

## PAPER DETAILS

TITLE: Investigation on Sintering Behaviour of Sol Gel Coated Seydisehir Alumina with TiO<sub>2</sub>

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## Sintering of Seydişehir Alumina from Sol Gel Method with TiO<sub>2</sub> Addition

TiO<sub>2</sub> ile Sol Jel Kaplanmış Seydişehir Alüminanın Sinterlenmesi

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### Abstract

In this study, we report the sinterability of Seydişehir  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> by coating TiO<sub>2</sub> colloidal particles by sol-gel method. In this context, efforts have been made to decrease the amount of impurities with washing process, to stabilize transformation with calcination and to reduce grain size by jet-mill grinding. It is aimed to increase the density of Al<sub>2</sub>O<sub>3</sub> by coating TiO<sub>2</sub> by sol-gel method. The ceramic powders were dry-pressed, they were sintered at 1580°C for different hours (1h, 3h and 6h). The role of TiO<sub>2</sub> content and sintering time on the microstructural properties and density of final products were investigated.

**Keywords:** Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, Sintering, Sol-Gel

### Öz

Bu çalışmada, Seydişehir  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> koloidal parçacıklar ile sol-jel yöntemiyle kaplanmış ve  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>'ün sinterlenebilirlik özellikleri rapor edilmiştir. Yıkama işlemi ile kirlilik miktarını azaltmaya, kalsine ile dönüşümü stabilize etmeye ve jet değirmen öğütme ile  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>'ün tane boyutu azaltılmaya çalışılmıştır. TiO<sub>2</sub> sol-jel yöntemi kullanılarak kaplama ile Al<sub>2</sub>O<sub>3</sub>'ün yoğunluğunun artırılması amaçlanmıştır. Seramik tozları kuru preslenmiş, farklı saatler (1 saat, 3 saat ve 6 saat) boyunca 1580 °C'de sinterlenmiştir. TiO<sub>2</sub> içeriğinin ve sinterleme süresinin nihai ürünün mikroyapısal özellikleri ve yoğunluğu üzerindeki rolü araştırılmıştır.

**Anahtar Kelimeler:** Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, Sinterleme, Sol-Jel

## I. INTRODUCTION

Alumina is a known ceramic material because of its high temperature stability, chemical inertness, strength, hardness, tribological, electrical and optical properties. The properties of alumina-based ceramics depend on the final microstructures which are affected by the characteristics of the starting powders[1-7].

Seydişehir Alumina has large particle size distribution and high impurity content. In recent years, many researchers focus on improving its sinterability properties by reducing the Na content, grinding and ceramic coating[2-4].

The ceramic coating improves the distribution of sintering aids, and also modify the rheological and consolidation behaviour of a ceramic suspension[5,8]. Sol-gel process is an useful method for the preparation of amorphous and structurally ordered materials and allows the synthesis of powders with a more controlled structure and morphology. It also improves the reactivity of the synthesized material such as porosity and surface area, to obtain homogeneous matrices[9-11]. Sol-gel method is highly preferred due to its low process cost, easy control of composition and relatively low calcination temperature[8,12,13]. The solid-state method requires a sintering process at high temperatures with a long holding time. This process may lead to sodium loss and exaggerated grain growth, which are deleterious to the mechanical strength. In order to decrease the sintering temperature, sol-gel method has been studied. The mixed oxides of TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> is a good alternative to overcome the problems of

the single phases like stabilization of porosity structure would be obtained at high temperatures. [14-18]. In recent years, synthesized TiO<sub>2</sub> powders with control over the crystalline phase, crystallite size, morphology and surface area have been used in various synthesized methods, such as sol-gel, hydrolysis, hydrothermal process, etc [19]. TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> composite materials that have several interesting physical properties protected metallic structural components against wear and corrosion due to their thermal, chemical and mechanical stability. TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> structures are used in various applications including catalysis, solar cells, photocatalytic, and self-cleaning [8,20].

A comparative study on density and morphological properties of Seydişehir Al<sub>2</sub>O<sub>3</sub> sol gel coated by TiO<sub>2</sub> is presented. The present approach results in good densification without significant grain growth.

## II. MATERIALS AND METHODS

The raw material, Seydişehir α-Al<sub>2</sub>O<sub>3</sub> powder (Al<sub>2</sub>O<sub>3</sub>(%98,5), SiO<sub>2</sub>(%0,030), Fe<sub>2</sub>O<sub>3</sub>(%0,035), Na<sub>2</sub>O(0,5) was jet milled for 30 min. Jet mill grinding is a mechanical method used for superfine grinding. The most important advantage is that it reduces grain size to 1-10 μm in a narrow distribution range. The Seydişehir alumina was fed to the dosing unit by means of air jets (8 units) with 7 bars of pressure produced in the screw compressor and milled at high speed. The samples were washed to reduce the Na<sub>2</sub>O content at 35°C and 70°C for 1 hour by heated magnetic stirrer. 450 ml distilled water ve 50 ml HCl acid were used as washing fluid. After washing, the cake filtered under vacuum was washed with pure water. The material was dried at 80 °C. % Na ratios of Seydişehir Al<sub>2</sub>O<sub>3</sub> before and after washing was given in Table 1.

