breakpoint Pressure, psi
As-milled	None	17.7	None
IPA	21	17.7	3
CCl_4	4	16.0	15
IPA, then distilled water	21,21	17.0	8
IPA, then hydrochloric acid(a)	21,11	15.8	50
IPA, then citric acid(a)	21,7	19.3	200
IPA, then acetic acid(a)	21,15	19.1	22

(a) pH = 3.

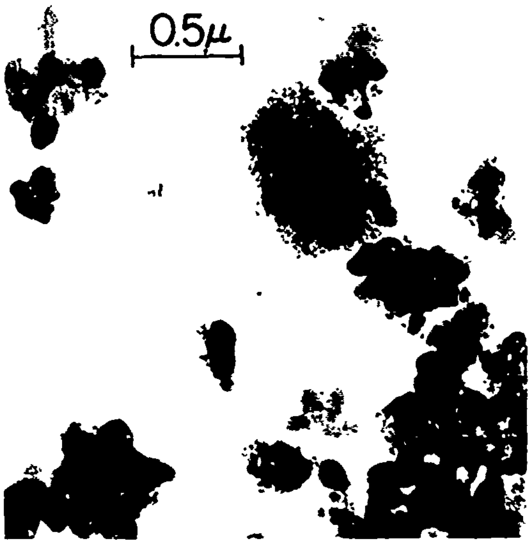

FIGURE 1. ALUMINA I AFTER 1 HOUR OF DRY BALL MILLING

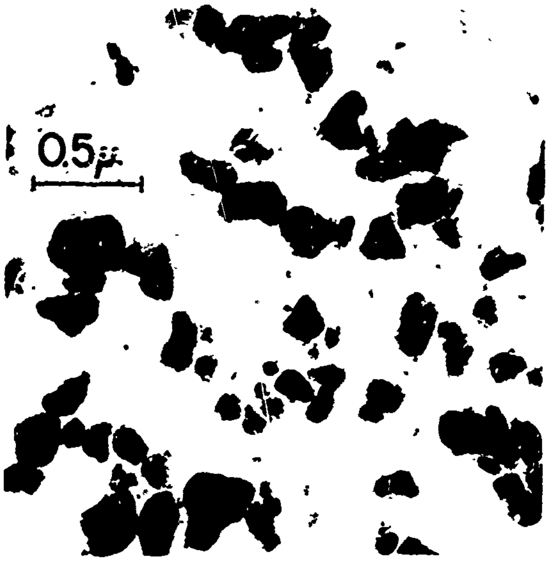

FIGURE 2. ALUMINA I AFTER 20 HOURS OF DRY BALL MILLING

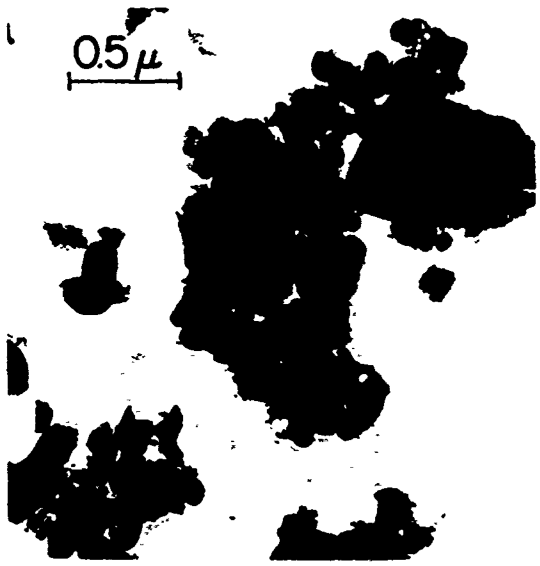

