PHILIPPINE ENGINEERING JOURNAL
PEJ 2005; **Vol. 26 No. 2**:41–56

The Relation Between Preparation, Microstructure and Mechanical Properties of Alumina Ceramics

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ABSTRACT

The starting alumina powders were synthesized by chemical method under varied pH conditions - pH 6.5 and pH 8.5. The resulting powders were characterized by fine particle sizes, high surface area and crystalline structure. Powders at pH 8.5 were noted to have finer particle size than at pH 6.5. Due to their fine characteristic, the powders agglomerated during preparation of compacts.

The alumina compacts were fabricated by (1) cold isostatic press (CIP) and sintered at 1550°C and 1650°C and (2) hot isostatic press (HIP) and also sintered at 1550°C and 1650°C. The CIP compacts showed large grains of alumina, whereas the HIP compacts were relatively fine-grained. The microstructure of both compacts exhibited abnormal grain growth more particularly in the CIP compacts.

The synthesized powders were contaminated with Ca which accounted for the abnormal grain growth in both alumina compacts. The Ca present in HIP fabricated alumina compacts at pH 8.5 and sintered at 1650°C, gave high flexural strength. This was due to the formation of fine-elongated grains of regular pattern in between the fine-grains in the alumina matrix. The Ca present in the CIP fabricated alumina compacts at pH 8.5 and sintered at 1650°C gave relatively low values of flexural strength. Flexural strength of alumina compacts fabricated by HIP at pH 8.5 significantly increased with an increase in sintering temperature.

For HIP alumina compacts at pH 8.5, fracture toughness increased with an increase in sintering temperature. Such increase in toughness was due to the growth of needle-like grains.

1. INTRODUCTION

Nano-crystalline α-alumina powder has considerable potential for a wide range of application including high performance engineering materials, electronic ceramics, bio-materials and

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Received December 6, 2004
Revised January 23, 2006
Accepted February 8, 2006

catalyst [1]. Alumina has excellent mechanical properties. These properties are very much dependent on the fabrication and preparation techniques used, purity of the starting materials and the temperature at which the powder is sintered [2]-[4]. The mechanical properties of alumina products strongly depend on the resulting microstructure: grain boundaries, presence of impurity, grain growth, etc [5]. In order to maximize its service life, its desirable qualities must be attained. A thorough understanding on the relationships between starting powder, preparation, microstructure and mechanical properties is necessary in order to design and fabricate alumina ceramics intended for a particular application.

In this study, alumina compacts were formed by cold isostatic pressing (CIP) and hot isostatic pressing (HIP). The study aims to evaluate the effects of the two 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 the strength.

2. MATERIALS AND METHODS

2.1. Powder Synthesis

The starting precursor was 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. 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.

2.2. Powder Characterization

The alumina powders were characterized using a Philips X-ray Powder Diffractometer with Cu anode (ModelPW3040/00) operating at 40 kV and 50 mA. The morphology (shape and size) of freshly prepared powders was analyzed using the transmission electron microscope model: TM 35 S.

2.3. Fabrication of Test Samples/Compacts

For CIP alumina compacts, the powder was pressed at 200 MPa, whereas for HIP samples, the powders were hot pressed at 12.41 MPa in the furnace (Model:Electrofuel 10 ton). All samples were sintered at 1550°C and 1650°C.

2.4. Bulk Density Measurement

The resulting bulk density of the sintered samples was taken by getting 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.

2.5. 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 2% H_2SO_4 in ethanol). These were air-dried for two hours 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.

2.6. Microstructural Examination

Samples of sintered alumina were polished and heat-treated (100°C lower than the sintering temperature). Microstructural examinations were conducted using a SEM Model Leis and laser microscope.

2.7. Flexural Strength and Fracture Toughness

Samples were cut by machine to dimensions: 36mm × 3mm × 4 mm. Specimens were then tested for flexural strength using a 3-point bend measurement with the Instron 4465 testing machine under Nitrogen gas. For fracture toughness measurement, a notch or crack on one 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.

3. RESULTS AND DISCUSSIONS

3.1. Particle size, morphology and structure of the synthesized alumina

The synthesized alumina powders were composed mainly of fine particles (typically < 0.02 micron particle size). Typical TEM micrographs of the powders prepared at pH 6.5 and 8.5 and at room temperature are shown in Figure 1. Much finer particles of alumina were observed at higher pH. The powders made at pH 8.5 gave higher surface area than those at pH 6.5. Figure 1 displays the image and diffraction pattern of the powders obtained from coprecipitation method. It is observed that the diffraction patterns for the powder made at pH 8.5 gave a more distinct and brighter ring. This indicates that the powder product is made up of fine and crystalline particles. The crystallographic orientation could not be measured due to the very fine particle sizes. Figure 1A suggests that the powder is amorphous since there is no clear view of rings in the diffraction pattern. This was also confirmed when the same powder was subjected to x-ray analysis (Figure 2).

