Int. J. Adv. Eng. Pure Sci. 2020, 32(2): 192-196
DOI: 10.7240/jeps.631637

RESEARCH ARTICLE / ARAŞTIRMA MAKALESİ

Sintering of Seydişehir Alumina from Sol Gel Method with TiO_2 Addition

TiO_2 ile Sol Jel Kaplanmış Seydişehir Alüminanın Sinterlenmesi

Zeynep TAŞLIÇUKUR ÖZTÜRK[1], Selin ENGÜRLÜ[2], Nilgün KUŞKONMAZ[3]

[1] *National Defence University,Turkish Naval Academy, Mechanical Engineering Department,34942, Istanbul, Turkey*

[2,3] *Yildiz Technical University, Faculty of Engineering, Metallurgy and Materials Engineering, Davutpasa Campus, Esenler, 34210, Istanbul, Turkey*

Abstract
In this study, we report the sinterability of Seydişehir α-Al_2O_3 by coating TiO_2 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_2O_3 by coating TiO_2 by sol-gel method. The ceramic powders were dry-pressed, they were sintered at 1580^{0}C for different hours(1h, 3h and 6h). The role of TiO_2 content and sintering time on the microstructural properties and density of final products were investigated.
Keywords: Al_2O_3, TiO_2, Sintering, Sol-Gel

Öz
Bu çalışmada, Seydişehir α-Al_2O_3, TiO_2 kolloidal parçacıklar ile sol-jel yöntemiyle kaplanmış ve α-Al_2O_3'nın sinterlenebilirlik özellikleri rapor edilmiştir. Yıkama işlemi ile kirlilik miktarını azaltmaya, kalsine ile dönüşümü stabilize etmeye ve jet değirmen öğütme ile α-Al_2O_3'nın tane boyutu azaltılmaya çalışılmıştır. TiO_2 sol-jel yöntemi kullanılarak kaplama ile Al_2O_3'ün yoğunluğunun arttırılması amaçlanmıştır. Seramik tozları kuru preslenmiş, farklı saatler (1 saat, 3 saat ve 6 saat) boyunca 1580 ^{0}C'de sinterlenmiştir. TiO_2 içeriğinin ve sinterleme süresinin nihai ürünün mikroyapısal özellikleri ve yoğunluğu üzerindeki rolü araştırılmıştır.
Anahtar Kelimeler: Al_2O_3, TiO_2, 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_2 and Al_2O_3 is a good alternative to overcome the problems of

Corresponding Author: Zeynep TAŞLIÇUKUR ÖZTÜRK, Tel: 0216 3952630(3160), e-posta: ztasli@gmail.com
Submitted: 10.10.2019, **Revised**: 26.12.2019, **Accepted**: 19.02.2020

the single phases like stabilization of porosity structure would be obtained at high temperatures. [14-18]. In recent years, synthesized TiO_2 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_2–Al_2O_3 composite materials that have several interesting physical properties protected metallic structural components against wear and corrosion dueto their thermal, chemical and mechanical stability. TiO_2–Al_2O_3 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_2O_3 sol gel coated by TiO_2 is presented. The present approach results in good densification without significant grain growth.

II. MATERIALS AND METHODS

The raw material, Seydişehir α-Al_2O_3 powder (Al_2O_3(%98,5), SiO_2(%0,030), Fe_2O_3(%0,035), Na_2O(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 Seydisehir 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_2O content at 35^0C and 70^0C for 1 hour by heated magnetic stirrer. 450 ml distilled water ve 50 ml HCI acid were used as washing fluid. After washing, the cake filtered under vacuum was washed with pure water. The material was dried at 80 ^{0}C. % Na ratios of Seydişehir Al_2O_3 before and after washing was given in Table 1.