**Table 1.** % Na ratios of Seydişehir Al<sub>2</sub>O<sub>3</sub> before and after washing

| Al <sub>2</sub> O <sub>3</sub> Samples                   | % Na  |
|----------------------------------------------------------|-------|
| Alcoa Al <sub>2</sub> O <sub>3</sub>                     | 0,174 |
| Seydişehir Al <sub>2</sub> O <sub>3</sub> before washing | 0,442 |
| Seydişehir Al <sub>2</sub> O <sub>3</sub> after washing  | 0,121 |

Seydişehir alumina was calcined at 1200°C for 2 hours to obtain % 100 corundum (α-Al<sub>2</sub>O<sub>3</sub>) in Linn High Therm furnace. After calcination, 9,6 gr Al<sub>2</sub>O<sub>3</sub> was subjected to coating with 0,4 gr TiO<sub>2</sub> colloidal particles by sol-gel method. 1,42 gr TIP (titanium (IV) isopropoxide), 2,84 gr 2-propanol, 250 ml distilled water and 2,5 ml HNO<sub>3</sub> were used as the starting material in the sol-gel method. During sol-gel reaction, water reacts with titanium isopropoxide molecules to form nano-sized TiO<sub>2</sub> particles as shown below in Equation(1).



This mixture is stirred for 24 hours in a magnetic stirrer. The powder is then precipitated in Nuve NF-400 Centrifuge. The precipitated mixture of Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> was dried at 80 °C. The forming process was performed by pressing 2 g samples of Alcoa Al<sub>2</sub>O<sub>3</sub>, Seydişehir Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> added Seydişehir Al<sub>2</sub>O<sub>3</sub> under a weight of 1600 kg. They were sintered at 1580°C for 1h, 3h and 6h, respectively. The microstructures of the samples were characterized by SEM (JEOL JAMP 9500F Field Emission Auger Microprobe). Particle size distributions of Seydişehir alumina and milled Seydişehir aluminas were carried out in Shimadzu SA-CP2 brand sedimentation and centrifugal grain size measuring device and Laser-ray detection principle Malvern-Mastersizer 2000S device. The density of sintered bodies was determined by Precise 205ASCS device with Archimedes principle.

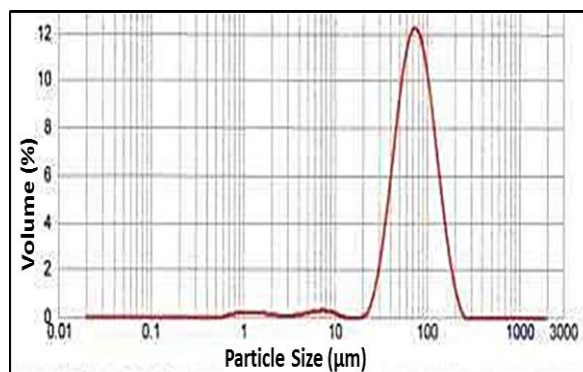
## III. RESULTS AND DISCUSSION

The chemical analysis of Seydişehir alumina is given in Table 1. Bulk density and absolute density of Seydişehir alumina are 1.00-1.10 gr/cm<sup>3</sup> and 3.30-3.60 gr/cm<sup>3</sup>, respectively.

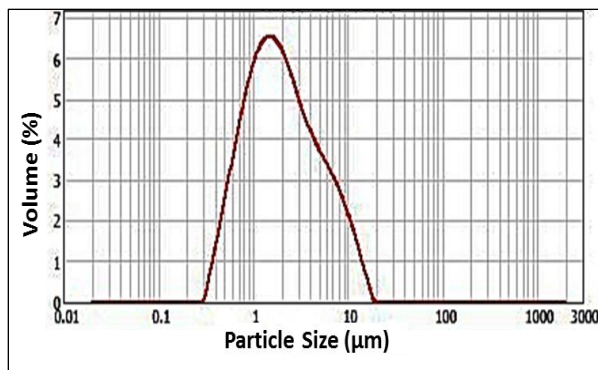
**Table 2.** Chemical analysis of Seydişehir alumina powder

| Chemical analysis | LOI (1100°C) | Al <sub>2</sub> O <sub>3</sub> | SiO <sub>2</sub> | Fe <sub>2</sub> O <sub>3</sub> | Na <sub>2</sub> O |
|-------------------|--------------|--------------------------------|------------------|--------------------------------|-------------------|
| (%) max           | 1            | 98.5                           | 0.030            | 0.035                          | 0.50              |

Grain refining process was applied to high grain sized alumina by jetmill grinding. The average grain size of the powder was 82.088 μm before jet-milling. After 30 min jet-milling, average grain size of the powder was 4.618 μm as given in the **previous study as shown in Figure 1[4]**.