Based on x-ray analysis (Figure 2), two types of structures 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). A higher concentration of OH- ions present in the solution yielded finer precipitates which were hard to filter [6].

3.2. Bulk Density Measurement

The synthesized powders were really fine in particle sizes even in the calcined form. The measured density of the CIP and HIP fabricated alumina compacts and the analysis of variance

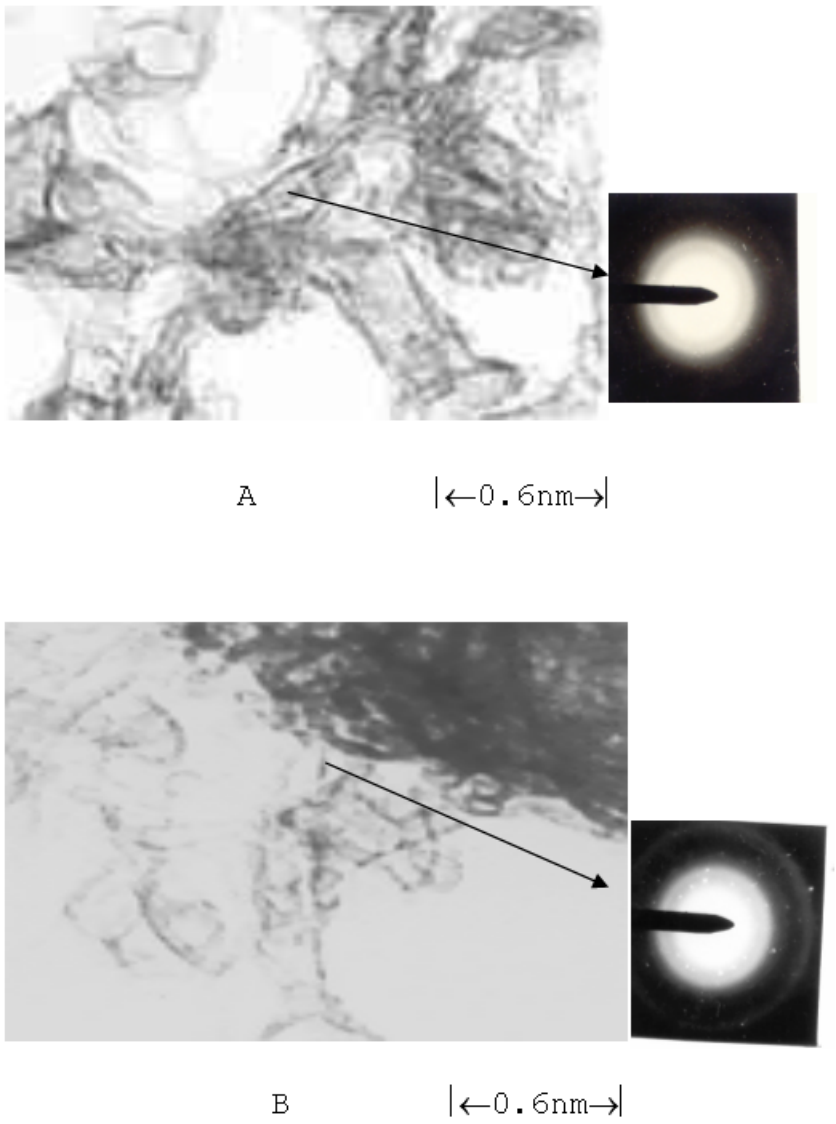

Figure 1. TEM micrographs of freshly prepared powders at: (A) pH 6.5 and (B) pH 8.5

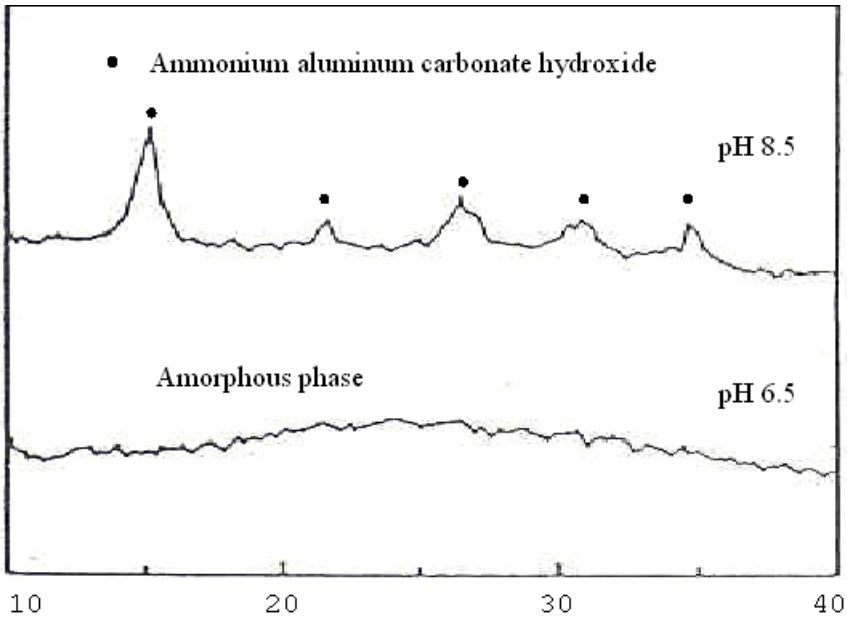

Figure 2. X-ray diffraction pattern of the synthesized alumina powder at pH 6.5 and pH 8.5

