Preparation and Mechanical Properties of the CIP and HIP Fabricated Alumina Ceramics

Lina dela Cuesta, Severino T. Bernardo, Manolo Mena, Girlie Naomi Sison, Seong Jai Cho and Keizo Uematsu

1Industrial Technology Development Institute, Taguig City, Philippines
2University of the Philippines, Diliman, Quezon City, Philippines
3Korea Research Institute of Standards and Science, Daejon, South Korea
4Nagaoka University of Technology, Nagaoka, Niigata, Japan

The starting alumina powders were prepared by chemical synthesis at pH 6.5 and pH 8.5. Powders made at pH 8.5 exhibited finer particle size, high surface area and crystalline structure. These powders were fabricated by (1) cold isostatic press (CIP) and (2) hot isostatic press (HIP) at 1550°C and 1650°C sintering temperatures. The microstructure of both compacts showed abnormal grain growth but to a greater extent in those prepared by CIP. This was attributed to the presence of Ca in the starting alumina powders. The HIP fabricated alumina compacts at pH 8.5 and sintered at 1650°C, gave high flexural strength and fracture toughness due to the formation of fine-needlelike grains in between the fine-grains of alumina. The CIP fabricated alumina compacts at pH 8.5 and sintered at 1650°C showed relatively low values of flexural strength due to the growth of large alumina grains.

Key Words: coprecipitation technique, surface area, microstructure, flexural strength, fracture toughness

INTRODUCTION

Nano-crystalline α-alumina powder has considerable potential for a wide range of applications including high performance engineering materials, electronic ceramics, bio-materials, and catalyst (Kim et al. 2002; Koga et al. 2001). Alumina has excellent mechanical properties that are very much dependent on the nature of fabrication and preparation techniques, purity of the starting materials, and the temperature at which the powder is sintered (Deng et al. 2001; Tanaka et al. 2002; Bonevich 1992). Alumina compacts may be formed in various ways, but those commonly used for good compaction are the cold isostatic pressing (CIP) and hot isostatic pressing (HIP).

The mechanical properties of alumina products strongly depend on their microstructure: particularly grain boundaries, presence of impurity, and grain growth (Cho et al. 2001; Koike 1996; Kruer 1998). This study aims to evaluate the effects of the 2 types of fabrication techniques on the properties of alumina powder in terms of pore morphology, microstructure, and mechanical properties. The study will also correlate grain boundary structures and the effect of impurity to microstructural property, particularly at high temperature deformation. The influence of the applied load will also be studied on the basis of mechanical properties.
MATERIALS AND METHODS

Powder Synthesis
The starting precursors were synthesized from equal volume of 0.1M ammonium aluminum sulfate (AA) and 1.5 M ammonium hydrogen carbonate (AHC) at pH 6.5 and pH 8.5 (Hayashi et al. 1990). The pH of the AHC solution was measured with a pH meter and was adjusted by the addition of 4 M ammonium hydroxide (for pH >7) or 1M HCl (for pH < 7). The reaction was carried out at room temperature. The resulting precipitate was vacuum filtered and dried. The dried powders were calcined at 1250°C to remove the combustibles in the forms of ammonia, water, and carbon dioxide and also to produce the α-alumina.

Fabrication of Test Samples/Compacts
Cold Isostatic Press (CIP)
Approximately 20 g of dried powders was weighed, placed in a mold, pre-pressed at 100 MPa for one minute and vacuum sealed. The sealed sample was then placed in an isostatic machine and pressed at 200 MPa for 2 minutes. The pressure was then slowly released to ensure good compaction.

Hot isostatic (HIP)
Approximately 60 grams of powder was placed into the graphite mold with diameter of 55 mm. This was then transferred to the hot press furnace (Electrofuel 10 ton) and hot pressed at 12.41 MPa.

All CIP/HIP alumina samples were sintered at 1550°C and 1650°C.

Bulk Density Measurement
The bulk density of sintered samples was determined by measuring the weight (g), height (cm) and the diameter (cm). Using the formula d=w/v, and substituting the known data, the approximate bulk density is calculated.