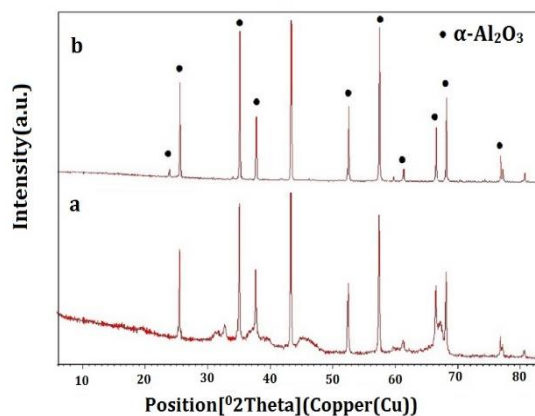
(a)



(b)

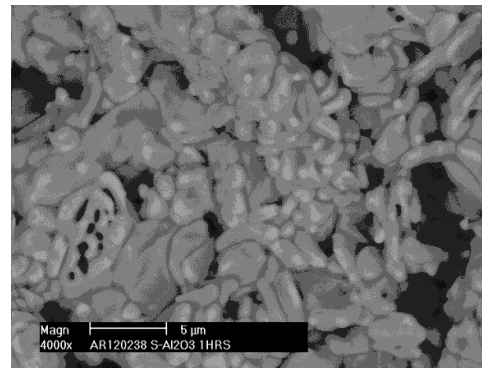
**Figure 1.** Particle size distribution of Seydişehir alumina a) before jet milling b) after jet milling[4]

According to XRD analysis in Figure 2, it was seen that Seydişehir alumina did not consist of completely  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> before calcination. After calcination at 1200 °C for 2 h, the transition phases transformed to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. Technical alumina ceramics could reach to the desired quality by calcination and grinding under controlled conditions[4]. % 100 corundum ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) was obtained after 2 hours calcination.

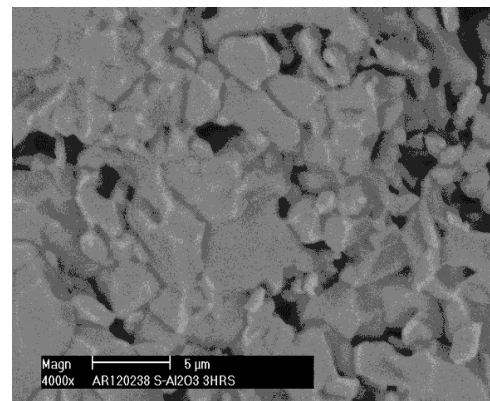


**Figure 2.** XRD patterns of the specimen a) before calcination b) after calcination at 1200°C for 2 h[4].

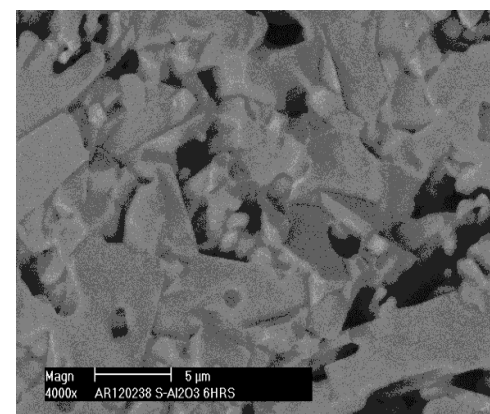
Calcined and milled alumina was sintered at 1580 °C for varying periods (1h, 3h and 6h). Figure 3 shows the SEM photographs of the sintered samples. Despite the increase of sintering time, porosity was still observed in the samples. Also, grain growth occurred during sintering. The effect of reaction time plays a great role in the morphology of the particles. Grain growth is considered to be undesirable due to adverse effects that such growth may have on mechanical properties[21].