Table 1. % Na ratios of Seydişehir Al_2O_3 before and after washing

Al_2O_3 Samples	**% Na**
Alcoa Al_2O_3	0,174
Seydişehir Al_2O_3 before washing	0,442
Seydişehir Al_2O_3 after washing	0,121

Seydisehir alumina was calcined at 1200^0C for 2 hours to obtain % 100 corundum (α-Al_2O_3) in Linn High Therm furnace. After calcination, 9,6 gr Al_2O_3 was subjected to coating with 0,4 gr TiO_2 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_3 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_2 particles as shown below in Equation(1).

$$Ti\{OCH(CH_3)_2\}_4+2H_2O \rightarrow TiO_2+4(CH_3)_2CHOH \quad (1)$$

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_2O_3 and TiO_2 was dried at 80 ^{0}C. The forming process was performed by pressing 2 g samples of Alcoa Al_2O_3, Seydişehir Al_2O_3 and TiO_2 added Seydişehir Al_2O_3 under a weight of 1600 kg. They were sintered at 1580^0C 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 Schimadzu 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.

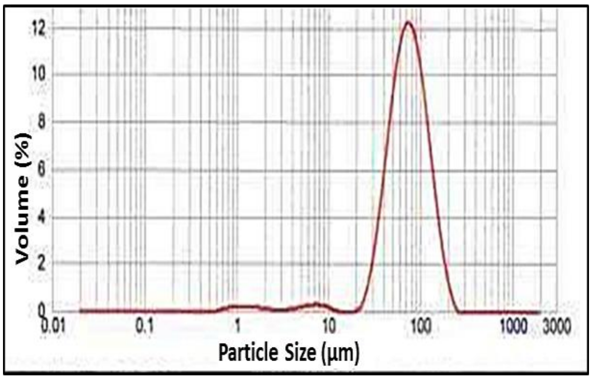
III. RESULTS AND DISCUSSION

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^3 and 3.30-3.60 gr/cm^3, respectively.

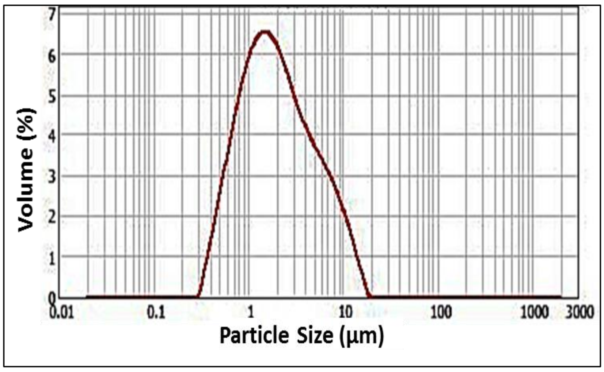
Table 2. Chemical analysis of Seydişehir alumina powder

Chemical analysis	**LOI (1100^0C)**	**Al_2O_3**	**SiO_2**	**Fe_2O_3**	**Na_2O**
(%) max	1	98.5	0.030	0.035	0.50

Grain refining process was applied to high grain sized alumina by jetmill grinding. The avarage 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 α-Al_2O_3 before calcination. After calcination at 1200 ^{0}C for 2 h, the transition phases transformed to α-Al_2O_3. Technical alumina ceramics could reach to the desired quality by calcination and grinding under controlled conditions[4]. % 100 corundum (α-Al_2O_3) was obtained after 2 hours calcination.