FIGURE 3. ALUMINA I AFTER 20 HOURS OF MILLING IN WATER WITH CITRIC ACID ADDITION

FIGURE 4. AGGREGATE STRUCTURE OF ALUMINA I PARTICLES

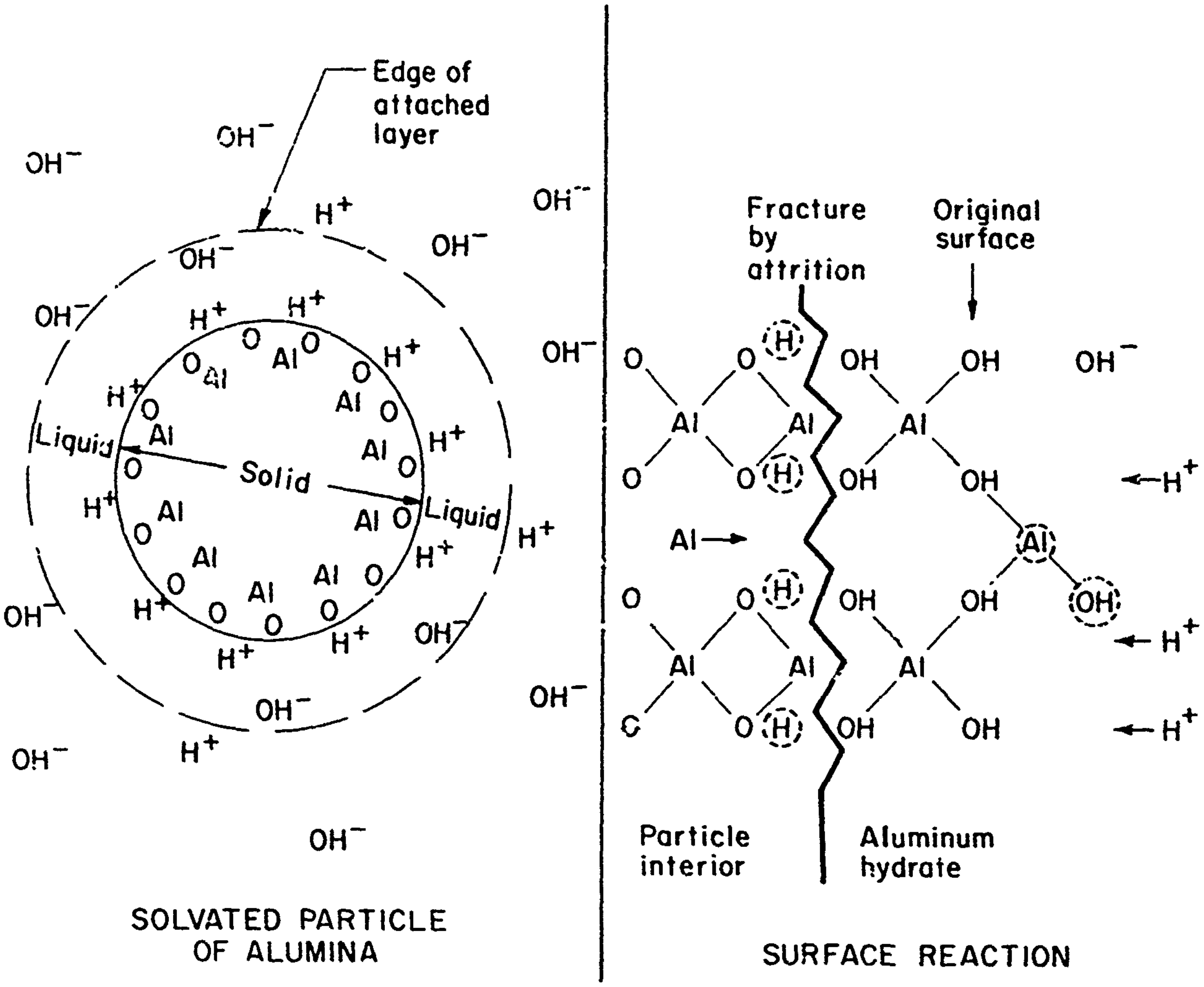

FIGURE 5. SCHEMATIC REPRESENTATION OF PROPOSED MECHANISM FOR REACTION OF ALUMINA DURING MILLING IN WATER

