



Effect of the Sintering Temperature on the Fabrication of Alumina Beads

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Abstract

In this study, kaolin bonded alumina-alginate composite beads were fabricated via a facile one-step sol-gel process by using sodium alginate. In order to achieve sintering of the beads at lower sintering temperatures a limited amount of CC31 commercial-grade kaolin was used as a sintering additive (Al_2O_3 :CC31 commercial-grade kaolin=14:1). Produced composite beads were heat treated at 1300°, 1400° and 1500°C for 1 hour to achieve partial densification of the beads. TG-DTA analysis of the CC31 commercial-grade kaolin showed that mullite phase formation took place approximately at 1000°C. However, XRD measurements revealed that there is only alumina phase in the sintered ceramic beads. Due to the low amount of CC31 commercial-grade kaolin, mullite formation was not detectable via XRD analysis. No significant grain growth was observed at the sintered samples depending on the increasing sintering temperature. However, when the sintering temperature was increased, densification ratio and mechanical properties of the produced beads were enhanced significantly. Microstructural investigations of the sintered beads shown that with the help of the liquid phase sintering process, a good chemical bonding was achieved between the alumina particles.



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Introduction

Porous alumina ceramics have attracted a significant attention due to their good thermal stability even at elevated temperatures, constructive surface properties, chemical stability, and relatively high strength.¹⁻¹⁰ Porous alumina ceramic materials are widely used for many applications such as

catalyst supports,¹¹⁻¹³ bone tissue engineering,¹⁴⁻¹⁶ membrane,¹⁷⁻¹⁹ high temperature filtration,²⁰ water desalination,²¹⁻²³ diesel particulate filters²⁴ and as an anodic oxide coating in tools.^{19, 25, 26} Recently ceramic microspheres either in the form of dense, hollow, and porous structures are very attractive materials. Owing to their unique characteristic properties

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such as high porosity, low density, mechanically and thermally stable structure, and providing an opportunity to use economical materials.²⁷⁻²⁹ Highly porous ceramic materials can be achieved in many different ways such as using fugitive additives,³⁰⁻³² partial sintering,^{2, 30, 32-34} polymeric sponge,^{20, 35, 36} etc. Using fugitive materials such as starches,^{20, 30, 31} saw dust^{37, 38} and carbon black³⁹⁻⁴¹ provide high open porosity and facilitate achieving highly interconnected porosity.

Ceramic-based microspheres can be used for various applications such as drug delivery, hard tissue regeneration, radiant burners, acoustic insulations, catalyst support, thermostable materials, filters, as reinforcement for foams for the structural applications, and sorbent materials.⁴²⁻⁴⁴ These microspheres have been used in many industrial applications in combination with a different

type of material. Fabrication of hollow/porous ceramic microspheres are carried out via various processing techniques such as template,⁴⁵⁻⁴⁸ multi-template,⁴⁹ hydro thermal processing,^{50, 51} spray drying,⁵²⁻⁵⁴ sono chemical,⁴⁹ solvo thermal process,⁵⁵⁻⁵⁷ pseudomorphic synthesis,⁵⁸ emulsion microencapsulation,⁵⁹ sacrificial core,⁶⁰⁻⁶² emulsion evaporation,^{63, 64} nozzle reactor and microwave-assisted solvo thermal synthesis.⁶⁵ Porous alumina ceramic beads can serve as an ideal filtration material due to its highly porous structure, controlled pore size, and distribution as well as its rigid structure.

In the current work, kaolin bonded alumina porous beads were fabricated via a facile, eco-friendly, and convenient route by using sodium alginate as an in situ gelling templates. A huge amount of investigations has been reported in literature dealing

