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Deagglomeration of High Purity Fine Alumina Powder Via pH Control*

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This paper presents results from a study on the effect of the pH of suspensions on the deagglomeration of a high-purity (99.99%), fine-grained alumina powder. The pH of the suspension was varied between pH 2 and 3. It is the aim of the study to determine the best pH for a successful dispersion of the alumina powders in the suspension. A series of rheological studies and analytical work under Scanning Electron Microscopy were conducted. It was found that the best pH was pH 2. Data obtained from rheological studies using a viscometer showed that the alumina suspension prepared at pH 2 was least viscous, which may be taken as a negative indicator of the presence of agglomerates. This hypothesis is validated by visual inspection using SEM. For the pH 2 samples, a successful removal of the agglomerates in the green compact has encouraged the sinterability of the samples and thus, resulted in an earlier sintering process at a low-firing temperature. In addition, the sintering characteristics and microstructures of the samples prepared with a pH 2 suspension are also presented.

Keywords: colloidal processing, fine alumina powders, pH control, rheology, sintering characteristics, microstructure

INTRODUCTION

Currently dominating the advanced materials era, advanced ceramics have played critical roles in numerous engineering applications that require materials with unique and reliable capabilities. Understandably, more and more research is devoted to further develop these technical ceramics; among which, alumina, is a continuous subject of interest. Due to its inherent brittleness, numerous studies are emphasized on the research and improvement of the fracture toughness properties of alumina (Misirli et al., 1994; Muchtar and Lim, 1998). As the characteristic properties are derived from the microstructure, a significant amount of the investigations involved were directed in improving the fabrication process and the starting materials needed such that resulting alumina products acquire better mechanical performance attributes.

One major breakthrough in ceramics research recently is the successful fabrication of fine-grained, high-purity alumina via colloidal processing. The technique has been used to produce agglomerate-free powder compacts, which generally exhibit superior sintering characteristics (Yeh and Sacks, 1988; Inada et al., 1990; Lim et al., 1997; Tari et al., 1998; Muchtar, 1999). As a result, the sintered products have a fine-grained structure, of the order of a

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few micrometers or less. However, the degree of agglomeration/deagglomeration of the powder particles is dependent upon the pH of the suspension and the adsorption of ions by the alumina particles. In distilled water, H^+ or OH^- ions are attracted to the oxide particles. If an acid, such as HCl, is added to the liquid, only the excess H^+ ions will be attracted to the particles, forming a layer of H^+ ions on the surface. As a result, the negatively charged chlorine ions, Cl^-, in the solution will be attracted to the positively charged particles, forming a thicker but negatively charged layer around the particles. This causes the particles to repel one another. In general, there exists an optimum pH whereby the oxide particles repel each other and thus do not form agglomerates (Nunes et al., 1992). The present work therefore attempts to fabricate alumina samples via the colloidal method with special emphasis on the study of the influence of pH on the deagglomeration of the powders. The colloidal processing technique should permit greater control of the microstructure and thus allow the prospect of engineering end products of superior quality. It is the aim of this study to determine the best pH for a successful dispersion of the alumina powders in the suspension. To obtain the answer, a series of rheological studies and analytical work under Scanning Electron Microscopy (SEM) were conducted. In addition, details of the microstructure and sintering characteristics of the samples produced at the optimum pH value were also presented.

METHODOLOGY

The initial starting powder was a commercially available α-alumina powder (TMDAR, Taimei Chemicals Co Ltd Japan) of 99.99 % purity with an average particle size of 0.17 mm as obtained via a laser particle size analyser (Malvern Mastersizer S). According to the manufacturer, the following is the impurity content in parts per million (ppm): Na – 1, K – 1, Fe – 5, Ca – 1, Mg – 1 and Si – 4. The BET surface area of the powder is given as 14.5 ± 1 m^2/g. A micrograph of the said powder taken by using a scanning electron microscope is shown in Figure 1. In attempting to remove the agglomerates, the powder was first colloidally processed. To start with, a suspension of 20% volume of solid content was prepared