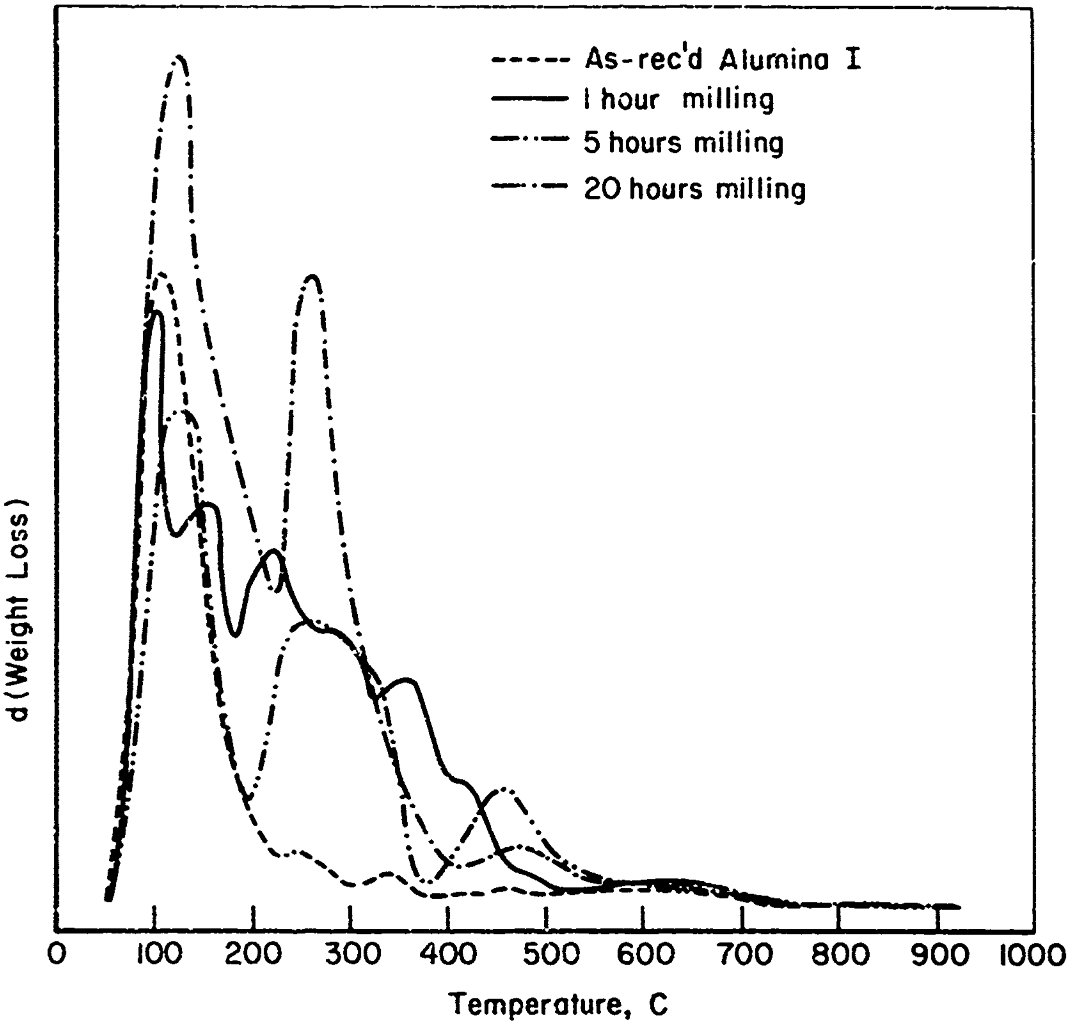

FIGURE 6. DIFFERENTIAL WEIGHT LOSS FROM THERMOGRAMS FOR ALUMINA I AFTER MILLING IN CITRIC ACID

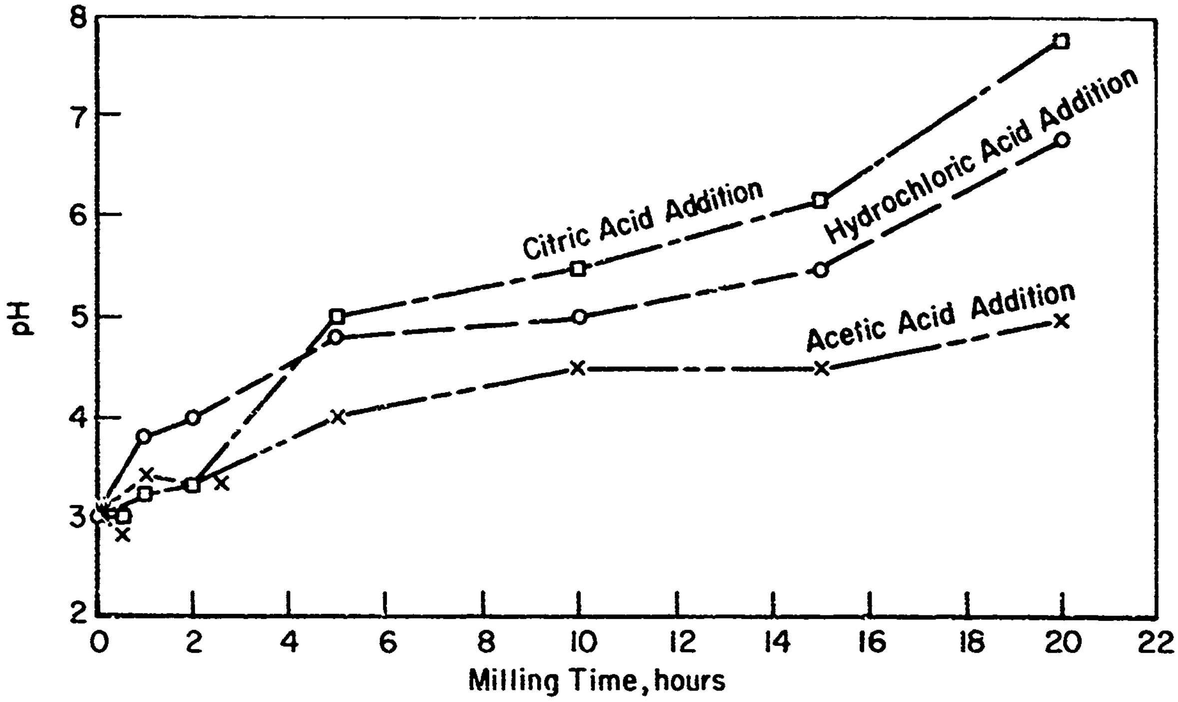

FIGURE 7. EFFECT OF MILLING TIME ON pH OF ALUMINA I SLURRIES

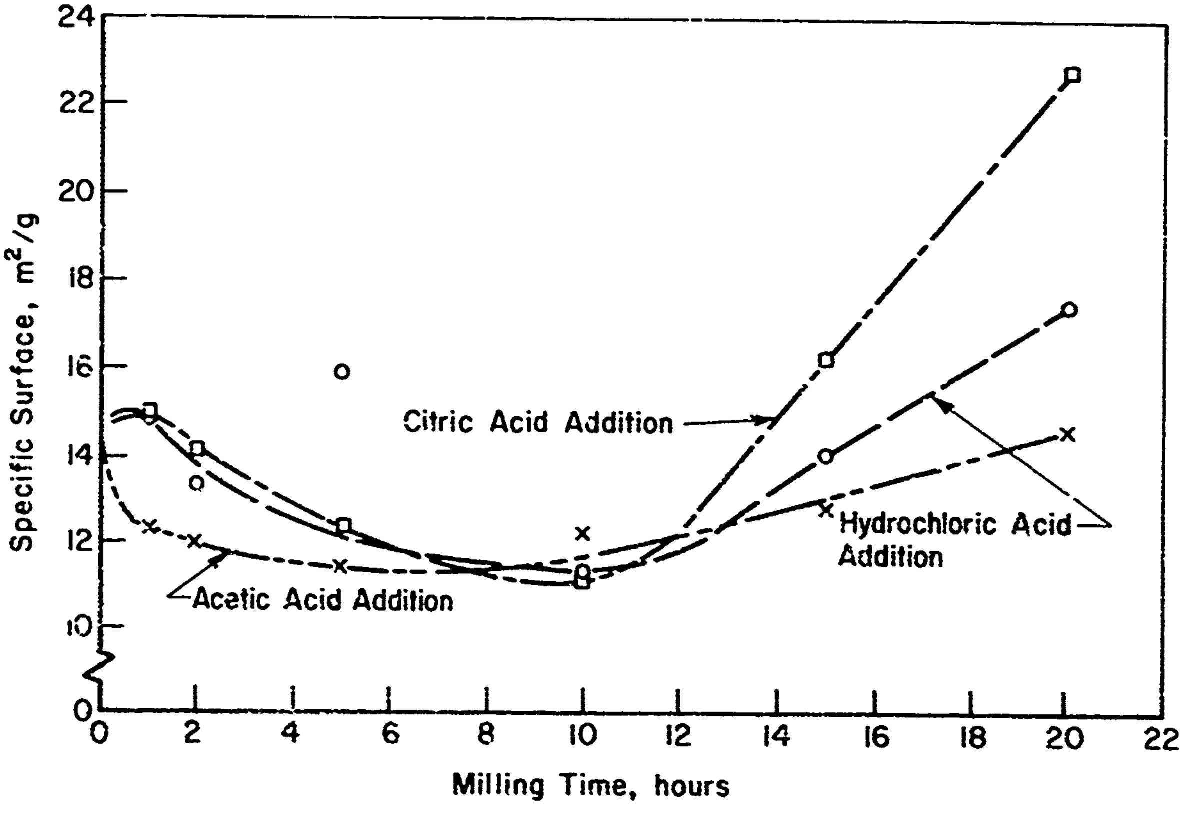

