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# SYNTHESIS OF MAGNESIUM ALUMINATE SPINEL DOPED $TiO_2$ FROM MAGNESITE WASTE

Magnesium aluminate spinel ($MgAl_2O_4$) is an important refractory material of magnesia origin. It is formed by the reaction of magnesium and aluminum oxides. In this study, $TiO_2$ was added to magnesite waste and alumina ($Al_2O_3$) powders in different proportions and the mixtures were sintered at different temperatures after shaping. The aim of this study was to produce spinel economically by recycling waste materials. Therefore, titanium dioxide ($TiO_2$) added magnesium aluminate spinel was produced and the products obtained were characterized by XRD and SEM-EDS analyses. In addition, bulk density, apparent porosity and microhardness values were measured and the effects of $TiO_2$ additive on magnesium aluminate properties were examined. The better values were determined in samples doped 4 wt.% $TiO_2$ at the sintering temperature of 1400°C.

*Keywords:* Magnesium aluminate spinel ($MgAl_2O_4$); Titanium dioxide ($TiO_2$); Magnesite waste; Alumina ($Al_2O_3$)

## 1. Introductıon

In recent years, magnesium aluminate spinel ($MgAl_2O_4$) has gained considerable importance both academically and industrially because of its favorable characteristics such as high melting point (2135°C), high hardness (16 GPa), relatively low density (3.58 $g.cm^{-3}$), high strength at room temperature (135-216 MPa) and high temperature (120-205 MPa at 1300°C), high resistance to chemical environments, high electrical resistance, relatively low thermal diffusion coefficient ($9\times10^{-6}$ $°C^{-1}$, between 30 and 1400°C), and high thermal shock resistance, excellent resistance to acid and bases and also excellent optical properties [1,2].

As a refractory material, spinel is important for iron and steel industry in steel ladles, transition zones and combustion zones of cement rotary kilns, and regenerators of glass tank furnaces. In addition to refractories, spinel is also used in the field of structural ceramics and has a wide variety of applications, such as missile domes, laser materials, moisture sensors, photocatalyst materials and catalyst support, dental materials, electroceramic materials, porous materials for high temperature applications, and transparent armor [3,4]. In addition to transparent armor, tough defense applications such as IR-transparent windows and domes, as well as commercial applications such as barcode scanners, clocks and high-temperature sight glasses can be listed among the various applications of transparent ceramics [5].

Magnesium aluminate spinel ($MgAl_2O_4$) is the main component of magnesia-based refractory materials. Since $MgAl_2O_4$ does not form naturally, it is produced by the reaction of magnesium and aluminum oxides. Its theoretical stoichiometric composition is 71.68% $Al_2O_3$ and 28.32% MgO by weight [6]. It is difficult to form a dense sintered structure due to a volume expansion of approximately 5% when magnesium aluminate spinel is produced by the reaction of the oxides. In addition, very high sintering temperatures are required [7]. Therefore, various studies have been carried out to achieve pressureless sintering at low temperatures. Some of these were carried out by adding sintering aids to reduce the sintering temperature. $TiO_2$, $MnO_2$, $Cr_2O_3$, and ZnO could be given as examples of sintering aids. Also, compounds of alkali/alkaline earth, transition metal and rare earth metals are used as additives [8]. Sarkar et al. [9] studied the effect of $Cr_2O_3$ addition on stoichiometric and non-stoichiometric compositions of magnesium aluminate. They found that the addition of $Cr_2O_3$ reduced the solid solubility temperature of the excess alumina in the alumina-rich spinel, enabled densification at 1550°C, and they confirmed the solid solubility of $Cr_2O_3$ in the spinel and stated that it dispersed evenly along both grain and grain boundaries. In a study by Tripathi et al. [10] it was found that $Dy_2O_3$ addition greatly improved the densification of spinel at 1600°C. Moreover, it was seen that the bulk densities of structures containing 2% and 4% of $Dy_2O_3$ by weight at

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1650°C were almost identical, and the apparent porosity values were almost zero. In addition, it was stated that higher amount of $Dy_2O_3$ addition increased the densification at 1550 and 1600°C. Yan et al. [11] studied the effect of $TiO_2$ addition to magnesium aluminate and found that $TiO_2$ strongly affected the formation of the liquid phase, and then porosity, pore size distribution and strength. They stated that the increase of $TiO_2$ amount increases the liquid phase formation at sintering temperature.