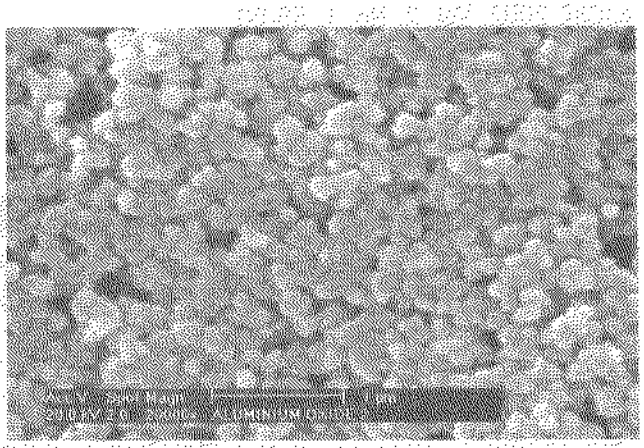

Figure 1 A micrograph of the starting α-Al_2O_3 powder used in this study.

using distilled water. This is followed by the addition of small amounts of hydrochloric acid (HCl) to break down the soft agglomerates (particles clustered loosely together by attractive forces such as the van der Waals and capillary forces) into individual particles. The pH of the suspension was varied between pH 2 and pH 3 to study the effect of the pH on the deagglomeration of the high-purity, fine-grained alumina powder. The suspension was next subjected to an ultrasonic bath (Transsonic 570/H) treatment for at least 10 minutes to enhance the deagglomeration process (Suzuki et al., 1998). Following the deagglomeration process of the soft agglomerates, the suspension was left in a quiet corner of the laboratory for a sedimentation period of 24 hours. This is to rid off the hard agglomerates (particles strongly bonded together by processes such as calcinations during powder manufacture). After the sedimentation period, the hard agglomerates formed a thin layer of sediment at the bottom of the suspension. The supernatant was then extracted using a dropper whilst being careful not to disturb the sediment at the bottom. The supernatant was then readjusted to the pH of interest through the addition of HCl.

Rheological studies were conducted on the suspension using a rotational viscometer (Haake VT 500). Next, the consolidation of the green compacts is achieved via the slip casting process. Cylindrical samples of diameter 6 mm were obtained by unidirectional slip casting in Teflon moulds placed on absorbent blocks of Plaster of Paris, as shown in Figure 2. The green samples were dried for a minimum of 72 hours. Samples were later fired at 1310°C with a soaking time of