FIGURE 8. EFFECT OF MILLING TIME ON SURFACE AREA OF ALUMINA I

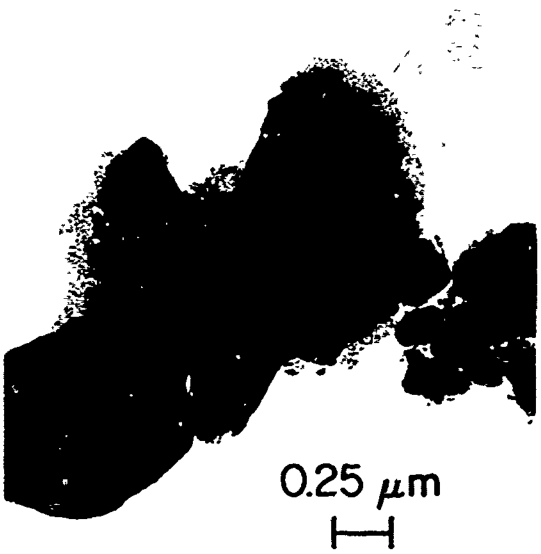

FIGURE 9. ELECTRON MICROGRAPH INDICATING EXTENSIVE ENCAPSULATION OF ALUMINA I PARTICLES BY REACTION PRODUCTS DURING MILLING IN CITRIC ACID AND DRYING