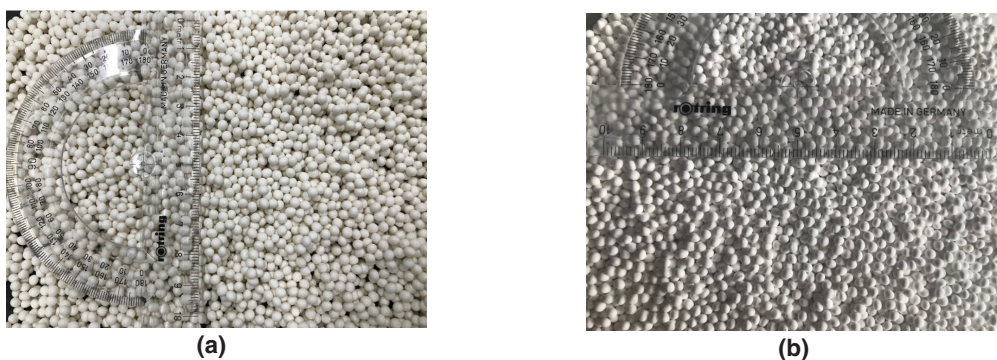


Fig. 1: (a) Al_2O_3 -kaolin-alginate green composite beads, and (b) alumina ceramic beads, produced via sintering at 1400°C for 1 hour

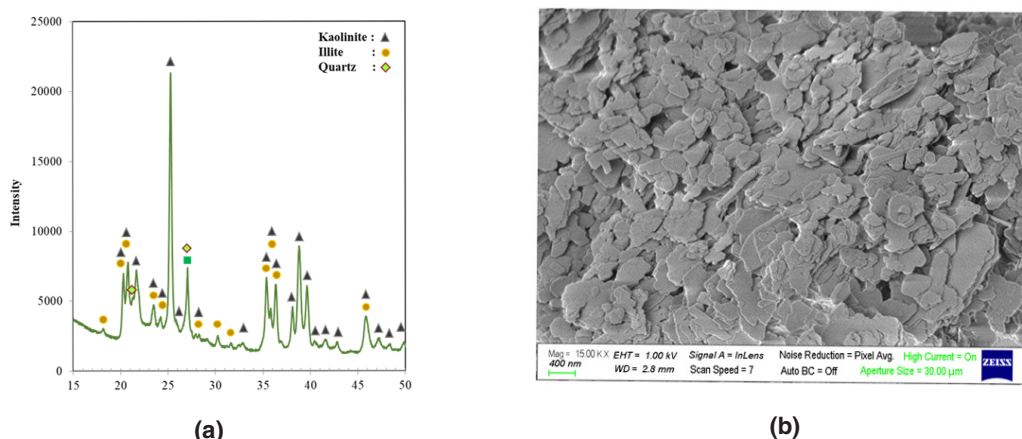


Fig. 2: (a) XRD pattern, and (b) microstructure of the CC31 commercial-grade kaolin

with the effects of the process parameters on the vibrational droplet technology in alginate systems. However, studies on the fabrication of high alumina ceramic loaded vibrational droplet technology is very limited. Alumina has a high melting temperature; thus solid-state sintering needs very high sintering temperatures and dwell times. In order to achieve partial sintering of alumina beads at low sintering temperatures in this study, a limited amount of CC31 commercial-grade kaolin was used as a sintering additive (Al_2O_3 :CC31 commercial-grade kaolin=14:1). Effect of the sintering temperature (1300°C – 1500°C) on the densification of the kaolin bonded porous alumina beads were investigated for the first time. It was determined that when the sintering temperature was $\geq 1400^\circ\text{C}$, the strength of the spherical ceramic beads significantly increased.

Experimental Procedure

CC31 commercial-grade kaolin (Esan Eczacibasi Group, Turkey) was used as a sintering additive to enhance densification of the Al_2O_3 (Esan Eczacibasi Group, Turkey) ceramic beads at relatively low temperatures. As-received kaolin powder content given by the manufacturer was Al_2O_3 (35.4 wt%), SiO_2 (50.7 wt%), K_2O (2.4 wt%), MgO (0.5 wt%), Fe_2O_3 (0.6 wt%), CaO (0.3 wt%) and Na_2O (0.5 wt%) with an ignition loss of 9.5 wt%. $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ is the empirical formula for kaolinite. Theoretical chemical composition of the kaolinite is Al_2O_3 , 39.50 %; SiO_2 , 46.54 %; and H_2O , 13.96 %. Thermal behavior of the

CC31 commercial-grade kaolin in air atmosphere was investigated via thermo gravimetry (TG) and differential thermal analysis (DTA) in a simultaneous TG/DTA analyzer (Netzsch STA 449F3) at a heating rate of $10^\circ\text{C}/\text{min}$.

