

LOW-TEMPERATURE SYNTHESIS OF BERLINITE-BONDED ALUMINA  
CERAMICS<sup>0</sup>

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## LOW-TEMPERATURE SYNTHESIS OF BERLINITE-BONDED ALUMINA CERAMICS

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### ABSTRACT

Alumina ceramics, in which berlinitite (aluminum orthophosphate,  $AlPO_4$ ) is the bonding phase, were synthesized at 150°C. Differential thermal analysis of a mixture of  $Al_2O_3$  and  $H_3PO_4$  solution indicated that a minimum temperature of 118°C was necessary for a chemical reaction to occur. Therefore, we hydrothermally cured a mixture of  $Al_2O_3$  and  $H_3PO_4$  solution between 130°C and 150°C to form a hard and dense berlinitite-bonded alumina ceramic. The intermediate phase of aluminum phosphate hydrate ( $AlH_3(PO_4)_2 \cdot H_2O$ ) was also identified. Physical and mechanical properties of this material are discussed.

### INTRODUCTION

High-alumina ceramics are preferred materials for a wide variety of applications. Their strength makes them valuable for high-load-bearing applications, and their resistance to corrosion in harsh high temperature environments makes them desirable for applications with steam and CO atmospheres (1,2). Alumina ceramics are also well known for their low electrical and thermal conductivity, thereby lending themselves to many practical applications that range from refractory bricks to electrical insulating components. Because of their technological importance, their low-temperature processing by chemical bonding deserves investigation.

Roy (3) defines chemically bonded ceramics as ceramics that rely on low temperature solid-liquid reactions to form new phases that serve as glue for holding ceramic particles together. Chemical bonding in phosphate ceramics occurs when acid phosphates react with oxides such as alumina, to create a bond of crystalline aluminum orthophosphate ( $AlPO_4$ ) (4). The resultant aluminum phosphate product can be described as "a covalent network solid of oxygen-

bridged alternating  $\text{PO}_4$  and  $\text{AlO}_4$  tetrahedra" (5). This structure is isomorphic with that of various forms of silica. Consequently, aluminum phosphate shares many of the chemical and physical properties of silica, yet  $\text{AlPO}_4$  is formed at much lower temperatures (5). This lower-temperature formation translates to an economic advantage in producing products suitable for high-temperature service at low processing costs (6). In addition, these lower-temperature materials are likely to develop less internal stress than their sintered counterparts.

The earliest studies of phosphate bonding by Kingery (7) involved room-temperature bonding of oxide-phosphoric acid mixtures that included alumina. Subsequently, other studies of the kinetics of formation of aluminum phosphate from solutions of phosphoric acid or monoaluminum phosphate were reported. (6,8-10). Bothe and Brown (8), and Lukasiewicz and Reed (10) studied the kinetics of formation of  $\text{AlPO}_4$  at low temperatures. O'Hara et al. (6) identified the intermediate phases that are formed during hydrothermal treatment of alumina with phosphoric acid. They identified the formation of monoaluminum phosphate ( $\text{AlH}_3(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ ) between 100 and 150°C and its conversion to  $\text{AlPO}_4$  above 150°C. The exact temperature of formation of intermediate phases may depend on the forms of alumina, with the most reactive ones reacting at lower temperatures (11). Singh et al. (12) formed alumina ceramics by boiling a mixture of alumina and phosphoric acid and then pressing the dried powder. This indicated that some reaction of alumina possibly occurred to form the intermediate phase of  $\text{AlH}_3(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  which then transformed into an  $\text{AlPO}_4$  bonding phase upon curing. We conducted a detailed study to understand the kinetics of formation of  $\text{AlPO}_4$  bonded alumina ceramics so that a reproducible process can be developed to manufacture such ceramics.

We demonstrate here that very high temperatures are not necessary to form monolithic ceramics. Using differential thermal analysis (DTA), we identified 118°C as the transition temperature to form an intermediate phase. X-ray diffraction (XRD) analysis of samples that were heated beyond 118°C confirmed that this phase, a gel, is monoaluminum phosphate hydrate ( $\text{AlH}_3(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ ). When the gel is heated to 150°C, the  $\text{AlH}_3(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  is converted into crystalline  $\text{AlPO}_4$  that bonds the alumina particles and forms a monolithic ceramic. This observation is important technologically because it indicates that it is possible to produce an  $\text{AlPO}_4$ -bonded alumina ceramic at warm temperatures.

## EXPERIMENTAL INVESTIGATIONS

A mixture of coarser and finer alpha-alumina was used for this study. The finer alumina was manufactured by Reynolds Chemical Company. Mean particle size of this alumina was 0.96  $\mu\text{m}$ , as measured with CILAS 1064 number 085. Alumina from Fisher Scientific, sieved to a mean particle size of 0.08 mm, was combined with the finer alpha-alumina powder to produce a mixture with an

$\text{Al}_2\text{O}_3$ :  $\text{H}_3\text{PO}_4$  weight ratio of 5. The alumina powder mixture became a slurry after we added a 50 wt.% phosphoric acid solution.