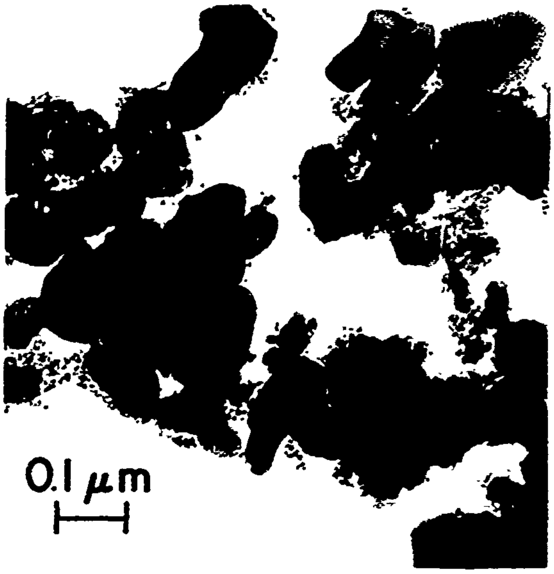

FIGURE 10. ELECTRON MICROGRAPH SHOWING MINIMAL FORMATION OF AGGREGATES DURING MILLING IN CITRIC ACID AND DRYING

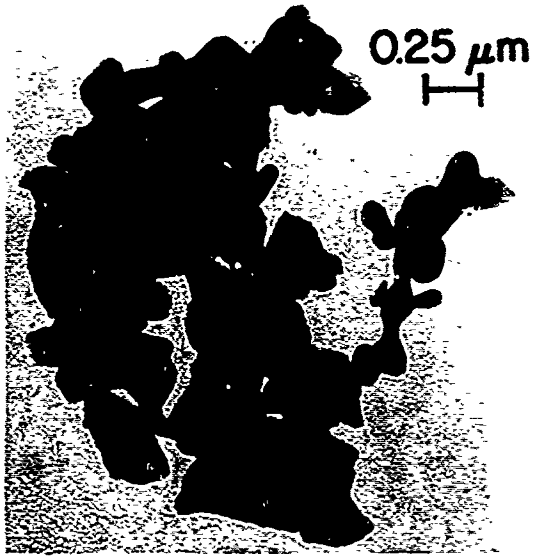

FIGURE 11. ELECTRON MICROGRAPH SHOWING EFFECT OF WASHING A POWDER MILLED IN CITRIC ACID, IN DILUTE HYDROCHLORIC ACID WITH A pH OF 1

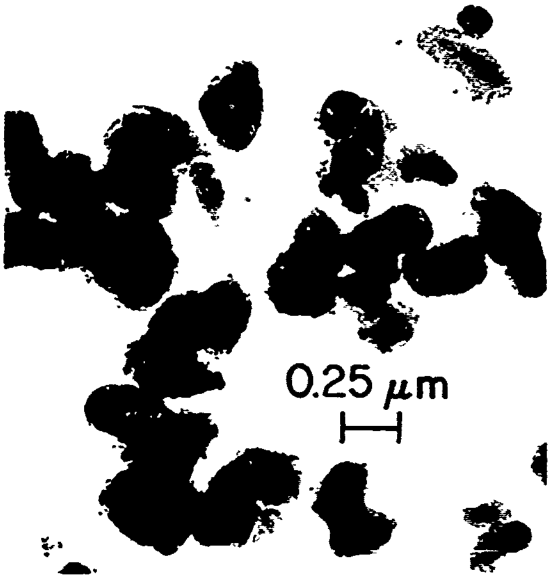

FIGURE 12. ELECTRON MICROGRAPH SHOWING EFFECT OF WASHING A POWDER DRY MILLED FOR 20 HOURS, FIRST IN IPA AND THEN IN DEIONIZED WATER