Bead production was carried out with the following procedure. Six grams of sodium alginate (SA) (Katki Donyasi, Turkey) was dissolved in 200 mL distilled water by magnetic stirring at room temperature for 24 hours. A homogenous slurry containing 70 g Al_2O_3 , 5 g CC31 and 150 mL SA solution, was prepared in a planetary ball mill at a rotation speed of 350 rpm for 45 minutes. The cross-linking solution was prepared via dissolving 1 wt.% calcium chloride (CaCl_2 , Katki Donyasi, Turkey) in distilled water by magnetic stirring at room temperature for 1 hour. Prepared aqueous SA + ceramic solution was added dropwise into CaCl_2 aqueous solution at room temperature using a 60 mL hypodermic syringe through a needle under constant stirring at room temperature. The alginate–ceramic composite beads are formed via cross-linking in the CaCl_2 solution for at least 30 minutes. Then beads are removed from the solution via sieving and washed with distilled water for many times. Fig. 1 displays fabricated Al_2O_3 –kaolin–alginate green composite beads and sintered beads. Macroscopic investigations depicted that the spherical beads kept their shape during the sintering process (Fig. 1-b).

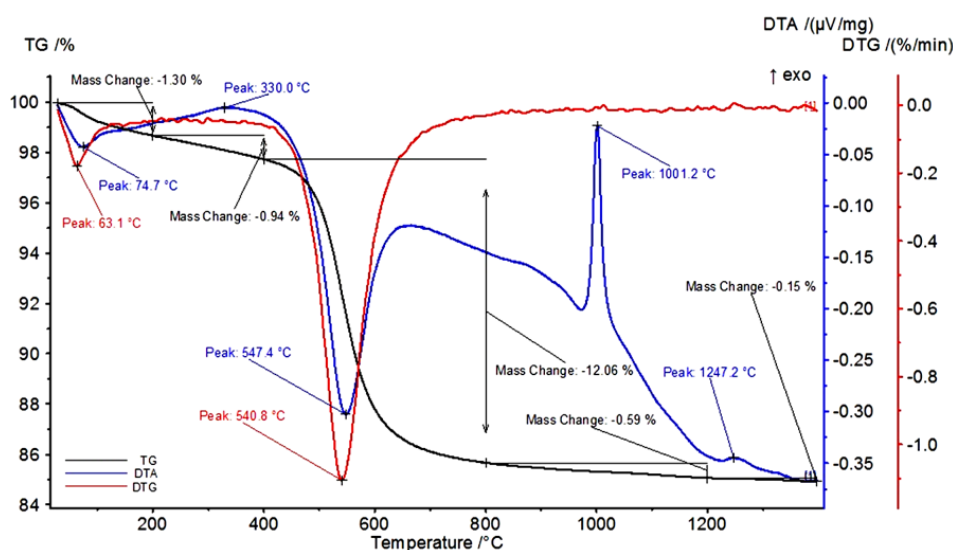


Fig. 3: TG/DTA simultaneous analysis result of the CC31 commercial-grade kaolin

Al_2O_3 -kaolin-alginate green composite beads were sintered at 1300°, 1400° and 1500°C for 1 hour with a 10°C/minute heating and cooling rate. Microstructural development of the alumina beads were investigated with scanning electron microscopes (SEM, Carl Zeiss/Gemini 300 and Tescan Vega3) in a secondary electron (SE) image mode. Elemental composition of the grain boundaries were investigated via an energy dispersive X-ray spectrometer (EDX, Bruker). Phase identification of the samples were performed by X-ray diffraction (XRD, Bruker AXS/Discovery D8), using monochromatic Cu-K_α radiation ($\lambda=1.5406\text{\AA}$).

