Effect of Starch Addition on Porosity in Reaction Sintering of Alumina and Magnesia

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Abstract

Porous magnesium aluminate ceramics were produced with a sintering process of α -Al₂O₃ and MgO. Up to 20% by weight of corn starch were used as a pore-forming agent. Pellets were prepared by powder metallurgy technique and produced by solid-state sintering route. The porosity of the sintered pellets was characterized with and without adding corn starch, respectively. In particular, the effects of corn starch additive on density, porosity, and microstructure were investigated. Almost full density was obtained in the samples without starch addition. The study results showed that corn starch addition increased the porosity of the sintered samples. Maximum porosity of 47.86 % was achieved with the addition of 20 wt. % corn starch of 1400°C sintering temperature.

Keywords: Porous MgAl₂O₄, Starch Addition, Microstructure, Sintering

Alümina ve Magnezyanın Reaksiyon Sinterlenmesinde Nişasta İlavesinin Gözeneklilik Üzerindeki Etkisi

Öz

Gözenekli magnezyum alüminat seramikler, α -Al₂O₃ ve MgO'nun sinterlenmesiyle üretilmiştir. Gözenek oluşturuca madde olarak ağırlıkça %20'ye kadar mısır nişastası kullanılmıştır. Peletler, toz metalurjisi tekniği ile hazırlanmış ve katı hal sinterleme yöntemiyle üretilmiştir. Sinterlenmiş peletlerin gözenekliliği, mısır nişastası eklenerek ve eklenmeden karakterize edilmiştir. Özellikle mısır nişastası katkısının yoğunluk, gözeneklilik ve mikro yapı üzerindeki etkileri araştırılmıştır. Nişasta ilavesi yapılmayan numunelerde hemen hemen tam yoğunluk elde edilmiştir. Çalışma sonuçları, mısır nişastası ilavesinin sinterlenmiş numunelerin gözenekliliğini artırdığını göstermiştir. 1400°C sinterleme sıcaklığında ağırlıkça % 20 mısır nişastası ilavesi ile % 47.86 gözeneklilik elde edilmiştir.

Anahtar Kelimeler: Gözenekli MgAl₂O₄, Nişasta İlavesi, Mikroyapı, Sinterleme

1. Introduction

In general, porous ceramics share many common properties such as high porosity, high chemical stability, good thermal shock resistance, and excellent thermal insulation, enabling their use in various applications, including gas and liquid filters, carriers, and insulation [1-4].

Porous magnesium aluminate spinel (MgAl_2O_4) is one of the refractory ceramics widely used as gas filters, catalytic supports, and separation membranes because of their high melting point (2135°C), high specific surface area, high thermal shock resistance, relatively low thermal conductivity and thermal expansion coefficient, and good chemical inertness [5-6].

Pore-forming agents are one of the most frequently used methods to produce porous ceramics with controlled microstructure (porosity and pore size) [7-9]. During the heating of the ceramics to the final firing temperature, these pore-forming substances burn, leaving empty pores in the ceramic. Among the various pore-forming agents, those of biological origin, especially starch, have gained a significant position [10-13]. Starch is inexpensive, non-toxic, environmentally friendly, and exhibits defect-free combustion between about 300 and 600°C [14]. Starch can be used as a pore-forming agent. It can be used as an additive in slip casting or as a combined pore-forming and body-forming agent in so-called starch consolidation [15]. In addition to these techniques, this study, it is aimed to form pores by adding corn starch to the anhydrous system.

In our previous work, the dense spinel ceramics with high strengths have been prepared using Al_2TiO_5 as an additive in reaction sintering of $\alpha\text{-Al}_2\text{O}_3$ and MgO [16]. Using the results obtained in the previous study, the composition showing a high densification tendency was chosen in this study. Accordingly, it is aimed to close the cracks that may occur due to the voids formed by the corn starch with high densification during sintering.

In this work, corn starch was utilized to prepare porous MA spinel ceramic materials with reactive sintering of $\alpha\text{-Al}_2\text{O}_3$ and MgO . The effects of starch ratio and sintering temperatures on the microstructure, density, and porosity were investigated.

2. Materials and Method

In this study, $\alpha\text{-Al}_2\text{O}_3$ (>99.7%, 2 μm , Nabaltec), MgO (>98%, Merck), and corn starch (Piyale, Turkey) were used as raw material and Al_2TiO_5 (AT) as an additive material. AT was prepared by solid-state sintering reaction by adding 10 wt. % MgO to the equimolar mixture of $\alpha\text{-Al}_2\text{O}_3$ and TiO_2 and sintering at 1450°C for 3 hours [16]. The samples obtained were powdered using a ring mill and used as an additive material in this study. After adding 10 % by weight of AT to equal mole amounts of $\alpha\text{-Al}_2\text{O}_3$ and MgO , the powders were mixed in an ethanol medium for 30 minutes in a porcelain mill. Then, it was kept in an oven at 80°C for 24 hours, and the ethanol was removed. Compositions were formed by adding 5, 10, and 20 % corn starch by weight to the dry powder mixture obtained. These compositions were homogenized by mixing for 10 minutes in a dry environment in a porcelain mill. The samples were formed into pellets by weighing 8 grams of powder and pressed under 30 MPa pressure in a steel mold (diameter = 30 mm) using a uniaxial semi-automatic press. Three samples were produced for each composition. The names and compositions of the prepared samples are given in Table 1.