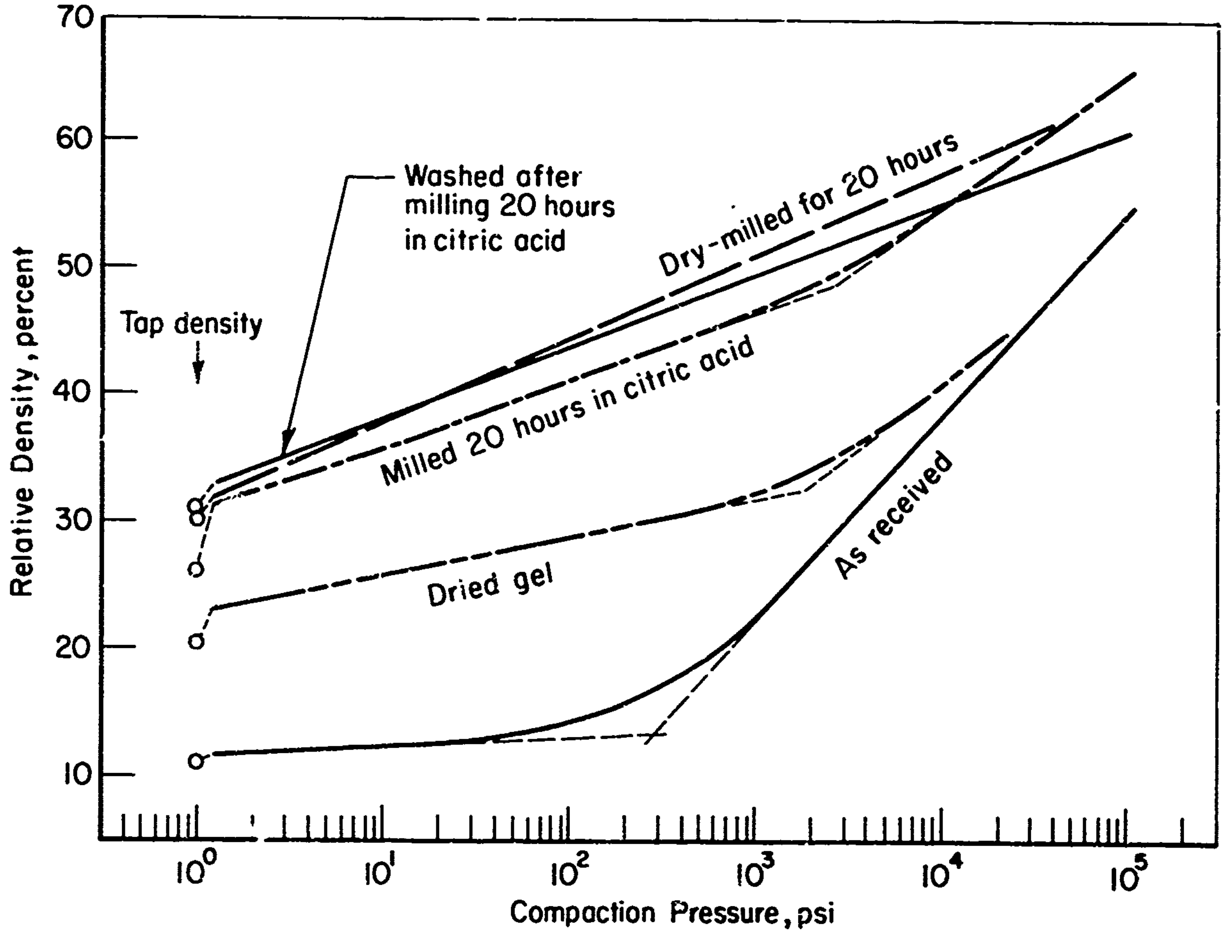

FIGURE 13. EFFECT OF POWDER PREPARATION PROCEDURE ON COMPACTION BEHAVIOR

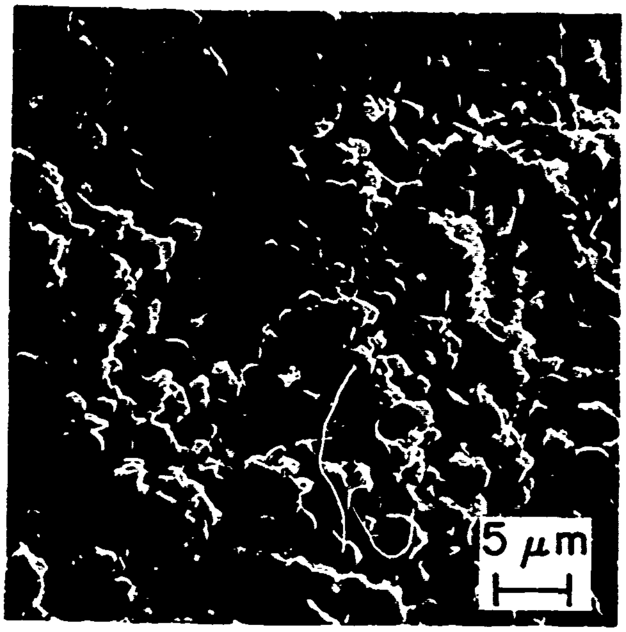

FIGURE 14. FRACTOGRAPH SHOWING AN ALUMINA COMPACT WITH ~8 PERCENT POROSITY FABRICATED BY ISOSTATIC PRESSING (100,000 PSI) AND SINTERING (2763 F-1 HOUR) OF ALUMINA I MILLED IN CITRIC ACID (2,000X MAGNIFICATION)

FIGURE 15. SECTION OF THE FRACTOGRAPH SHOWN IN FIGURE 14 (10,000X MAGNIFICATION)