Samples	Density(g/mL) (% Theoretical Density)			
	CIP		HIP	
	1550°C	1650°C	1550°C	1650°C
pH 6.5	3.7257	3.8810	3.9299	3.9365
	3.7268	3.8732	3.9200	3.9402
	3.7015	3.8991	3.9300	3.9940
pH 8.5	3.8815	3.8916	3.3516	3.8920
	3.8713	3.9121	3.3190	3.8990
	3.9005	3.9032	3.3498	3.9010

Table I. Bulk densities of fabricated compacts

are shown in Table I and Table II, respectively.

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. These powders were agglomerated. As a result, pores were formed, of irregular shape from the low-density regions at the boundaries of the granules. According to Zhang *et al.* [6], these pores are attributed to the aggregation of

Source of Variation	Df	Sum of Sq	Mean Sq	F Value	Pr(F)
process	1	0.0269675	0.0269675	101.1365	2.539e-008
temp	1	0.2233589	0.2233589	837.6653	0.000e+000
pH	1	0.0799607	0.0799607	299.8773	8.710e-012
process:temp	1	0.0609538	0.0609538	228.8773	6.784e-011
process:pH	1	0.25855658	0.25855658	969.7021	0.000e+000
temp:pH	1	0.0536855	0.0536855	201.3373	1.752e-010
process:temp:pH	1	0.1711126	0.1711126	641.7254	2.000e-014
Residuals	16	0.0042663	0.0002666		

The ANOVA table suggests the presence of two-factor interaction of process and temperature, process and pH as well as temperature and pH. The three factor interaction between process, temperature and pH is also evident. It also shows a significant main effect of all the three factors.

Table II. Analysis of Variance of Density

the granules and/or the non-uniform packing of the granules.

3.3. Microstructural analysis

Figure 3 shows the structure of CIP alumina compacts fired at 1550°C and 1650°C. The arrows show the presence of pores. The morphology of these large pores changed with the sintering temperature.

In the specimen prepared at pH 6.5, majority of the large defects have a clear boundary, whereas, when the pH increases to pH 8.5, extremely large pores exhibited an unclear boundary. The structure of the CIP alumina produced an equiaxed grain, whereas, the others (pH 8.5 at 1650°C) developed elongated grains. Elongated grains developed as a result of differences in the growth rates of the bounding interfaces, the relative growth rates of the bounding grain boundaries (or surfaces planes) determine the evolution of the grain [8]. The development of faceted grains in ceramics is often associated with the presence of wetting grain-boundary phase which could be brought about by glassy phase accumulation in the form of impurities at the grain boundaries [9].

The effect of sintering temperature (under air) on the densification and occurrence of abnormal grain growth (AGG) is also very significant in the sintering of alumina compacts. From the microstructures, significant number of pores were trapped in the abnormally grown grains [10], thus, the porosity appeared to be large for sample made at pH 6.5. The same was also observed in alumina compacts made at pH 8.5. The difference in the porosity could be attributed to the sintering temperature applied for each specimen and also to the degree of compaction of the powder granules. Furthermore, the results indicate that the densification process have been affected by the presence of an impurity that had enhanced grain growth. The measured grain size of the sintered compacts and its analysis of variance are presented in