DTA was used at a rate of 50°C/hr up to 400°C to determine phase changes at various temperatures. The DTA output is presented in Fig. 1. The endotherm slightly above 100°C indicates evaporation of water, but the one near 118°C indicates a phase transformation.

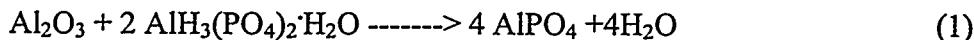
To identify phases that were formed near 118°C, the slurry was heated in an oven at 130°C and cured at that temperature for 1, 2, and 4 days in a closed container to avoid evaporation of water. The product was a thick puttylike material (gel), which was kept at ambient temperature for a week so that some crystalline growth would occur. Crystalline phases in the gel were then identified by XRD analysis. The output of the DTA of the 130°C samples is shown in Fig. 2.

The XRD output in Fig. 3 shows clear peaks of unreacted  $\text{Al}_2\text{O}_3$  and the reaction product  $\text{AlH}_3(\text{PO}_4)_2\text{H}_2\text{O}$ . Formation of this reaction product is consistent with observations made by earlier investigators (6). Formation of sharper and taller peaks in samples cured for a longer time indicate that the concentration of the reaction product in the gel is time-dependent. This implies that in order to form a chemically bonded ceramic, sufficient hydrothermal curing is necessary to allow reactions to occur between the acid solution and the alumina and for the dissolution of alumina to take place. Thus, our results confirm Bothe and Brown's work concerning the importance of the role of water in these reactions (8).

When completely dried, the samples were hard monoliths, indicating that  $\text{AlH}_3(\text{PO}_4)_2\text{H}_2\text{O}$  acted as the binding phase between the alumina particles. However, all of these samples disintegrated when placed in water. This indicates that no significant durable insoluble phases such as  $\text{AlPO}_4$  were formed.

Because Gonzalez and Halloran (12) noted that the berlinitic phase is formed at approximately 150°C, the samples were heated to that temperature. Significant porosity developed in the monoliths as bound water escaped through an increasingly viscous slurry. The DTA output of the samples cured at 150°C is shown in Fig. 4, and the XRD patterns of the resultant ceramics are shown in Fig. 5.

The sample heated at 150°C for one day shows the emergence of berlinitic peaks, which are taller in samples heated for two and three days. No peaks of  $\text{AlH}_3(\text{PO}_4)_2\text{H}_2\text{O}$  are visible. This observation indicates  $\text{AlH}_3(\text{PO}_4)_2\text{H}_2\text{O}$  was transformed to berlinitic.



In each case, the resultant ceramic appeared to be a very hard monolith with dense phases separated by large pores. The top portion of each monolith was

covered with a thin soft layer of acid phases that precipitated during heating. When these layers were sliced off with a diamond saw and the rest of the sample was soaked in water, the samples did not dissolve, nor did they lose significant weight when soaked in water for several days. Also, the pH of the water remained near neutral, indicating a lack of soluble acid phosphates in the leachate.

### CHARACTERIZATION OF THE CERAMIC

Scanning electron microscopy (SEM) was used to determine the microstructure of the ceramic. Figure 6 shows a typical photomicrograph of a fractured surface. The photomicrograph reveals that the individual particles are glued together by a binding phase that may be AlPO<sub>4</sub>. Due to the small grain size of individual particles, energy dispersive X-ray analysis (EDX) could not be used to distinguish between the phases of Al<sub>2</sub>O<sub>3</sub> and AlPO<sub>4</sub>. However, EDX patterns clearly revealed a homogenous distribution of AlPO<sub>4</sub> as shown by a constant aluminum-to-phosphorus ratio. This indicates that all of the particles have been coated with AlPO<sub>4</sub>.

Unconfined compression strength testing was also performed in a uniaxial mode with an Instron machine. An average strength of 6824 psi was measured on samples of 20.9 vol.% open porosity. If we ignore the berlinitic phase and use the density of alumina (3.97 g/cm<sup>3</sup>), it is possible to estimate the total porosity in the sample as 37.3 vol.%. Subtracting the measured from the theoretical porosity, we obtain an estimate of 16.4 vol.% of closed porosity.

### CONCLUSIONS

This study identifies a method to form a monolithic alumina ceramic at warm temperatures with berlinitic (AlPO<sub>4</sub>) as the bonding phase. AlH<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O is an intermediate phase that acts as a precursor to the formation of the AlPO<sub>4</sub> bonding phase. The formation of sufficient amounts of this precursor phase to form the AlPO<sub>4</sub>-bonded alumina ceramic depends on the hydrothermal curing time and temperature. More investigations are needed to develop dense chemically bonded alumina ceramics because bound water from the precursor generates significant porosity in the ceramic product.