Impurity Determination
The cut test specimens were first polished to mirror-like surface. The polished surface was cleaned with alcohol, dried and dipped into the etching solution (a mixture of 2% H2SO4 in ethanol). These were air-dried for 2 h and coated with gold by sputtering technique. The gold-coated samples were viewed under SEM for EDAX examination, i.e. presence of Si and Ca.

Microstructural Examination
Two sets of sintered alumina samples were polished and heat-treated 100°C lower than the sintering temperature. The first set was mounted on a glass slide and directly viewed under the laser microscope. The other set was gold-coated and viewed under the SEM. Microstructural examinations were conducted using the SEM Leis Model.

Flexural Strength and Fracture Toughness
Flexural Strength Measurement
Samples were cut by machine to dimensions: 36mm x 3mm x 4 mm. Specimens were then tested for flexural strength using the Instron 4465 testing machine under Nitrogen gas.

Fracture toughness measurement
A notch or crack on 1 side at the middle portion of the sample was made using the Vickers Hardness Tester (Model: DVK-28) with a load of 10 kg or 98 N. The notched sample was then placed on the metal holder for strength determination.

RESULTS AND DISCUSSION

Powder Synthesis
The alumina particles formed from the above preparations were composed mainly of fine particles (typically <0.02 μm particle size). The average particle size of the synthesized alumina powder was estimated on the assumption that all particles have the same spherical shape and size. The calculated particle diameter gave a value of 25 nm based on the formula: D = 6/(Ssp)(ρo) where: D is the diameter of the synthesized alumina powder in nm, Ssp is the measured specific surface area equivalent to 233 m2/g, and ρo is the true density of the alumina powder equal to 1.01 g/cc). This particle size diameter was found consistent with the TEM micrographs (Figure 1). Finer particles of alumina were observed at higher pH. At pH 6.5, the reaction between the aqueous solutions of AA and AHC resulted to an agglomerated mass of particles. The white precipitate, which was soft, of foamy structure and very porous, was formed with effervescence shown in the following reaction:

\[ \text{NH}_4\text{HCO}_3 + (\text{NH}_4)_2\text{SO}_4 + \text{Al}_2\text{(SO}_4)_3 + 24\text{H}_2\text{O} \rightarrow 2\text{Al(OH)}_3 + 3\text{NH}_3 + \text{CO}_2 + 4\text{H}_2\text{SO}_4 + 19\text{H}_2\text{O} \]
In this reaction, the $\text{Al}^{3+}$ also acts as a Bronsted-Lowry acid. The specie neutralizes the negatively charged hydroxo complexes, resulting to an agglomerated mass of $\text{Al(OH)}_3$ that tends to settle quickly (Kneen 1972). Adjusting the pH of the AHC solution to 8.5 resulted to the formation of small particles and negatively charged complexes such as $\text{OH}^-$, $\text{HCO}_3^-$, and $\text{AlO(OH)}_2^-$. At this pH, individual particles, which acquired negative surface charge remained dispersed in the solution and later formed a gelatinous precipitate. The amount of interparticle repulsion (Wu 2000) was greatest in solution containing higher concentration of the $\text{OH}^-$ ions. Hence, the precipitate formed at pH 8.5 has finer particle size and took longer time to settle compared to that made at pH 6.5, consequently lowering the filterability of the precipitate.

Based on x-ray analysis (Figure 2), two types of structure were formed. The precipitate was amorphous at lower pH, whereas, at higher pH the white residue was crystalline due to the formation of ammonium aluminum carbonate hydroxide (AACH). The more $\text{OH}^-$ ions present in the solution, the finer the precipitate and the harder to filter.