A high-temperature furnace (Protherm) with a MoSi_2 heating element was used for sintering. The samples were sintered at 1400 and 1500°C for 1 hour in an air atmosphere. The heating rate of the furnace was $5^\circ\text{C}/\text{min}$, and the cooling rate was $2^\circ\text{C}/\text{min}$. According to Archimedes' principle, bulk density, apparent porosity, and water absorption values were calculated. The Archimedes method tests were verified with three samples. A powder diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$) and a secondary graphite monochromator was used for phase analysis (Shimadzu, XRD-6000). X-ray diffraction (XRD) spectra were obtained by scanning from 25° to 70° angles (2θ), at a goniometer speed of $1.25^\circ/\text{min}$, at an accelerating voltage of 40 kV and a current of 30 mA. The fractured surfaces of the samples were coated with carbon and investigated with a scanning electron microscope (SEM) (LEO-1430VP).

Table 1. Corn starch ratios and sintering temperature of the samples.

Sintering Temperature/ Corn Starch Ratio (wt. %)	0	5	10	20
Sintered at 1400°C (1h)	M014	M514	M1014	M2014
Sintered at 1500°C (1h)	M015	M515	M1015	M2015

3. Results and Discussion

The bulk density values of the samples determined by the Archimedes' method are given in Figure 1. Corn starch addition decreased the bulk density as expected. The theoretical density of MA spinel is 3,58 g/cm³. The bulk density of the M015 sample was measured as 3.336 g/cm³. The apparent porosity of this sample, which was sintered at 1500°C without adding corn starch, was measured as 0.159 % and the water absorption percentage as 0.047. It can be said that the MA spinel that will form the skeleton approaches almost full density at this composition and sintering temperature. The sample sintered at 1400°C without corn starch addition has a bulk density of 2.464 g/cm³. At the sintering temperature of 1400°C, these samples did not show full densification and had porosity without adding corn starch. Figure 2 shows the apparent porosity of the sintered samples. Porosity decreased with increasing sintering temperature [17-18]. At the same time, the porosity values increased with the addition of corn starch. With the addition of 20 % corn starch, approximately 50 % porosity was obtained in the samples sintered at 1400°C.

The water absorption % of the samples is given in Figure 3. With the increase of sintering temperature, the water absorption values showed a significant decrease. With the addition of corn starch to the system, the increase in water absorption values became evident. Water absorption values are lower than the apparent porosity. This indicates the presence of both open and closed pores in the system.

Figure 1. Bulk density of the sintered pellets.

Water absorption values are an indirect indicator of the amount of open pores. If the water absorption values of a material with a specific porosity value are very close to the apparent porosity values, the existing pores in the material are primarily open pores. However, if the difference between these values is large, the material has both open and closed pores. The relationship between water absorption and apparent porosity values can be explained in this way.

Figure 2. Apparent porosity of the sintered pellets.

Figure 3. Water absorption of the sintered pellets.

XRD phase analyzes of sintered samples are given in Figure 4. The main phases were determined by performing XRD analyzes on samples without starch additives. The primary phase is MA spinel. A high amount of MA spinel phase was formed at both sintering temperatures. In this case, the starting powders α - Al_2O_3 and MgO reacted to form the MA phase. The sintered samples contain a small amount of the Al_2TiO_5 phase. Al_2TiO_5 phase was used as an additive to increase the densification. As the sintering temperature increased, the intensities of the minor peaks decreased.

Figure 4. XRD phase analysis of the sintered samples.

Figure 5. SEM micrographs (M015), BSE micrograph (left), SEM-EDX mapping micrograph (right).

SEM-BSE micrograph of the fractured surface of sample M015 is shown in Figure 5. It is seen that the sample has a dense structure. Unreacted AT grains appear in white, MA grains appear in gray. In addition, although overgrown MA grains are visible, the sample contains few pores. These results are consistent with the bulk density and porosity values obtained with Archimedes'.

Figure 6. SEM-SE micrographs, a) Sample without starch additive sintered at 1400°C, b) Sample with starch additive sintered at 1400°C, c) Sample without starch additive sintered at 1500°C, d) Sample with starch additive sintered at 1500°C.

SEM-SE micrographs of the fractured surface of the samples are given in Figure 6. Samples sintered without starch additives have very little porosity. Grain growth is observed as the sintering temperature rises from 1400°C to 1500°C. Even overgrown grains are evident. The porosity is seen in the samples in which corn starch is added to the composition. It can be thought that corn starch burns during sintering and forms voids in its positions. According to DTA analysis, during heating, corn starch dehydrates up to about 115°C and loses 11.50 % of its weight. The second weight loss between 275 and 325°C occurs with the combustion of amylopectin groups, and 65.29% of the starch weight is lost. Finally, with the removal of the amylose group between 325-525°C, it loses 22.66% of its weight and completely disappears from the system [19-20].

4. Conclusions and Recommendations

This study carried out MA spinel production with porosity successfully using corn starch. Corn starch acted as a pore former.

As a result of sintering the starting powders by trying a composition that will create a high density, MA spinel with a value close to the theoretical density was produced according to Archimedes' results in the samples without starch. These results were in agreement with the XRD phase analysis.

According to the SEM results, very few pores were detected in the samples without starch. The porosity of the samples increased due to the voids formed due to the removal of starch from the system.

Approximately 50% porosity was obtained in the samples sintered at 1400°C with the addition of 20 % by weight of corn starch.

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