Results and Discussion

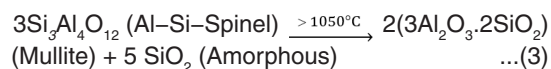
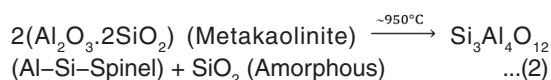
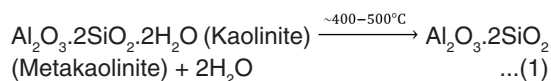
Densification of alumina ceramics via solid state sintering requires very high temperatures. Thus CC31 commercial-grade kaolin was used as a liquid phase sintering aid to decrease the sintering temperature of the alumina-based ceramic beads. XRD analysis of the as-received CC31 commercial-grade kaolin revealed that kaolinite, illite, and free quartz phases exist in the powder (Fig. 2-a). Microstructural investigation of the CC31 commercial-grade kaolin revealed that the particle size of the kaolin is very fine (Fig. 2-b). To avoid exaggerated grain growth Al_2O_3 :CC31 commercial-grade kaolin weight ratio was kept constant as 14:1.

Stability and thermal behavior of the sintering aid was determined by simultaneous thermo gravimetric

and differential thermal analysis (TG-DTA). TG-DTA results of the CC31 commercial-grade kaolin (Fig. 3) revealed that desorption of the water took place at low temperature. The endothermic peak, determined at 74.7°C represents the removal of the absorbed water. The endothermic peak observed at 547.4°C represents dehydration of the kaolin. The exothermic peak observed at 1001.2°C represents the formation of the mullite phase. Mullite formation temperature is determined as 980°C in a study carried out by Chakraborty and Ghosh.⁶⁶ Chen *et al.*,⁶⁷ reported this exothermic mullite formation reaction temperature as 1006.5°C. In the literature kaolin to mullite reaction series have been intensively investigated. It is reported that the reaction temperatures can change depending on various parameters. Particle size and distribution of the kaolin, source of the kaolin, the crystallinity of kaolin, heating rate, and impurity content can change the reaction temperatures.⁶⁸⁻⁸⁵ Depending on the decreased particle size of the kaolin, also reaction temperatures are decreased. The impurity content of the kaolin considerably affects the composition and rheological properties of the liquid phase in the system which mullite formation takes place in it. The impurity content has a significant effect on the kaolin to mullite reaction series.

Phase analysis of the monolithic CC31 commercial-grade kaolin sintered at 1300°, 1400° and 1500°C depicted that kaolin to mullite reaction series were completed in all these temperatures. Mullite phase was detected in all samples (Fig. 4).

Kaolin to mullite reaction series can be explained by the following reactions:



Fracture surface microstructure investigations of the alumina beads densified via liquid phase sintering

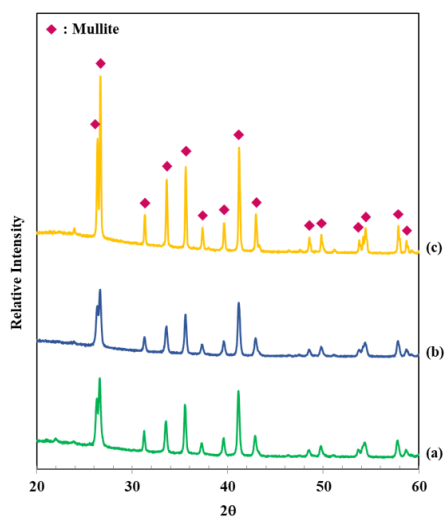
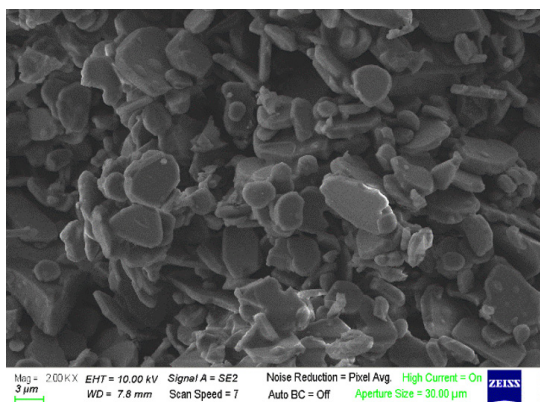