**Bulk Density Measurement**

The synthesized powders were made up of fine particles even in the calcined form. During the preparation of compacts, it was noted that powders (in particular for pH 8.5) would easily be blown or got stuck on the gloves that were used during handling. When the powders underwent either the CIP or HIP, pores were still present and significantly affected the density of the sintered compacts. The measured bulk density of the CIP and HIP fabricated alumina compacts is shown in Table 1.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Density (g/mL)</th>
<th>CIP</th>
<th>HIP</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 6.5</td>
<td>1550°C</td>
<td>3.7257</td>
<td>3.8810</td>
</tr>
<tr>
<td></td>
<td>1650°C</td>
<td>3.7268</td>
<td>3.8732</td>
</tr>
<tr>
<td></td>
<td>1550°C</td>
<td>3.7015</td>
<td>3.8991</td>
</tr>
<tr>
<td>pH 8.5</td>
<td>1550°C</td>
<td>3.8815</td>
<td>3.8916</td>
</tr>
<tr>
<td></td>
<td>1650°C</td>
<td>3.8713</td>
<td>3.9121</td>
</tr>
<tr>
<td></td>
<td>1550°C</td>
<td>3.9005</td>
<td>3.9032</td>
</tr>
</tbody>
</table>

The bulk density of alumina compacts is affected by various factors namely: the sintering temperature, the fabrication process employed, and the pH used during powder preparation. The bulk density for compacts (3.9569 g/mL) fabricated at pH 6.5, HIP and 1650°C was greater than the compacts (3.7180 g/mL) fabricated at pH 6.5, CIP and 1550°C. The same was true for compacts (3.9266 g/mL) at pH 6.5, HIP and 1550°C and those (3.9023 g/mL) fabricated at pH 6.5, CIP and 1650°C. Based on the ANOVA of the bulk density values, the effect of the fabrication process and temperature, fabrication process and pH, as well as, the combination of temperature and pH, were significant. In addition, the bulk density (3.8973 g/mL) of compacts fabricated at pH 8.5, HIP and pH 1650°C was also greater than those compacts (3.7180 g/mL) fabricated at pH 6.5, CIP and 1550°C. Thus, the
effect of the fabrication process, temperature and pH on the bulk density of the alumina compacts was considered highly significant. All calculations were made at 5% level of acceptance.

The discrepancy in the density of the fired-compacts was attributed to the morphology of the starting powders particularly those made at pH 8.5. At this pH, the powders were agglomerated. This resulted in the formation of pores with irregular shape from the low density regions at the boundaries of the granules. According to Zhang et al. (1999), these pores are attributed to the aggregation of the granules and/or the non-uniform packing of the granules.

Impurity analysis
The microstructures of the CIP/HIP alumina compacts have demonstrated the effect of an impurity in the original synthesized powders. Figure 3 shows the laser micrographs of the HIP fabricated and sintered at 1650°C alumina compacts. The sample prepared from pH 8.5 contained fine elongated needle-like grains in between other fine grains, whereas, the pH 6.5 was composed of irregular large grains in fine-grained matrix.

EDAX analysis (Figure 4) of the starting powders made at pH 6.5 showed a peak of Ca and also an absence of the same peak for powder made at pH 8.5. But this did not mean that Ca was not present in the powder (pH 8.5), since grain growth was also exhibited in the HIP/CIP fabricated samples. The amount of Ca in the powder may be very minimal or less than 0.01% such that EDAX could no longer detect it. Ca, even in a very minimal or trace amounts, can likely enhance grain growth. This is because Ca acts as a catalyst to the growing alumina grains at high temperature.

In an alkaline solution (pH 8.5), Ca is quite stable due to the hydrogen bonding that exists in the solution. In this condition, the AACH (the alumina rich-mineral formed at pH 8-10) was also formed in agglomeration such that the calcium becomes homogeneously mixed with the AACH. The agglomeration was brought about because of electrostatic forces, van der Waals forces, capillary forces and others. Upon heating, the precipitated alumina showed the formation of needle-like structure in between the alumina grains due to Ca that brought about grain growth.