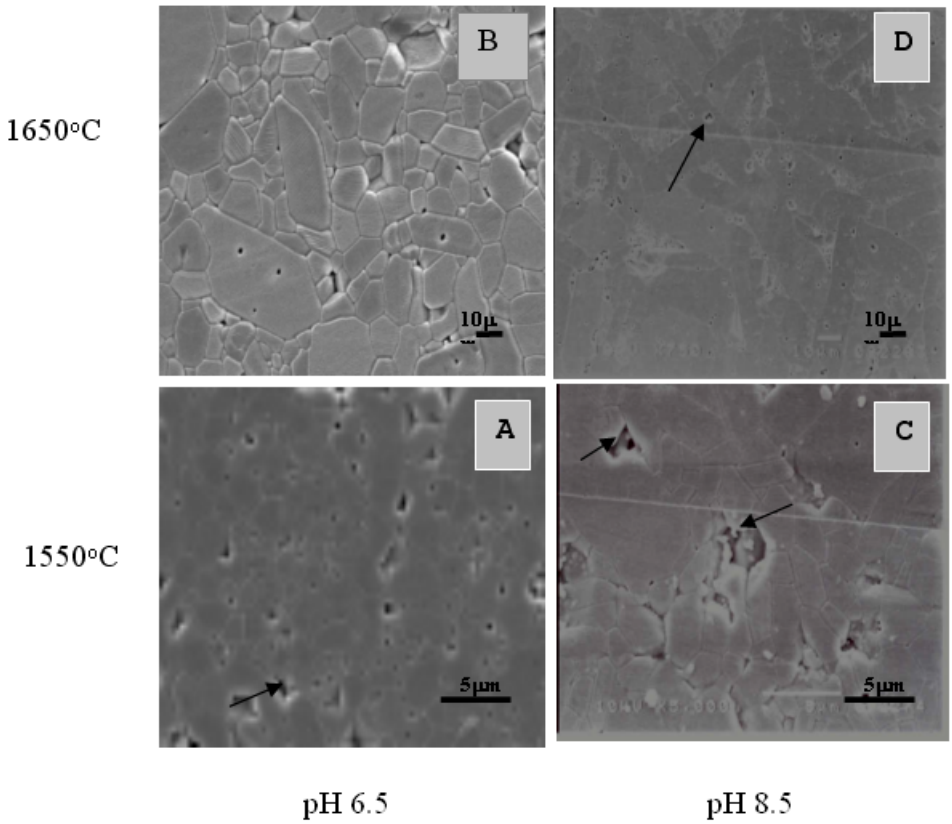

Figure 3. Microstructure of CIP alumina compacts made at pH 6.5: sintered at (A) 1550°C (B) 1650°C, and pH 8.5 at (C) 1550°C (D) 1650°C (arrows show the pores).

Table III and Table IV, respectively.

For pH 6.5 compacts, the microstructures at 1550°C and at 1650°C showed different grain sizes and pores in-between the grains. More pores were exhibited by samples sintered at 1550°C compared to those fired at 1650°C. The average grain size at 1550°C and at 1650°C was measured $\geq$ 0.5 um and $\geq$0.9 um, respectively. Both samples contained equiaxed grains.

The results obtained from the microstructures explained that the abnormal grain growth occurring in the test compacts was due to a small amount of impurities. Compared to the samples prepared at pH 6.5, the amount of impurities was found very distinct in samples made at pH 8.5. This may be due to the alkaline nature of processing the alumina powder. It is also noted that the grain sizes were smaller before the occurrence of abnormal grain growth. On further sintering, the impurities accumulating at the grain boundaries has already reached its solubility limit, thus, causing the grains to grow [11]. On the other hand, other boundaries also affected with impurities may not have yet attained the solubility limit, show fine grain matrix. The latter is observed for compacts prepared at pH 6.5. As a result, few grains with liquid films have grown to abnormally large size with large capillary driving forces provided

Samples	Average grain size (micron)			
	pH 6.5		pH 8.5	
	1550°C	1650°C	1550°C	1650°C
CIP	0.80	1.003	0.97	0.89
	0.72	0.92	0.95	0.89
	0.76	1.09	0.94	0.92
HIP	0.587	0.643	0.520	0.596
	0.558	0.662	0.587	0.615
	0.587	0.634	0.569	0.625

Table III. Measured grain size in sintered compacts

Source of Variation	Df	Sum of Sq	Mean Sq	F Value	Pr(F)
process	1	0.5612042	0.5612042	398.5943	0.00000
temp	1	0.0368167	0.0368167	26.1490	0.0001041
pH	1	0.0004860	0.0004860	0.3552	0.5650541
process:temp	1	0.0017682	0.0017682	1.2558	0.2789799
process:pH	1	0.0075615	0.0075615	5.3705	0.0340560
temp:pH	1	0.0368167	0.0368167	26.1490	0.0001041
process:temp:pH	1	0.0298215	0.0298215	21.1807	0.0002944
Residuals	16	0.0225274	0.0014080		

The ANOVA table indicates the significant three factor interaction and a two-factor interaction between process and pH as well as between temperature and pH. However, an insignificant two factor interaction effect between process and temperature is manifested. The main effect of process and temperature is significant while that of pH is not significant but this does not mean that pH should be eliminated in future studies because there exists an interaction effect between pH and the other two variables, ie. process and temperature.

Table IV. Analysis of Variance of Density

by fine matrix grains.

For HIP alumina compacts, the corresponding microstructure is presented in Figure 4. The alumina developed grains that appeared columnar. The faceted grain boundaries increased as the pH increases from pH 6.5 to pH 8.5. These changes in grain morphology was accompanied by the creation of microcrack-like voids to triple points adjacent to the elongated grains [12]. Such pores appeared predominant in compacts made at pH 8.5.