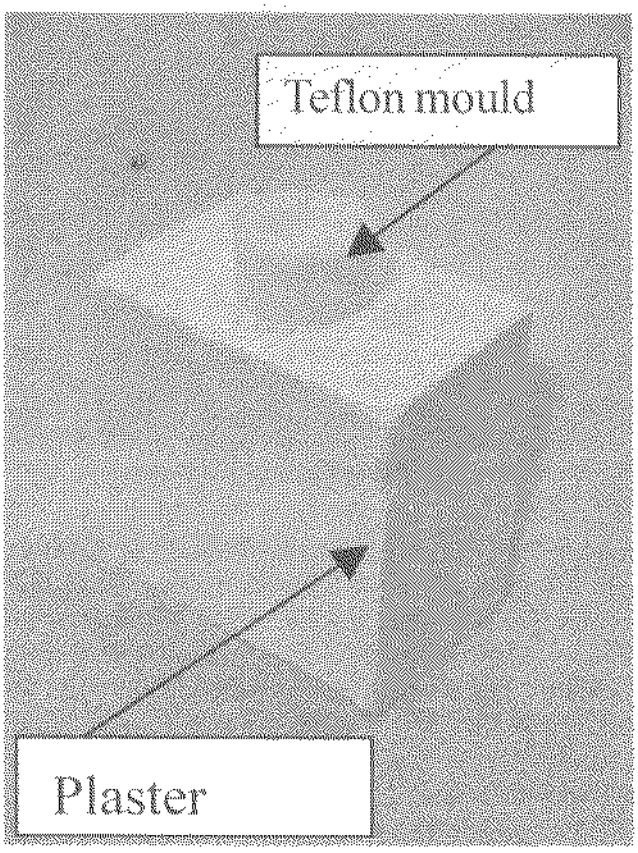

Figure 2 Teflon mould sitting atop the plaster block during slip casting

one hour (LINN High Term, VMK 1800). Samples that have been prepared at the optimum pH value were also sintered at various other sintering temperatures in order to view the effects of the sintering temperature on the microstructure and properties of the samples. Microstructural analysis was conducted using a scanning electron microscope (Philips XL30).

RESULTS AND DISCUSSION

Previous works have shown that the agglomeration of oxide powders in suspensions is influenced by its pH values (Inada et al., 1990; Nunes et al., 1992). Similarly, in the present work, the viscosity of the suspensions is found to be a function of the pH. Figure 3 shows the viscosity curves for the various Al_2O_3 slips at pH 2, 2.5 and 3. All three suspensions displayed shear-thinning characteristics, whereby the apparent viscosity decreases with increasing shear rate. This is generally the favourable rheological behaviour for slips used in slip casting. In theory, a less agglomerated suspension will yield lower

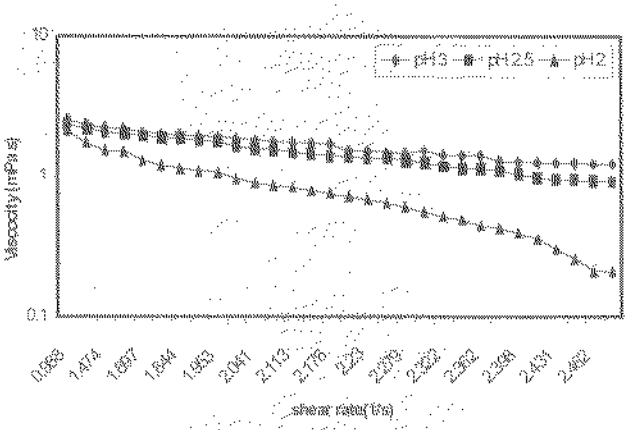

Figure 3 Viscosity as a function of pH in the suspensions

viscosities compared to slips with a higher degree of agglomeration. Accordingly, it demonstrates that the pH 2 suspension is least agglomerated compared to the other two suspensions of pH 2.5 and 3.

Further analytical work is then carried out by examining sintered samples under the scanning electron microscope (SEM). Figure 4 demonstrates the difference between the microstructure of samples prepared at pH 2 and pH 3. It is noted that SEM micrographs of samples prepared at pH 2.5 indicated similar microstructures to those of pH 3 samples, and therefore not shown here. In much the same way as previously manifested in Figure 3, the pH 2 samples behaved differently from the others, showing a microstructure that is completely different compared to those samples prepared at the higher pH values. Whereas, there is hardly any evidence of an onset of sintering on the top micrograph of Figure 4, which is for a sample prepared at pH 3, the micrograph on the right shows that the initial sintering process has already begun. Fusion between some of the particles is clearly evident with grains forming a more angular shape. In contrast, the particles on the pH 3 sample are still well rounded, much like the initial starting powder. This highlights an increased sinterability of the pH 2 samples as compared to the others. Additionally, the pH 3 samples showed the agglomeration of the particles whereas there is no clear evidence of agglomeration in the pH 2 samples. Again, it is noted that the sintered pH 3 samples exhibited the same characteristics as the pH 2.5 samples. Therefore, it is very interesting to note the striking difference between the pH 2 and pH 2.5 samples