On the other hand, the alumina powder processed at pH 6.5 contained Ca in some areas of the grain boundary due to the occurrence of grain growth. Generally, some grains grew depending on the amount of Ca. Previous investigations (Kaysser 1987; Handwerker 1989) suggested that impurities, notably silicon and calcium, play a decisive role for the abnormal grain growth of Al₂O₃. AGG (abnormal grain growth) is one of the reasons for the reduction of the mechanical property of sintered ceramics.
Microstructural Analysis
The structure of the starting powders were very fine and agglomerated, particularly those prepared at pH 8.5, resulting to the non uniform packing of the granules. Non-uniform packing generated voids/spaces in between particles that resulted to the formation of pores when the formed compacts were sintered. This manifested the occurrence of pores in the CIP alumina compacts (Figure 5) sintered at 1550°C and 1650°C. For compacts made at pH 6.5, the microstructure showed different grain sizes and pores in-between the grains. More pores were exhibited by samples that were sintered at 1550°C compared to those fired at 1650°C. However, large grains appeared in samples sintered at 1650°C.

For compacts prepared at pH 8.5, the microstructure appeared differently compared with compacts prepared at pH 6.5 at the same sintering temperature. The compacts at pH 8.5 showed grain growth but pores were greatly reduced since significant numbers of these pores were trapped in the abnormally grown grains. Hence, the porosity appeared to be large for compacts made at pH 6.5. The difference in the porosity can be attributed to the sintering temperature and morphology of the powders.

All compacts prepared by HIP and sintered at 1550°C and 1650°C showed the presence of pores (microstructure shown in Figure 6). Presence of pores, however, was greatest in the compact made at pH 8.5 and sintered at 1550°C. The presence of these pores could be associated with the low density of the compacts (refer to Table 1) and morphology of the powders. Powders prepared at pH 8.5 showed smaller particle sizes than those made at pH 6.5. Compaction was relatively higher for powders made at pH 6.5, resulting to lesser pores.

The formation of abnormal grain growth in all the compacts was due to a small amount of impurities (refer to impurity analysis). Compared to the samples prepared at pH 6.5, the amount of impurities was found homogeneously mixed in compacts made at pH 8.5. This may be due to the alkaline nature of processing the alumina powder. On further sintering, the impurities accumulating at the grain boundaries has already reached its solubility limit, thus, causing the grains to grow (Johnson & Stein 1975). Thus, the presence of Ca in powders at pH 8.5 greatly effected the microstructure due to the occurrence of more inter-connecting grains particularly at higher sintering temperature (1650°C).

Sintering temperature (under air) largely affects also the densification and occurrence of abnormal grain growth of alumina compacts. When the CIP alumina compacts were annealed in air, the grains reacted with oxygen and resulted to the subsequent reduction of dragging force (Gupta 1982). The outcome of such reaction explains the formation of grain growth. On the other hand, sintering under reducing atmosphere or under nitrogen atmosphere definitely controls grain growth (Mutoh & Inone 1993). In such case, grain growth in HIP compacts were controlled.

Mechanical Properties (Flexural Strength and Fracture Toughness)
Typically, the higher the purity of the alumina sample, the higher is the sintering temperature for densification. Since grain growth of alumina is sensitive to sintering temperature, abnormal grain growth in alumina usually

![Figure 5. SEM micrograph of CIP fabricated alumina compacts prepared at pH 6.5 and pH 8.5 and sintered at 1550°C and 1650°C](image)

![Figure 6. SEM micrograph of HIP fabricated alumina compacts made at pH 6.5 and pH 8.5 and sintered at 1550°C and 1650°C](image)
occur in the final stage of densification. The flexural strength and wear resistance of pure alumina increase with decreasing grain size.

Figure 7 shows the effect of sintering temperature and pH on the flexural strength of alumina compacts fabricated by CIP and HIP. For HIP fabricated compacts, an increased in the pH from 6.5 to 8.5 at a sintering temperature of 1550°C resulted to a decrease in the flexural strength. However, for both compacts, the flexural strength values increased when sintering at 1650°C.