All of the hot pressed samples fired at 1550°C and at 1650°C showed the presence of pores,

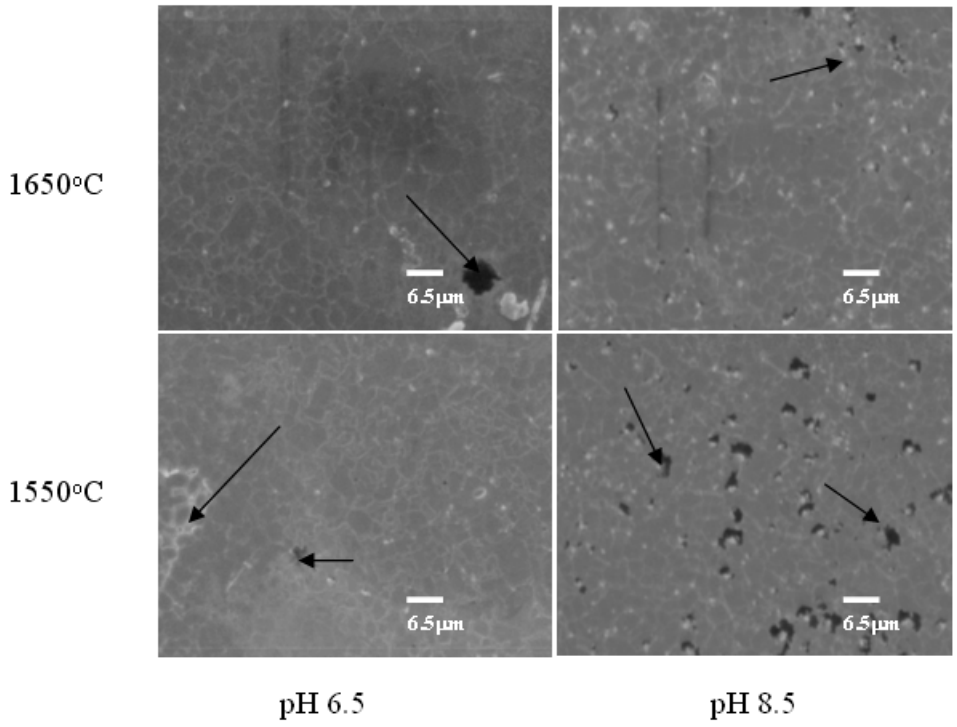

Figure 4. SEM micrograph of HIP fabricated alumina compacts made at pH 6.5 and pH 8.5 and sintered at 1550°C and 1650°C (arrows show the pores).

although, pores were greatest in the compact made at pH 8.5 and fired at 1550°C. The presence of these pores could be associated with the low density of the compacts.

At higher temperature, the connectivity of the grains became higher and the microstructure is more uniform. Sintering under reducing atmosphere or under nitrogen or argon atmosphere definitely controls grain growth [13]. However, when these compacts were subjected to laser microscopy (Figure 5), tests showed that the HIP fabricated and sintered at 1650°C alumina compacts underwent growth of grains. The sample prepared from pH 8.5 contained needle-like grains in between other fine grains, whereas, at pH 6.5, the sample was composed of irregular big grains in a fine-grained matrix.

3.4. Impurity analysis

The results taken from the microstructure of the CIP/HIP alumina compacts demonstrated the effect of an impurity in the original synthesized powders. EDS analysis (Figure 6) of the starting powders made at pH 6.5 showed a peak of Ca and also the 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 compacts. Unlike for the finer powder prepared at pH 8.5, the impurity is distributed evenly. This observation was supported by the work of Cho [2] where he demonstrated that the high concentration of impurities was