### ACKNOWLEDGMENTS

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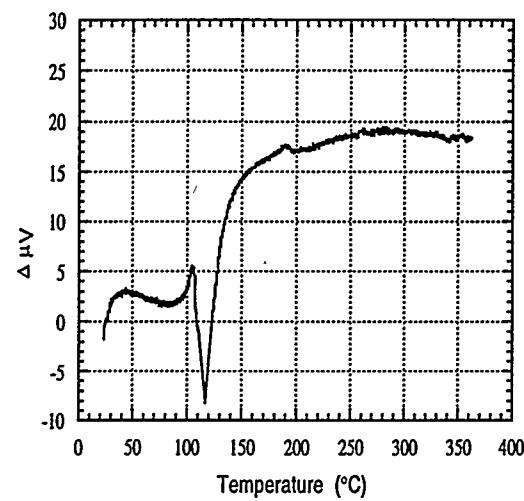


Fig. 1. DTA output of a mixture of alumina and phosphoric acid solution

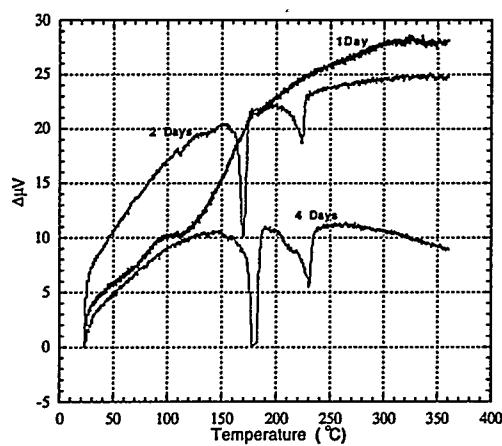


Fig. 2. DTA of  $\text{Al}_2\text{O}_3$  and  $\text{H}_3\text{PO}_4$  solution hydrothermally heated at 130°C

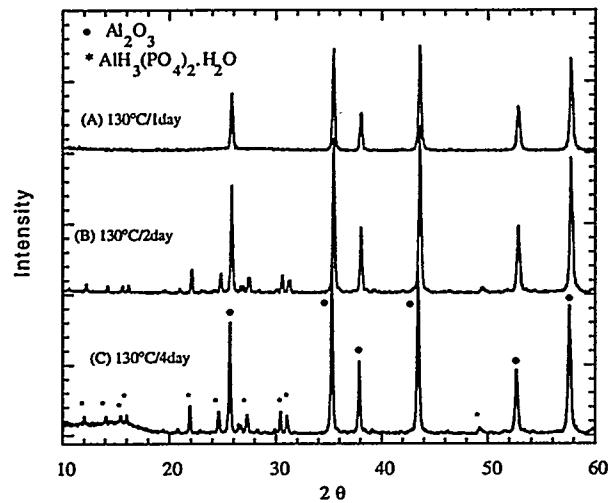


Fig. 3. X-ray diffraction pattern of a specimen cured at 130 °C

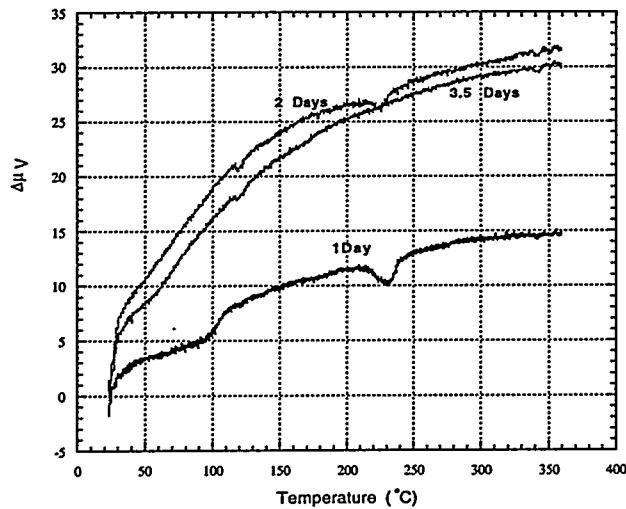


Fig. 4 DTA of  $\text{Al}_2\text{O}_3$  and  $\text{H}_3\text{PO}_4$  solution hydrothermally cured at 150 °C

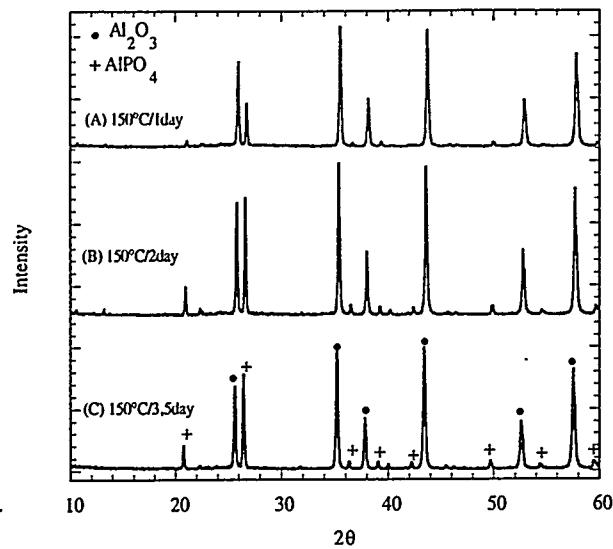


Fig. 5. X-ray diffraction pattern of a specimen cured at 150 °C



Fig. 6. SEM photomicrograph of a berlinitite-bonded alumina ceramic