(a)



(b)



(c)

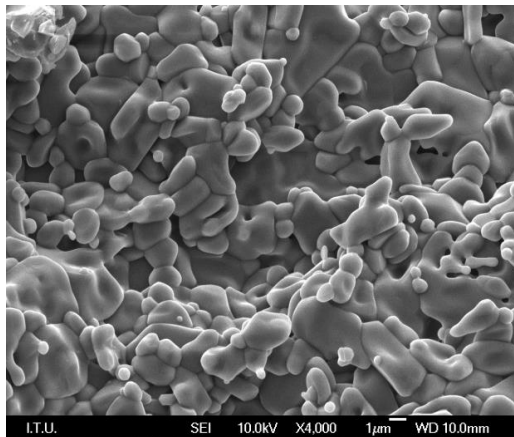
**Figure 3.** SEM photograph of the samples sintered at 1580°C for varying periods a)1 hour b) 3 hour c) 6 hour

Table 2 shows the density of the samples sintered at 1580 °C for 1, 3, 6 hour and density of the coated samples with TiO<sub>2</sub> colloidal particles by sol-gel method sintered at 1580°C for 1, 3, 6 hour.

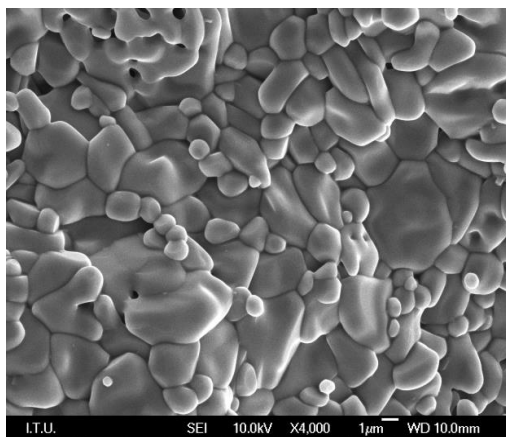
**Table 3.** Density of the samples sintered at 1580 °C and coated samples with TiO<sub>2</sub>

| Time(h) | Density of the samples sintered at 1580 °C (g/cm <sup>3</sup> ) | Density of the coated samples with TiO <sub>2</sub> sintered at 1580 °C (g/cm <sup>3</sup> ) |
|---------|-----------------------------------------------------------------|----------------------------------------------------------------------------------------------|
| 1       | 3,539                                                           | 3,879                                                                                        |
| 3       | 3,544                                                           | 3,880                                                                                        |
| 6       | 3,548                                                           | 3,900                                                                                        |

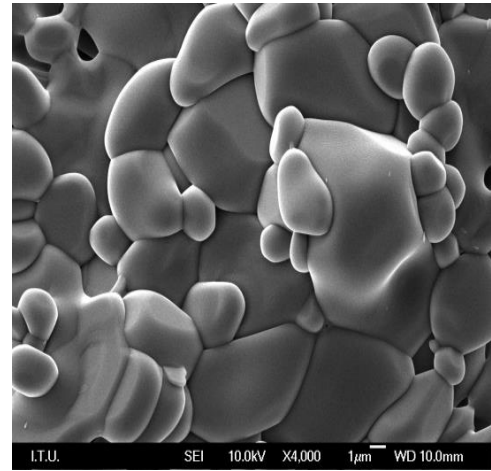
Density of the coated samples with TiO<sub>2</sub> increased and this result was supported by SEM images in Figure 2. TiO<sub>2</sub> coated alumina is effective in enhancing grain growth when compared with an uncoated material. No microcracks are observed in any of the samples. TiO<sub>2</sub> grains are uniformly dispersed in the Al<sub>2</sub>O<sub>3</sub> matrix. The increase of sintering time caused an increase in grain size of the samples as can be seen from the coarser grains in the microstructures (Figure 4). The grain size of the samples sintered for 6 hours was found as 10 microns.



(a)



(b)



(c)

**Figure 4.** SEM photograph of the TiO<sub>2</sub> coated samples sintered at 1580 °C for varying periods a) 1 hour b) 3 hour c) 6 hour

#### IV. CONCLUSION

In this study, it is aimed to increase the sintering ability of Seydişehir alumina powder. Therefore, alumina powder was washed to decrease the amount of impurities, calcined to stabilize the transformation and jet-milled to reduce the grain size. Al<sub>2</sub>O<sub>3</sub> is coated with TiO<sub>2</sub> by sol gel method. The density and the grain size of sintered samples increase with increasing sintering time. TiO<sub>2</sub> plays an important role in the densification of the resulting samples. Tests made on TiO<sub>2</sub> doped alumina have been observed to increase in density. As a result of the study, density of the coated samples with TiO<sub>2</sub> was reached a max value as 3,9 g/cm<sup>3</sup>. However, no difference was observed between 3 hours and 6 hours. Therefore, it can be said that sintering time did not cause an increase in density. In order to increase the density more, it is necessary to reach higher temperatures.

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