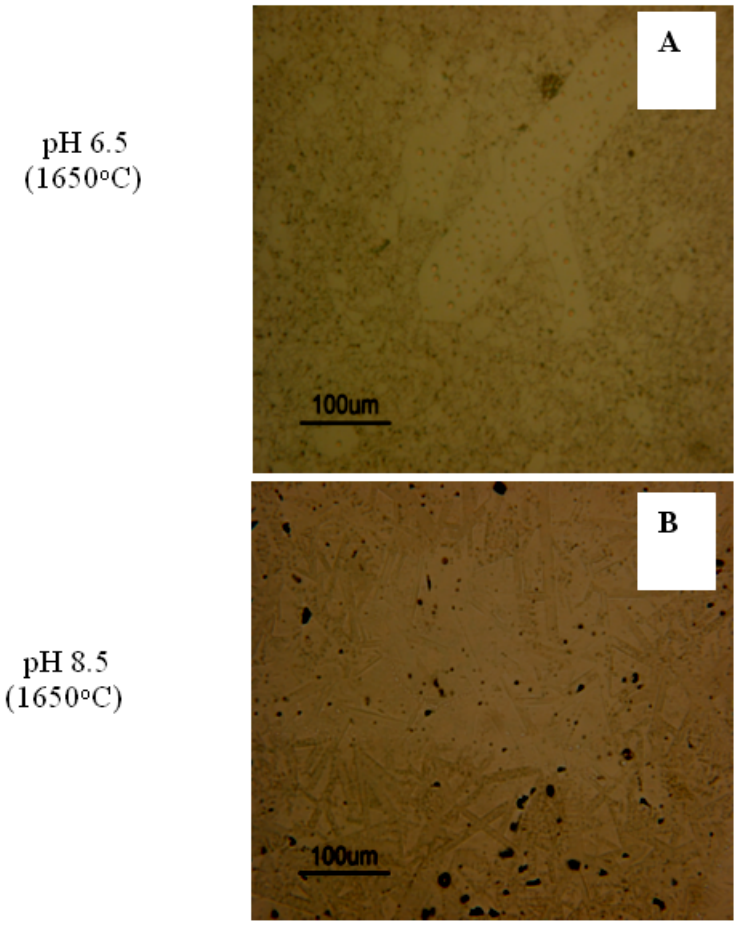

Figure 5. Laser micrographs of HIP alumina compacts aintered at 1650°C:A) ph 6.5 and (B) pH 8.5.

associated with the aggregate form of the powder. In effect, the particle aggregates causes abnormal grain growth (AGG) during sintering.

In an alkaline solution (pH 8.5), Ca in the form of $CaOH^{2+}$ and $CaOHCO_2^+$ are quite stable in the solution. In this same condition, the AACH is also formed in agglomeration such that the calcium becomes homogeneously mixed with the AACH. The agglomeration is brought about by 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 which brought about grain growth.

On the other hand, the alumina powder processed at pH 6.5, a peak that corresponded to the presence of Ca was observed. This implied that greater concentration of contamination in some parts of the grain boundary occurred due to the presence of grain growth. Other parts in the grain boundary did not exhibit grain growth but maintained finer grains (Figure 6A), which

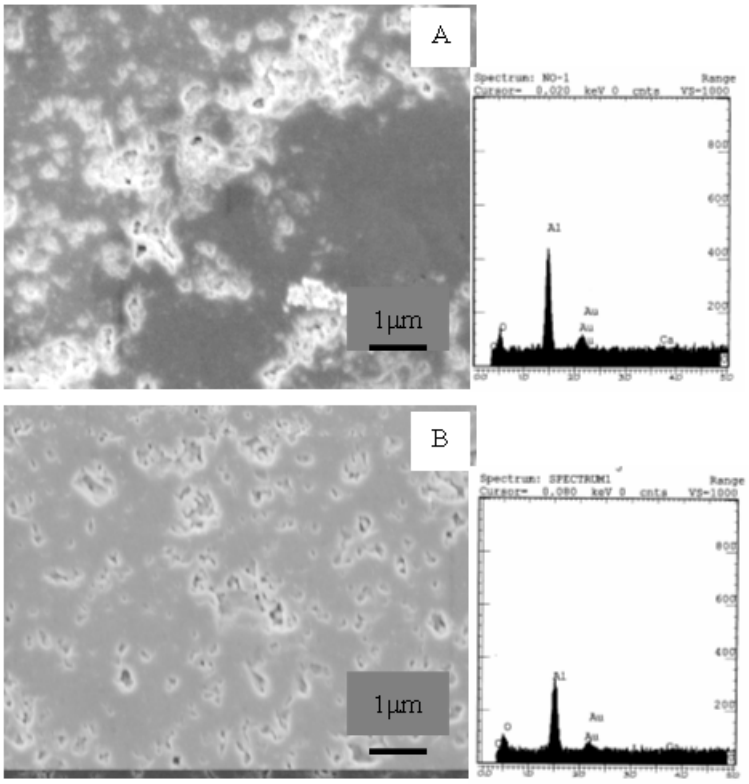

Figure 6. EDS measurement of Ca impurity in (A) pH 6.5 and (B)pH 8.5 samples

indicated that Ca was absent. Thus, Ca in powder pH 6.5 was not homogeneously present.

3.5. Mechanical Properties (Flexural Strength and Fracture Toughness)

Grain growth of alumina is sensitive to sintering temperature. If sintering temperature is too high, flexural strength and wear resistance of alumina are greatly affected. The flexural strength and wear resistance of pure alumina increased with decreasing grain size [16].

Figure 7 shows the effect of sintering temperature and pH on the flexural strength of alumina ceramics for the CIP and HIP fabricated samples. It is observed that increasing the pH from 6..5 to pH 8.5 for HIP fabricated compacts, the flexural strength decreased at the same sintering temperature (1550°C), whereas, the same compacts increased in strength when sintered at higher temperature (1650°C).

In the case of the CIP fabricated alumina compacts, samples sintered at 1550°C, showed an increase in flexural strength, whereas, at 1650°C, the same compacts exhibited also an increased strength. At pH 6.5 and 1650°C sintering temperature, compacts fabricated by CIP and HIP did not show significant difference in strength. The above results clearly indicate that grain size and porosity had a significant influence on the flexural property other than the density. Based on the microstructures of the alumina compacts, the HIP fabricated compacts

contained pores which were the main factors contributing to low density and strength.