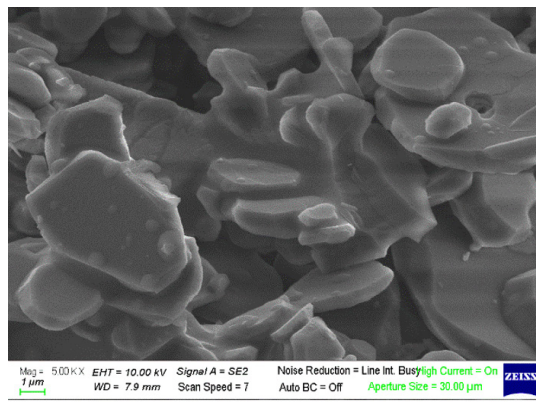
Fig. 4: XRD patterns of the CC31 commercial grade kaolin sintered at (a) 1300°C, (b) 1400°C and (c) 1500°C for 1 hour

at different sintering conditions are given in Fig. 5. Depending on the sintering temperature densification ratios of the samples are slightly changed. Porosity

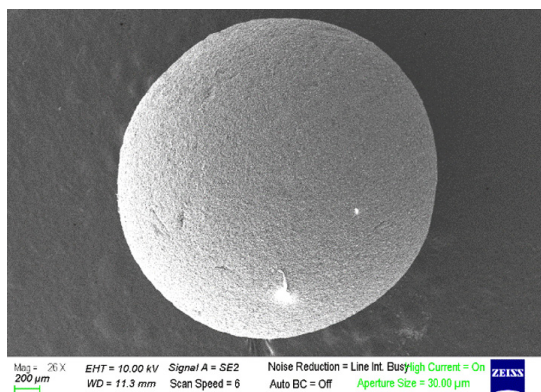
amount and pore size decreased with the increased sintering temperature. SEM investigations confirmed that the highest densification ratio was achieved at



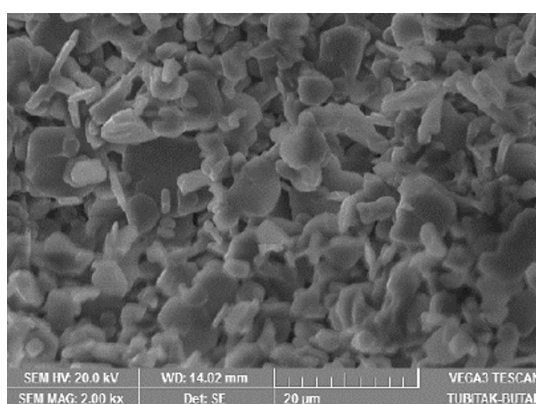
(a)



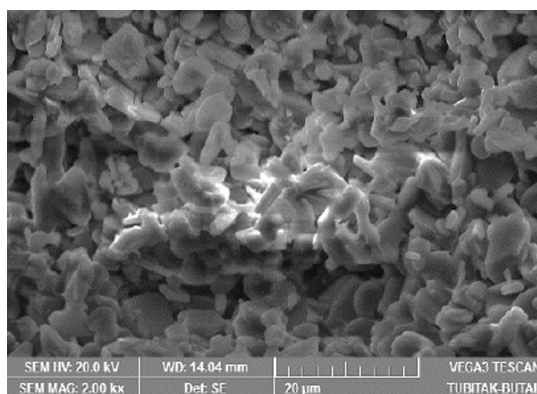
(b)



(c)



(d)



(e)

Fig. 5: Scanning electron microscopy images of kaolin bonded alumina beads produced via sintering at (a, b) 1300°C, (c, d) 1400°C, and (e) 1500°C for 1 hour

1500°C for 1 hour. When the sintering temperature of the beads was $\geq 1400^\circ\text{C}$, it was observed that the strength of the ceramic beads increased significantly due to enhanced densification ratio. Macroscopic and microscopic investigations revealed that the morphology of the ceramic beads did not change during the sintering step (Fig. 1–b and 5–c). As clearly observed in Fig. 5–b, with the help of liquid phase sintering process, a good chemical bonding was achieved between the alumina particles.

EDX analysis of the sample sintered at 1400°C for one hour is given in Fig. 6. The chemical analysis

of the grain boundary phases revealed that there is some silicon and sodium at the grain boundary phases due to CC31 commercial-grade kaolin sintering aid.