In the case of the CIP fabricated alumina compacts, samples sintered at 1550°C and at 1650°C showed an increase in flexural strength. Furthermore, at pH 6.5 and sintering temperature of 1650°C, compacts fabricated by CIP and HIP did not show significant difference in flexural strength values. However, samples at pH 8.5 and fabricated both by CIP and HIP methods produced high strength when sintered at 1550°C and 1650°C. As the sintering temperature was increased from 1550°C to 1650°C, the HIP compacts at pH 8.5 showed a significant increase in flexural strength; CIP fabricated compacts exhibited a minimal reduction in strength. On the other hand, the HIP compacts at pH 6.5 exhibited low flexural strength values compared to compacts at pH 8.5; no significant change was noted on the flexural strength values of CIP compacts. These results clearly indicate that grain size, porosity, and morphology of the starting powders have a significant influence on the flexural strength property of the compacts other than the density.

The microstructures of the HIP alumina compacts contained pores. High porosity is the main factor contributing to low density and strength. And these were attributed by the particle morphology of the powders prepared at pH 6.5 and pH 8.5. However, there was an observed inconsistencies of the measured strength, that is, reduced strength at pH 6.5 and an increased strength in pH 8.5 (from 1550 °C to 1650 °C). This is primarily due to the abnormal grain growth as evidenced by the laser micrographs (Figure 3). At 1650 °C the grains of compacts at pH 6.5 were very large compared to the compacts at pH 8.5. The latter showed fine grains with faceted and needle-like structure in-between the grains. According to Yasuoka et al. (1994), as grain size decreased, high flexural strength increases. The impurities found in the HIP compacts prepared at pH 8.5 did not result in the growth of large grains, instead,
formed small needle-like grains that in a way improved the strength. A homogeneous mixture containing small amount of impurity coupled with the sintering under nitrogen atmosphere inhibited the formation of large abnormal grain.

The measured fracture toughness of the alumina compacts is presented in Figure 8. For pH 8.5 / HIP compacts, sudden increase in toughness was observed as the temperature was increased from 1550°C to 1650°C. However, the same sets of compacts fabricated by CIP at pH 8.5 showed slight decrease in toughness. On the other hand, pH 6.5/HIP fabricated compacts appreciably increased in toughness, but the CIP compacts showed insignificant change.

The significant increase in the toughness of the HIP compacts was attributed to the presence of large grains for compacts at pH 6.5, and with the growth of grains in the form of needle-like grains for compacts at pH 8.5. These abnormal grain growths for all alumina compacts (CIP/HIP) were enhanced by the presence of Ca. These grains act as “bridging grains”, which then prevent the propagation of crack (Yasuoka 1993). As a result, the fracture toughness of alumina compacts was improved by the presence of second phases in the microstructure promoting crack deflection and crack bridging.

CONCLUSIONS

The 2 powders synthesized were fine and agglomerated especially when prepared at pH 8.5. Because of this morphology, the CIP and HIP alumina compacts have not attained good compaction and resulted to low sintered densities.

The microstructures for the CIP and HIP alumina compacts showed the presence of pores and growth of grains. Grain growth was more enhanced in the CIP samples due to the oxygenation of the grain boundaries and also to the effect of Ca. As the temperature was increased, the growth of the grains also increased.

The pH at which the powder was prepared showed a significant effect on the growth of grains. At pH 8.5, the Ca was homogeneously mixed with the alumina forming a regular growth of grains when HIP fabricated. The

![Figure 8. Fracture Toughness (FT) of Alumina Compacts in relation to pH, sintering temperature, and fabrication process.](image)

Note: Dotted line represents mean fracture toughness for CIP, and the line represents mean fracture toughness for HIP. Significant differences are observed in all FT of alumina compacts except for those fabricated using the 2 processes (HIP and CIP) at pH 8.5 and 1650 °C where no significant difference is observed.
measured high values for the flexural strength and fracture toughness of the HIP (pH 8.5/sintered 1650 °C) was attributed to the formation of fine-grained microstructure with faceted/needle-like growth in between the grains which was effective in increasing the strength of the material.

REFERENCES