Although these samples contained fine microstructures as shown by the SEM micrographs, the inconsistencies of the measured strength, that is, reduced strength in pH 6.5 and an increased strength in pH 8.5 (from 1550°C to 1650°C) is primarily due to the abnormal grain growth as evidenced by the laser micrographs. The grains in pH 6.5 compacts (1650°C) were very large compared to the pH 8.5 compacts. The latter showed fine grains with needle-like structure in-between the other grains. According to Yasuoka [16], high flexural strength increased appreciably with decreased grain size. The homogeneous mixture of Ca (in small amount) plus the sintering under nitrogen, definitely inhibited the formation of large abnormal grain.

The measured fracture toughness of the alumina compacts similar to those subjected to flexural strength determination is presented in Figure 8. Here, different observations were seen in the behaviour of the alumina compacts. For pH 8.5/HIP compacts, there was a sudden increase in the toughness when the temperature went up from 1550°C to 1650°C. However, the same sets of samples fabricated by CIP showed little decrease in toughness. On the other hand, pH 6.5/HIPfabricated compacts appreciably increased in toughness but the CIP compacts showed insignificant change.

The significant increase in the toughness of the HIP compacts was associated with the presence of large grains (pH 6.5 samples) and growth of grains in the form of needle-like grains for the pH 8.5 compacts. These grains then act as "bridging grain" which then prevented the propagation of crack. In some investigations conducted, Yasuoka [16] found that the fracture toughness of ceramics is improved by the presence of elongated grains or second phases in the microstructure, promoting crack deflection and crack bridging.

All CIP compacts contained large grains which could have been attributed to the presence of an impurity and also due to the sintering condition (oxidation atmosphere) employed. In a way, these factors enhanced grain growth and resulted to good toughness strength.

4. CONCLUSIONS

The two powders synthesized were fine-grained and agglomerated especially that one 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 was 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, thus, exhibiting grain growth for HIP fabricated compacts. The measured high values for the flexural strength and fracture toughness of the HIP samples (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.

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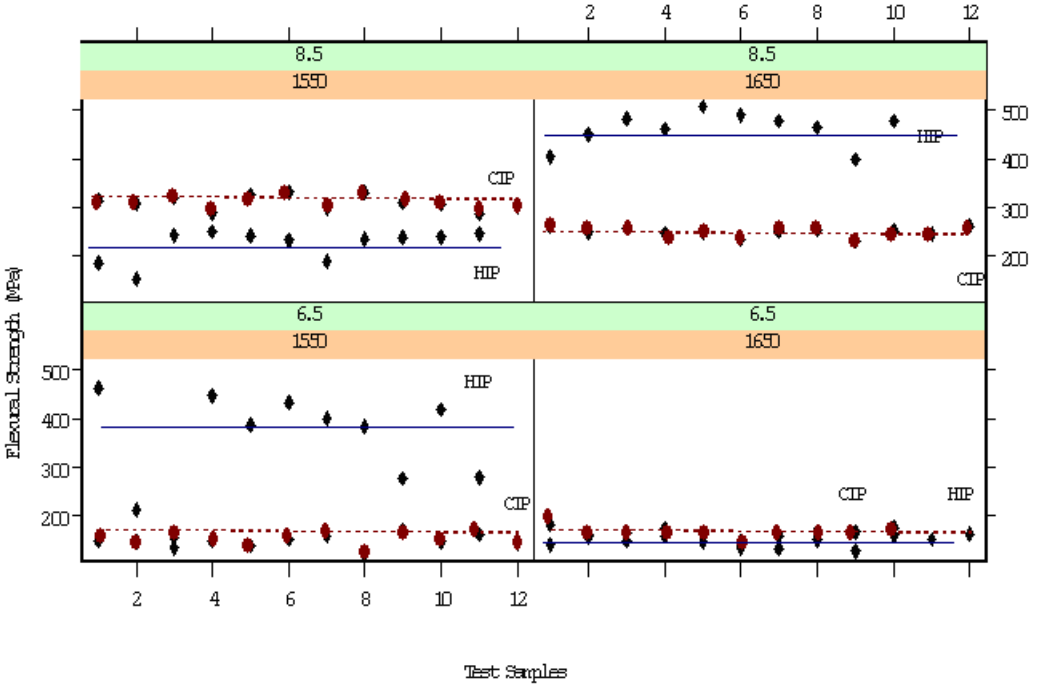
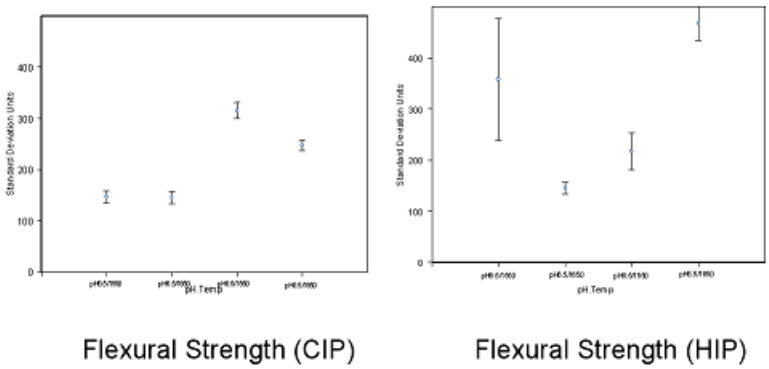