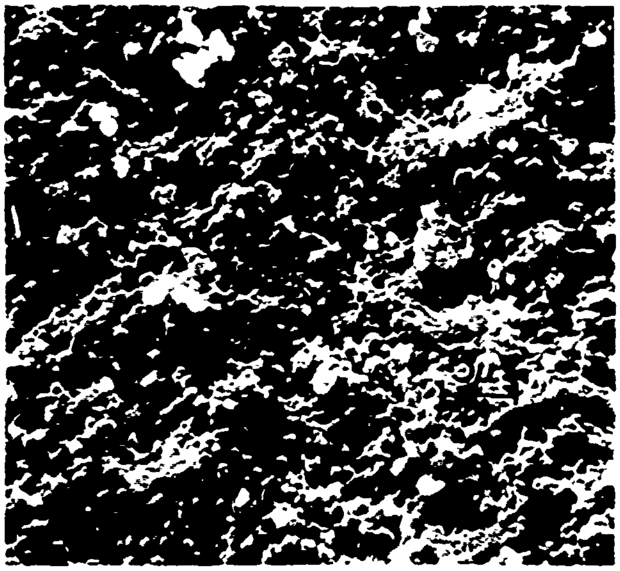

FIGURE 16. FRACTOGRAPH OF 96 PERCENT DENSE COMPACT FABRICATED BY ISOSTATIC PRESSING (100,000 PSI) AND SINTERING (2568 F - 1 HOUR) OF ALUMINA I DRY MILLED FOR 20 HOURS

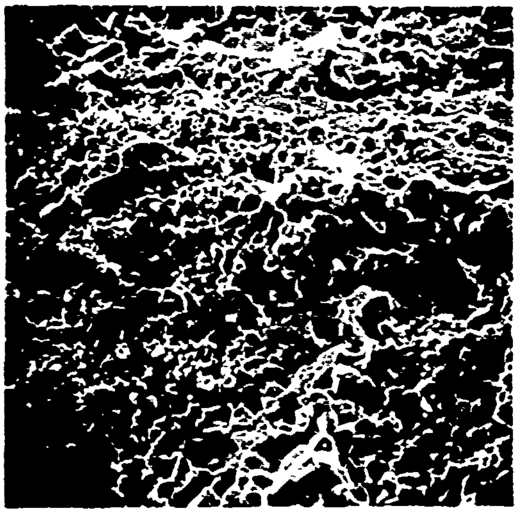

FIGURE 17. FRACTOGRAPH OF 95 PERCENT DENSE COMPACT FABRICATED BY ISOSTATIC PRESSING (100,000 PSI) AND SINTERING (2751-1 HOUR) OF AS-RECEIVED ALUMINA I