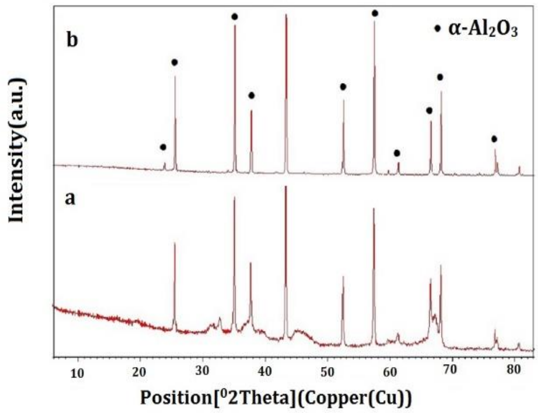
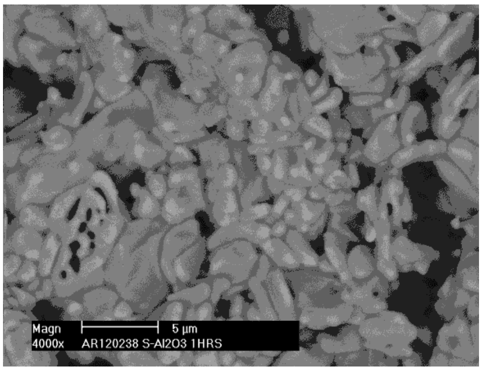
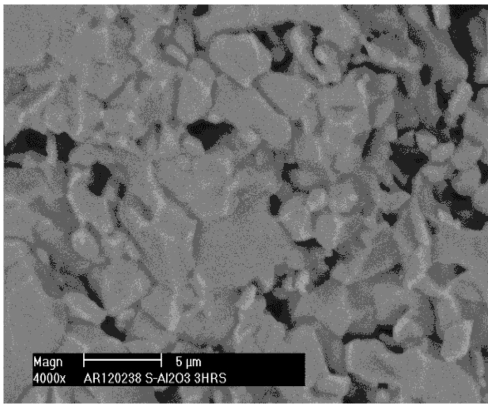


Figure 2. XRD patterns of the specimen a) before calcination b) after calcination at 1200°C for 2 h[4].

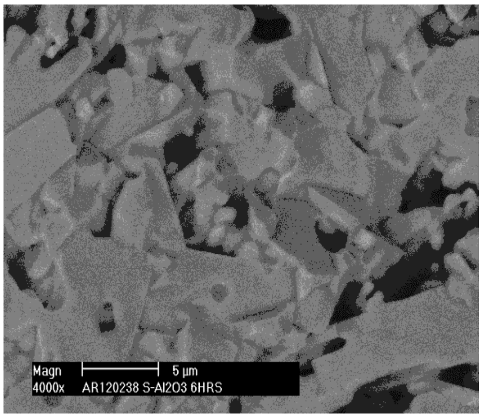
Calcined and milled alumina was sintered at 1580 ^{0}C for varying periods (1h, 3h and 6h). Figure 3 shows the SEM photographs of the sintered samples. Despite the increase of sintering time, porosity was still observed in the samples. Also, grain growth occured during sintering. The effect of reaction 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)

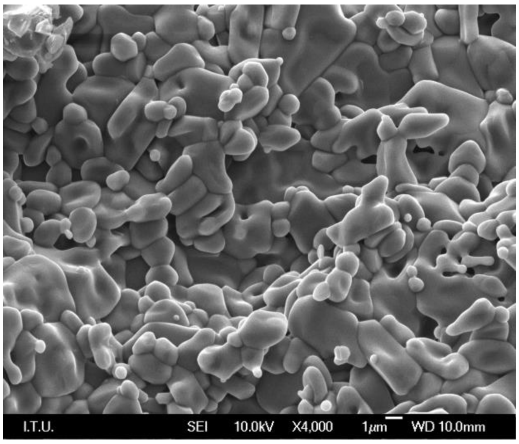
Figure 3. SEM photograph of the samples sintered at 1580^{0}C for varying periods a)1 hour b) 3 hour c) 6 hour

Table 2 shows the density of the samples sintered at 1580 ^{0}C for 1, 3, 6 hour and density of the coated samples with TiO_2 colloidal particles by sol-gel method sintered at 1580^{0}C for 1, 3, 6 hour.

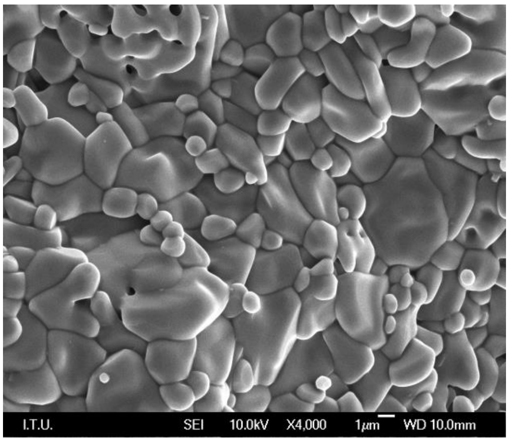
Table 3. Density of the samples sintered at 1580 ^{0}C and coated samples with TiO_2