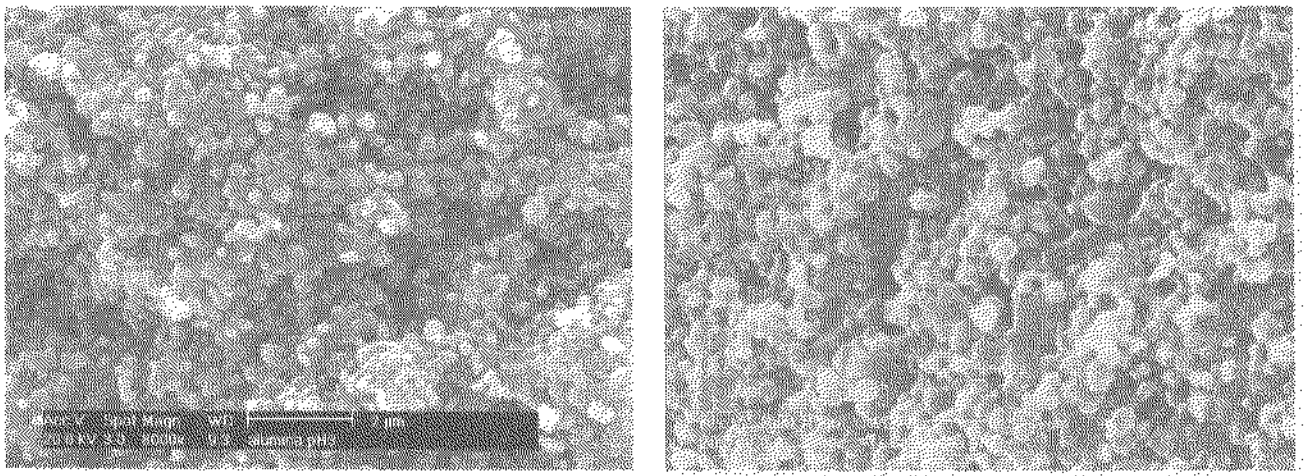

Figure 4 Microstructure of the fired compacts (1310°C) from the pH = 3 (top) and pH = 2 (bottom) suspensions

when in fact the pH difference of their respective suspensions is only marginal. Previous investigations (Inada et al., 1990; Nunes et al., 1992) have also shown the influence of pH on the powder agglomeration of alumina suspensions but their works were conducted on a wider range of pH values, focussing on pH 2, 4, 6, 8 etc. The present study, on the other hand, has shown that a marginal difference in pH of 0.5 can affect the agglomeration of powders and subsequently, the sinterability of the compacts.

Upon obtaining the above results, some additional work was undertaken to examine further the sintering characteristics and microstructure of the alumina powders colloidally processed in slips at pH 2 and subsequently consolidated into green compacts via slip casting. These were then sintered at varying temperatures of 1310, 1350, 1425, 1500 and 1550°C. Once sintered, the samples were polished to a mirror finish quality prior to thermal etching at 1200°C with a soaking time of 3 hours. Examples of the resulting SEM micrographs taken are shown in Figure 5. Sintered densities measured by the Archimedes technique yielded >99.2 % theoretical density for all samples prepared using the pH = 2 suspension and subsequently sintered at temperatures of 1310°C and above.

In Figure 5, the micrographs exhibit narrow-size-distributed equiaxed grains with no exaggerated grain growth, even at the highest sintering temperature of 1550°C. As expected, the elimination of the agglomerates resulted in a narrow grain size distribution. The average final grain size measured using the linear intercept technique, is 0.3 mm for the lowest temperature and about 2.2 mm for the highest temperature used, as shown in Figure 6. The results of an earlier work (Muchtar, 1999) on another alumina powder, TM-5D from Taimei Chemicals Co. Ltd,