In this study, magnesite waste, which is a waste as a raw material was used as starting powders in magnesium aluminate spinel production instead of pure oxide powders to make the process more economical. In addition to being cost efficient, it was thought that the oxide residues in the magnesite waste would act as a sintering aid to promote densification and facilitate sintering at lower temperatures. Furthermore, the effect of $TiO_2$ added as sintering additive on the densification and some other properties of magnesium aluminate spinel was also examined. Although the addition of $TiO_2$ has been widely studied in the literature, it has been added as a sintering aid to spinel produced from waste material in this study.

## 2. Experimental studies

Magnesite waste, alumina ($Al_2O_3$), and titanium dioxide ($TiO_2$) powders were used as raw materials in this study. Magnesite waste was obtained from KÜMAŞ A.Ş., $Al_2O_3$ was obtained from KALEMADEN and 99.9% pure $TiO_2$ was obtained from Alfa Aesar. The compositions of the starting raw materials used are given in TABLE 1.

TABLE 1

The chemical compositions of the starting raw materials

| **Compound (wt.%)** | **$SiO_2$** | **CaO** | **$Al_2O_3$** | **$Fe_2O_3$** | **MgO** | **$Na_2O$** | **L.O.I*** |
|---|---|---|---|---|---|---|---|
| **Magnesite waste** | 15.56 | 1.79 | 0.28 | 3.36 | 45 | — | 33.96 |
| **Alumina** | | | 99.85 | | | 0.06 | 0.29 |

* Loss on ignition

For the production of magnesium aluminate, magnesite waste, $Al_2O_3$ powder and 1%, 2%, 3% and 4% $TiO_2$ powder by weight were dry-mixed in the ball mill for 10 hours according to the stoichiometric ratio of 78% $Al_2O_3$-22% MgO. The prepared mixtures were shaped by dry pressing under 60 MPa pressure and then sintered at 1300, 1350, 1400 and 1450°C for 1 hour. Flow chart of magnesium aluminate production from magnesite waste was given in Fig. 1. Bulk densities and % apparent porosity values of sintered products were measured by the Archimedes method. Firstly, dry mass of sintered samples were weighed ($Wa$). The weights in water ($Wb$) of the samples were then measured. Finally, the samples were removed from the water and roughly dried, and their weights were measured ($Wc$) one more time. Bulk density and % apparent porosity values were calculated according to the following formulas ($dw$: density of water was taken as 1):

$$\text{Bulk density} = \frac{Wa}{Wc - Wb} \cdot dw \tag{2.1}$$

$$\%\ \text{Apparent porosity} = \frac{Wc - Wa}{Wc - Wb} \cdot 100 \tag{2.2}$$

In addition, other samples produced under the same conditions were first prepared metallographically and then polished. The Vickers hardness of the polished specimens was measured under 500 g load. The samples were then thermally etched at temperatures 50°C below the sintering temperature. SEM and EDS analyses were performed on the polished and etched surfaces for microstructural and elemental analysis. Therefore, based on the results obtained in this study, optimum conditions for the production of magnesium aluminate spinel with the starting materials used and the effects of $TiO_2$ addition were investigated.

## 3. Results and discussion

The bulk densities of the samples obtained from the mixtures prepared in suitable compositions for producing magnesium aluminate spinel after sintering at different temperatures (1300, 1350, 1400 and 1450°C) for 1 hour are shown in Fig. 2. In general, increasing the temperature up to 1400°C increased the density in all compositions (with 1 wt.%, 2 wt.%, 3 wt.% and 4 wt.% $TiO_2$ doped), and at 1450°C there was a decrease in densities. When different amounts of $TiO_2$ additives are compared, it can be seen that high densities are obtained with 4 wt.% $TiO_2$ addition. In another study [12], density and porosity values were measured by adding spinel and $SnO_2$ into MgO. The density values of the samples with spinel addition were approximately