Time(h)	Density of the samples sintered at 1580 ^{0}C(g/cm^3)	Density of the coated samples with TiO_2 sintered at 1580 ^{0}C(g/cm^3)
1	3,539	3,879
3	3,544	3,880
6	3,548	3,900

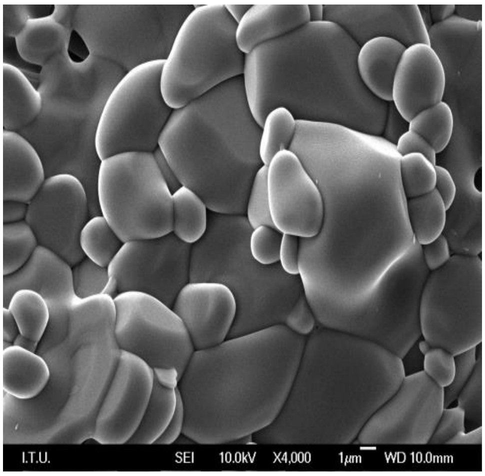
Density of the coated samples with TiO_2 increased and this result was supported by SEM images in Figure 2. TiO_2 coated alumina is effective in enhancing grain growth when compared with an uncoated material. No microcracks are observed in any of the samples. TiO_2 grains are uniformly dispersed in the Al_2O_3 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_2 coated samples sintered at 1580 ^{0}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_2O_3 is coated with TiO_2 by sol gel method. The density and the grain size of sintered samples increase with increasing sintering time. TiO_2 plays an important role in the densification of the resulting samples. Tests made on TiO_2 doped alumina have been observed to increase in density. As a result of the study, density of the coated samples with TiO_2 was reached a max value as 3,9 g/cm^3. 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.

ACKNOWLEDGMENT

This work is financially supported by Project number 2011-07-02-YÜLAP06. The authors wish to acknowledge the Scientific Research Project Coordination of Yildiz Technical University.

REFERENCES

[1] Yong, Y., You, W., Zheng, W., Gang L. and Wei, T. (2008). Preparation and sintering behaviour of nanostructured alumina/titania composite powders modified with nano-dopants. *Mater. Sci. Eng. A.*, 490, 457-464.

[2] Erten, R., Emrullahoğlu, C.B., Yazıcı, Z.O. and Emrullahoğlu, Ö.F. (2004). An investigation on injection moulding of Seydişehir alumina. *Key Eng. Mater.*, Vols. 264-268, 2523-2526.

[3] *Palacı, Y.(2001). Alüminanın özelliklerine, şekillendirme yönteminin, katkılarının ve sinterleme sıcaklığının etkisi. Doktora Tezi, İstanbul Teknik Üniversitesi, Türkiye, p. 8-10.*

[4] Engürlü, S., Taşlıçukur Öztürk, Z. and Kuşkonmaz, N. (2017). Investigation of the production of β-Al_2O_3 solid electrolyte from Seydişehir α-Al_2O_3. *Süleyman Demirel Üniversitesi Fen Bilimleri Enstitüsü Dergisi*, Cilt 21 (3),816-819.

[5] Jayasankar, M., Ananthakumar, S., Mukundan, P., Wunderlich, W. and Warrier, K.G.K.(2008). Al_2O_3 @ TiO_2-A simple sol–gel strategy to the synthesis of low temperature sintered alumina–aluminium titanate composites through a core–shell approach. *J. Sol. St. Chem*., 181,2748–2754.

[6] Avcı, G.G., Mısırlı, Z. and Günay, V. (1996). Processing and characterization of microfiltration supports prepared from alumina powders. *Cer. Inter.,* 22, 23-26.

[7] Ahmed, M.A., Abdel-Messih, M.F. (2011). Structural and nano-composite features of TiO_2–Al_2O_3 powders prepared by sol–gel method. *J. Alloys Comp.,* 509,2154–2159.