XRD results of the kaolin bonded alumina beads revealed that the beads contain alumina phase. There is only a very small peak (showed with a red arrow in Fig. 7) which belongs to mullite phase. Mullite phase forms in the sample as an in-situ phase via the reactions of kaolin at elevated temperatures. However, the beads contain a very low amount of kaolin (alumina:kaolin weight

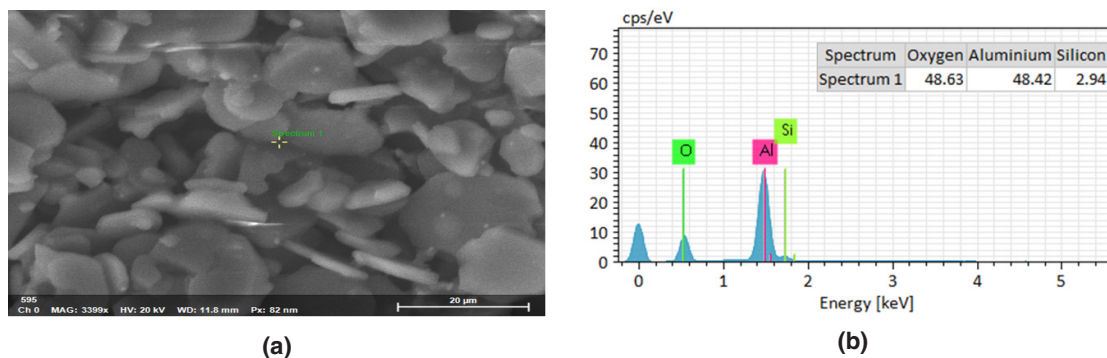


Fig. 6: (a) Investigated region (shown as “Spectrum 1”), and (b) the corresponding EDX spectra achieved for “Spectrum 1” point and the associated element quantification

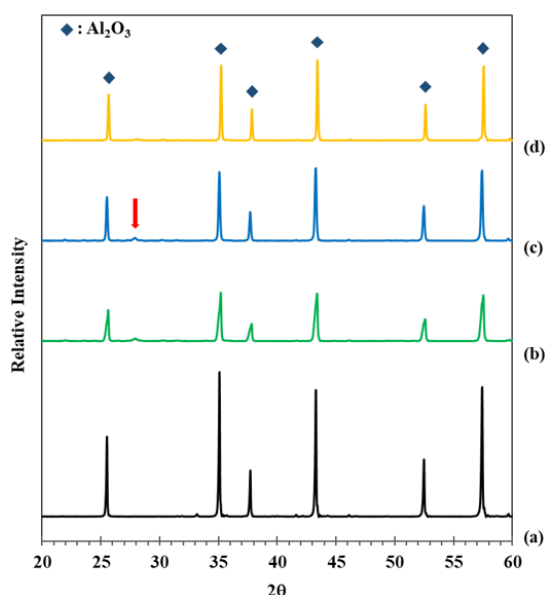


Fig. 7: X-ray diffraction patterns of the (a) Al_2O_3 powder, and ceramic beads produced via sintering at (b) 1300°C , (c) 1400°C , and (d) 1500°C for 1 hour

ratio is 14:1); thus the formation of mullite phase is also very low. As a result, detection of the mullite phase in the samples via XRD is not accurately possible.

Conclusion

- Kaolin bonded alumina porous ceramic beads were produced via a facile, eco-friendly, and convenient route by using sodium alginate as an in situ gelling template for the shaping process and partial sintering for the densification.
- Macroscopic and microscopic investigations revealed that the shape of the produced alumina beads did not change significantly during the sintering step and spherical sintered alumina beads were achieved.
- Sintering studies were carried out between 1300°–1500°C. When the sintering temperature of the beads was $\geq 1400^\circ\text{C}$ it was noticed that strength of the spherical ceramic beads significantly increased due to enhanced liquid phase sintering process.

- Produced porous alumina ceramic beads can be promising materials for various applications such as desalination, water treatment, refractory applications, and a versatile reinforcement for the different polymer, metal or ceramic matrix composite structures.

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Conflict of Interest

The authors have no conflicts of interest to disclose.

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