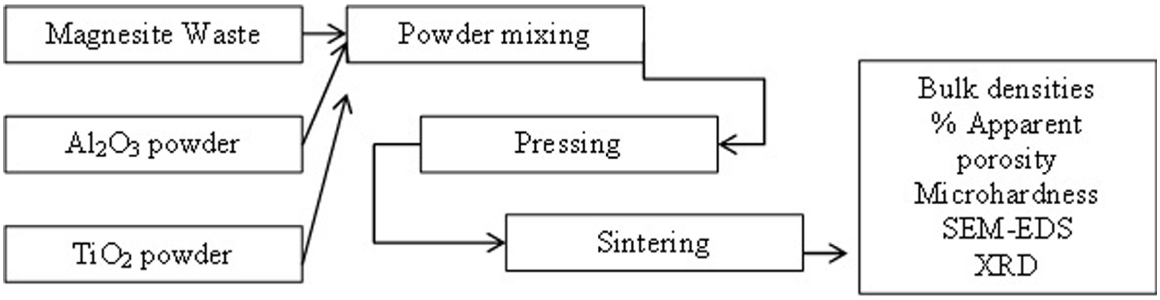


Fig. 1. Flow chart of magnesium aluminate production from magnesite waste

between 2.75 and 2.81 gr.cm$^{-3}$, and density values of the samples with $SnO_2$ addition were approximately 3.2 gr.cm$^{-3}$. The highest density value of the samples produced in this study was obtained as 3.05 gr.cm$^{-3}$ at 1400°C in 4% $TiO_2$ doped mixture. The density of the 1 wt.% doped mixture produced under the same conditions was 2.84 g.cm$^{-3}$, and thus it was clearly demonstrated that increasing the $TiO_2$ additive had a positive effect on the density. Naghizadeh et al. [13] examined the effect of $TiO_2$ addition to $MgAl_2O_4$ spinel and stated that new phases were formed on the grain boundaries and a dense structure was formed due to liquid phase sintering.

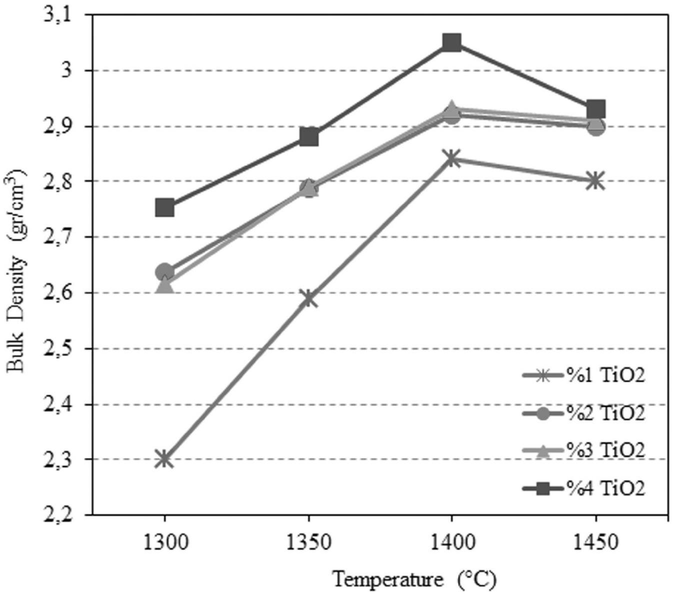


Fig. 2. Bulk densities at different sintering temperatures

Fig. 3 shows the % apparent porosity values calculated based on the amount of $TiO_2$ added. It is evident here that with increasing temperature the number of pores decreases in all compositions. This change is due to the increase in density caused by the increase in sintering temperature and therefore consistent with the results shown in Fig. 2. The lowest apparent porosity was obtained as 0.3% at 1400°C in 4 wt.% $TiO_2$ doped system, and this result was also consistent with the highest density value. When we compare this result with 10.73% porosity at 1 wt.% $TiO_2$ doped system, it can be said that the change in apparent porosity obtained by increasing temperature and $TiO_2$ amount in the system is considerable.

The change in microhardness values of the samples produced with different amounts of $TiO_2$ at different sintering temperatures is given in Fig. 4. As can be seen from the graph, increasing the sintering temperature caused an increase in the hardness of the samples. At the same time, increasing the amount of $TiO_2$ generally increased the hardness. The highest hardness value was measured as 1510 HV at 1400°C sintering temperature in 4 wt.% $TiO_2$ doped system. When compared with the density and apparent porosity graphs given in Fig. 2 and Fig. 3, it can be seen that the results are consistent. Therefore, considering the bulk density, apparent porosity, and hardness values of magnesium aluminate spinel produced with $TiO_2$ additive, the best result is obtained at a sintering temperature of 1400°C in 4 wt.% $TiO_2$ doped system. Sarkar and Bannerjee [14] investigated the effects of $TiO_2$ addition to MgO and $Al_2O_3$ mixtures in different compositions for spinel production. They stated that the presence of $TiO_2$ increased the density at 1550°C but worsened the properties at higher temperatures due to grain growth. They also found that low temperature strength increased but high temperature strength decreased, and this was explained by the presence of $TiO_2$ at the grain boundaries.