[8] Arıer, U.Ö.A. and Tepehan, F.Z. (2013). Influence of Al_2O_3:TiO_2 ratio on the structural and optical properties of TiO_2–Al_2O_3 nano-composite films produced by sol gel method. *Comp.: Part B.,* 58, 147–151.

[9] Toygun, Ş., Köneçoğlu, G. and Kalpaklı, Y. (2013). General principles of sol – gel. *J. Eng. Nat. Sci. Sig.,* 31, 456-476.

[10] Dascalescu, T., Todan, L., Rusu, A., Preda, S., Andronescu, C.,Culita, D.C., Munteanu, C. and Zaharescu, M. (2014). Nanosized Al_2O_3-TiO_2 oxide powder with enhanced porosity obtained by sol-gel method. *Rev. Roum. Chim.,* 59 (2), 125-134.

[11] Farias, R.F., Arnold, U., Martı´nez, L., Schuchardt, U., Jannini, M.J.D.M. and Airoldi, C. (2003). Synthesis, characterization and catalytic properties of sol–gel derived mixed oxides. J. Phys. Chem. Sol., 64, 2385–2389.

[12] Jung, Y., Kim, D., Kim, Y., Park, E. and Baeck, S. (2008). Synthesis of alumina–titania solid solution by sol–gel method. *J. Phy. Chem. Sol.,* 69, 1464–1467.

[13] Leblebicier, Y., Yüzer, H. and Emrullahoğlu, Ö.F. (2000). Sol Jel metodu ile mikronaltı incelikte alümina üretimi. *Afyon Kocatepe University J. Sci.,* 2 (1),1-12.

[14] Shi-Jie, S., Li-Ping, Y., Xiao-Min, L., Xiao-Ling, W., Hui, Y. and Xiao-Dong, S. (2013). Preparation and characterization of TiO_2 doped and MgO stabilized Na–β″-Al_2O_3 electrolyte via a citrate sol–gel method. *J. All. Comp.,* 563, 176–179.

[15] Yang, L.P, Shan, S., Wei, X., Liu, X., Yang, H. and Shen, X. (2014). The mechanical and electrical properties of ZrO_2–TiO_2–Na-β/β″-alumina composite electrolyte synthesized via a citratesol–gel method. *Cer. Inter.,* 40 9055–9060.

[16] Habibpanah, A.A., Pourhashem, S. and Sarpoolaky, H. (2011). Preparation and characterization of photocatalytic titania–alumina composite membranes by sol–gel methods. *J. Eur. Cer. Soc.,* 31, 2867–2875.

[17] Akbarnezhad, Sh., Mousavi, S.M. and Sarhaddi, R. (2010). Sol-gel synthesis of alumina-titania ceramic membrane: Preparation and characterization. *Ind. J. Sci. Tech.,* Vol. 3 No. 10 ISSN: 0974- 6846, 1048-1051.

[18] Mohammadi, M.R. (2014). Semiconductor TiO_2–Al_2O_3 thin film gas sensors derived from aqueous particulate sol–gel process. *Mater. Sci. Semi. Proc.,* 27,711–718.

[19] Cheng-Li, W., Weng-Sing, H., Hsueh-Liang,C., Huey-Jiuan, L., Horng-Huey, K. (2016). Kinetics of anatase transition to rutile TiO_2 from titanium dioxide precursor powders synthesized by a sol-gel process. *Cer. Inter.,* 42, 13136–13143.

[20] Vanessa, D., Homero, M., Mariana, F., Anderson, L., Rodrigo, P., Fernanda, M. (2019). Atomic layer deposited TiO_2 and Al_2O_3 thin films as coatings for aluminum food packaging application. Mater.,12, 682**.**

[21] Dorian, A.H.H., Wanqiang, X., Michael, F. and Charles, C.S. (2012). Abnormal grain growth of rutile TiO_2 induced by $ZrSiO_4$. *J. Cry. Grow.,* Volume 359 83-91.