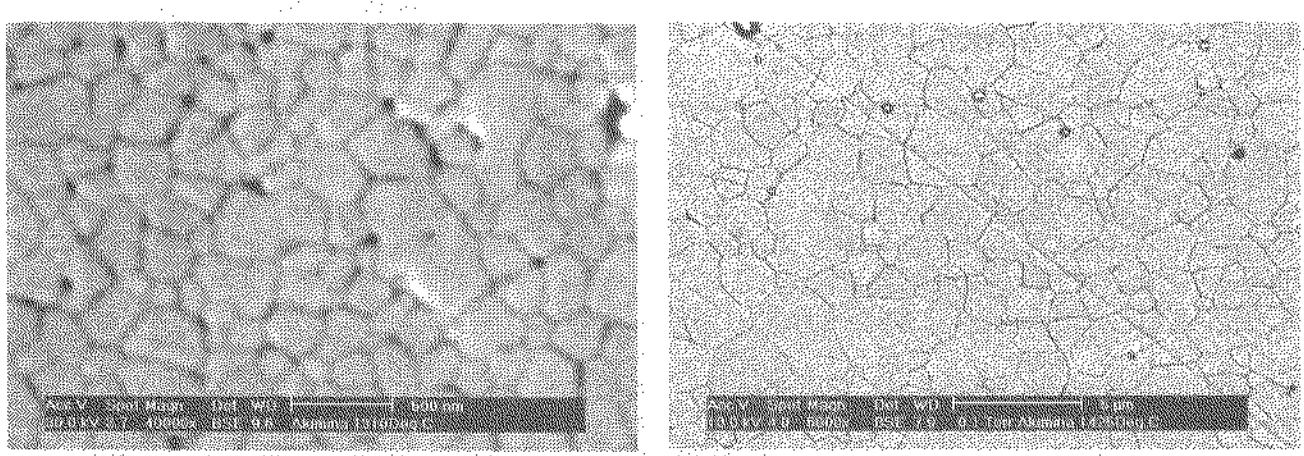

Figure 5 Polished microstructure of high-purity fine-grained alumina prepared at pH = 2 suspension and sintered at 1310°C (left) and 1425°C (right)

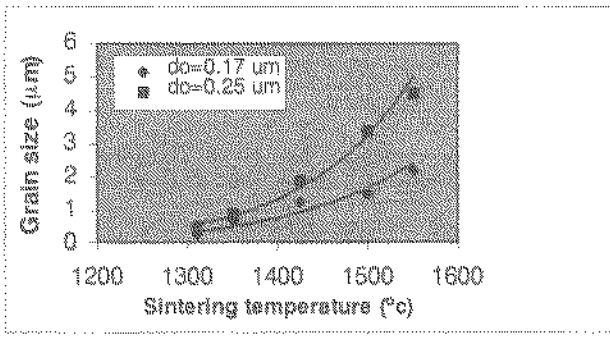

Figure 6 Grain size of samples sintered at varying sintering temperatures for similar alumina powders with the initial particle size, d_o = 0.17 mm as used in the present study and the d_o = 0.25 mm used in a previous study (Muchtar, 1999)

Japan with an average initial particle size of 0.25 mm is also depicted in the figure. The TM-5D powder suspension was also prepared at pH 2 and followed the same processing route as the powder used in the present study. It is clearly evident that the initial particle size of the alumina powders determines the final grain size of the sintered samples. A smaller initial particle size results in a smaller fired grain size. This emphasizes the significance of using a starting material with a smaller initial particle size. As all other things being equal, the mechanical performance of polycrystalline alumina improves with a reduction in grain size (Muchtar and Lim, 1998; Lange, 1989; Miyahara et al., 1992).

CONCLUSION

The result of this study has proven that a careful pH control of the suspension is necessary for the deagglomeration of high-purity and fine-sized alumina powders, ensuring a successful colloidal processing of the powders. The rheological work has indicated that the pH 2 suspensions have a much lower viscosity compared to those of pH 2.5 and 3. Upon comparing the SEM micrographs of the fired samples, the pH 2 samples showed little or no agglomeration. In contrast, samples which were not processed at pH 2 showed much agglomeration of the alumina particles. It is also shown that at a low-firing temperature of 1310°C, the pH 2 samples have already started the sintering process whereas the other samples have yet to manifest the onset of sintering. In conclusion, the present work has shown that fine-grained, high-purity alumina was successfully deagglomerated via colloidal processing at pH 2 and subsequently sintered to full density at a low temperature of 1310°C with one hour soaking time.

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