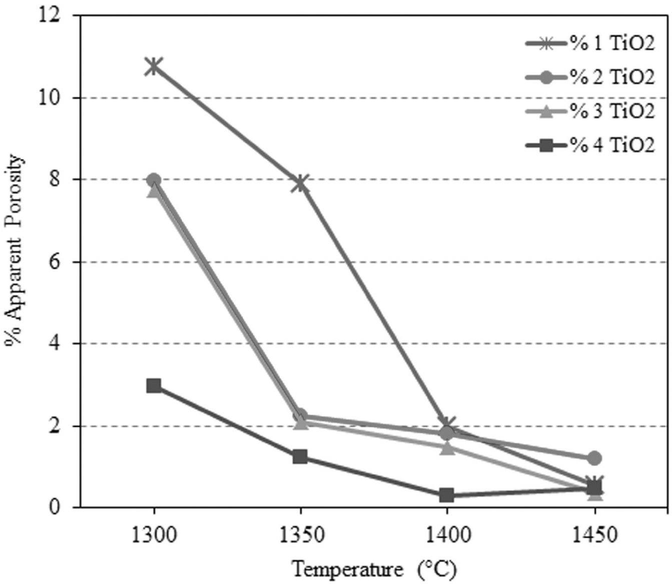


Fig. 3. Apparent porosity (%) values of sintered samples

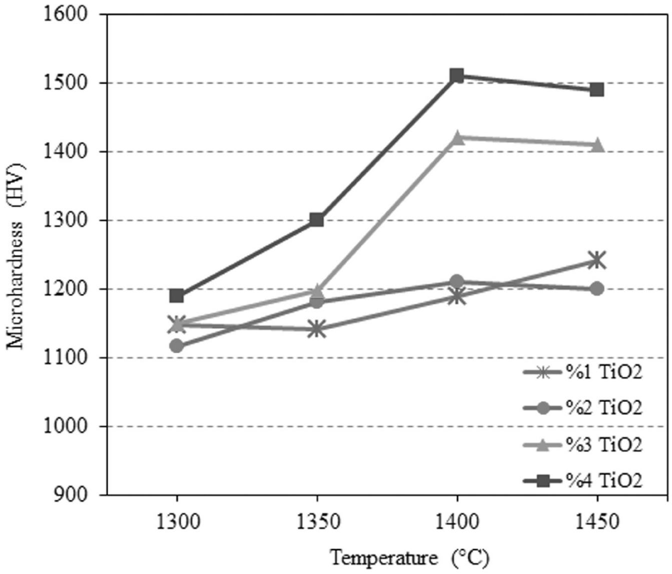
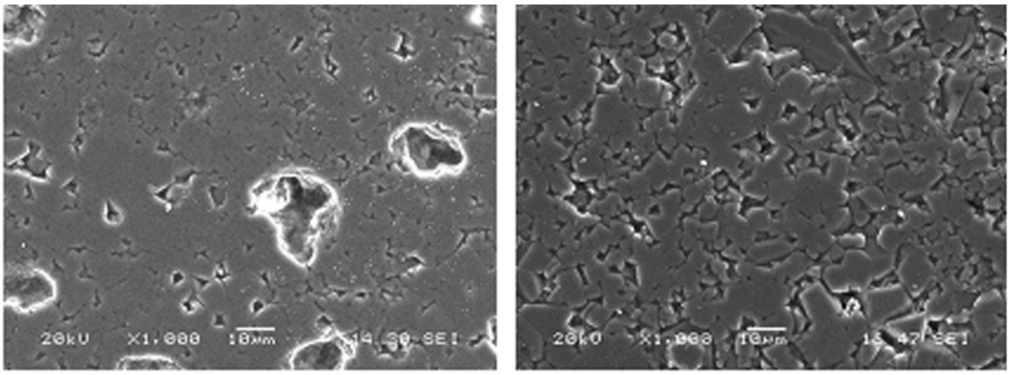
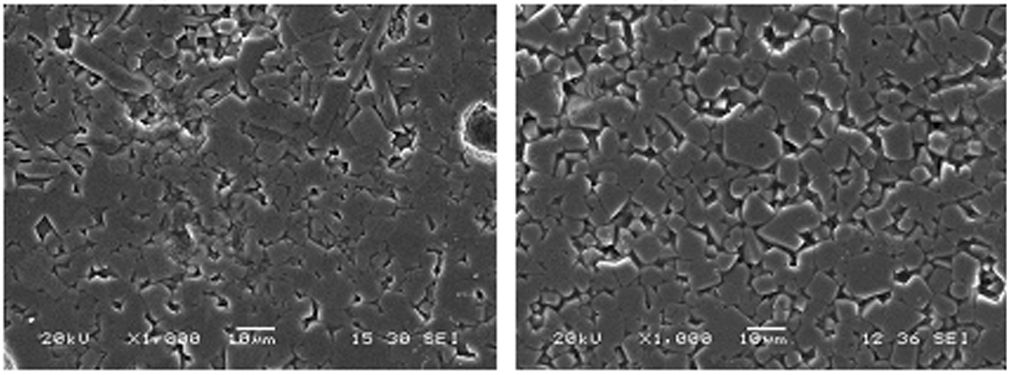