Figure 7. Flexural Strength (FS) of Alumina Compacts in Relation to pH, Sintering Temperature and, Fabrication Process

Error Bars:



The mean flexural strength of the alumina compacts using CIP is highest when produced at pH 8.5 and temperature of 1550°C followed by that produced by the same process at the same pH of 8.5 and a higher temperature of 1650°C and lowest at pH 6.5, temperatures 1550°C and 1650°C. The error bars show minimal variations of the flexural strength measurements in all the trials at different combinations of pH and temperature

The mean flexural strength of the of the alumina compacts using HIP is highest when produced at pH 8.5 and temperature of 1650°C followed by that produced by the same process at a lower pH of 6.5 and a lower temperature of 1650°C, then by that produced at pH 8.5 and temperature of 1550°C and lowest when produced at pH 6.5 and temperature 1650°C. The error bars show minimal variations of the flexural strength measurements in the trials at combination 6.5 pH and 1650°C temperature and greatest in the trials at combination 6.5 pH and 1550°C temperature.

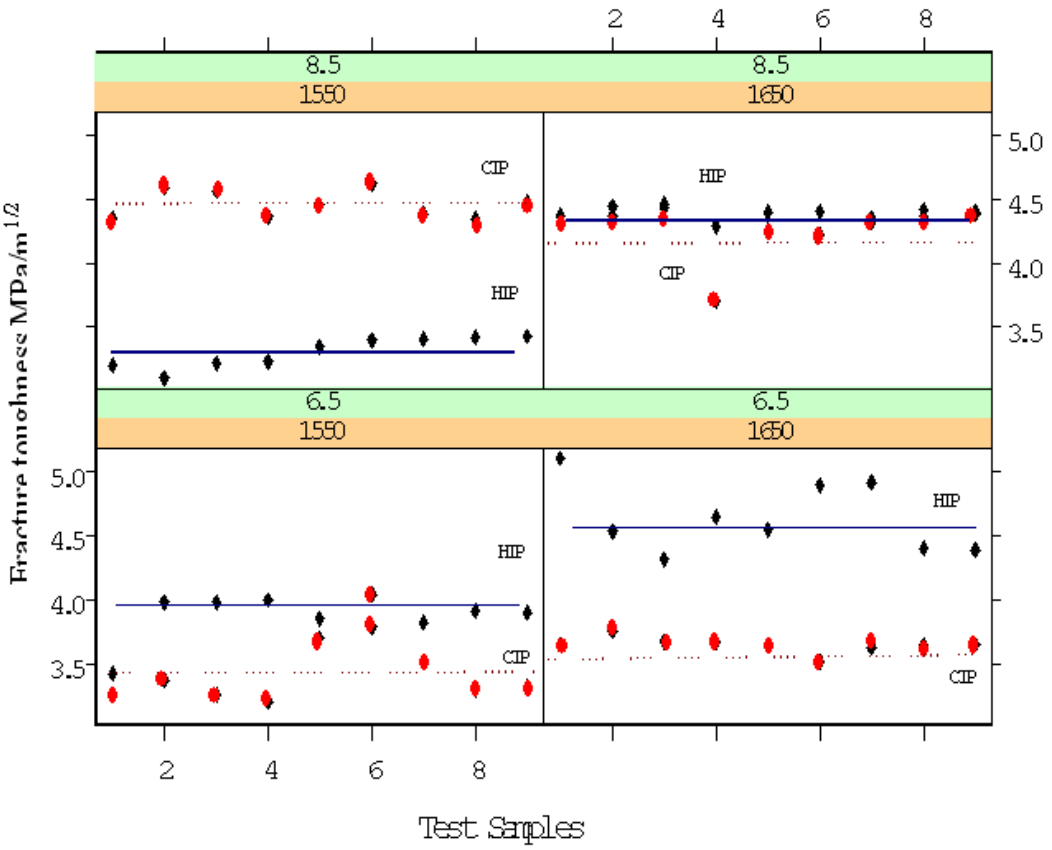


Figure 8. Fracture Toughness (FT) of Alumina Compacts in Relation to pH, Sintering Temperature and, Fabrication Process.

Note: Large dotted line represents mean fracture toughness for CIP and small dotted line represents mean fracture toughness for HIP. Significant differences are observed in all FT of alumina compacts except for those fabricated using the two processes (HIP and CIP) at pH 8.5 and 1650o C where no significant difference is observed.

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