Fig. 4. Microhardness values at different sintering temperatures

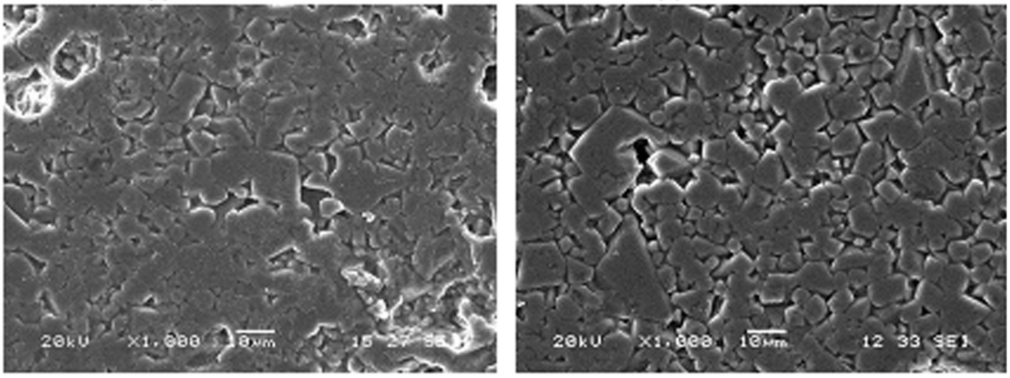
Fig. 5 shows SEM images of samples sintered at 1300°C and 1400°C for 1 hour with different $TiO_2$ additions. The purpose of showing only these images is to observe the microstructure changes depending on the amount of additive in samples sin-



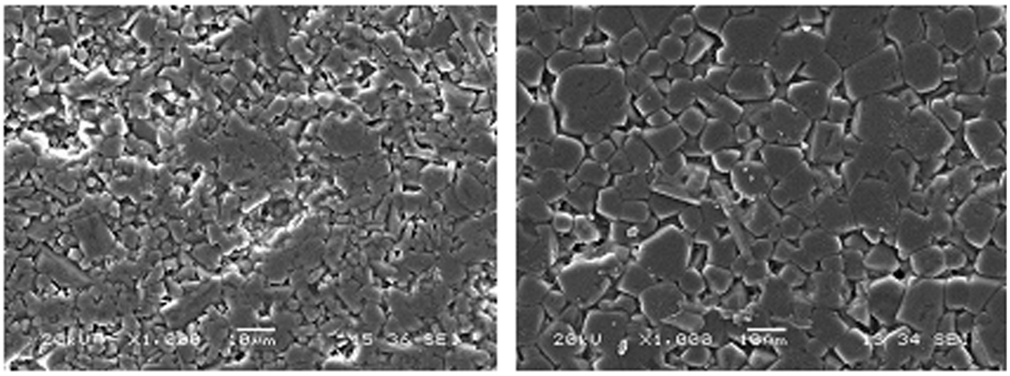
(a) %1 TiO$_2$ – 1300°C (b) %1 TiO$_2$ – 1400°C



(c) %2 TiO$_2$ – 1300°C (d) %2 TiO$_2$ – 1400°C



(e) %3 TiO$_2$ – 1300°C (f) %3 TiO$_2$ – 1400°C



(g) %4 TiO$_2$ – 1300°C (h) %4 TiO$_2$ – 1400°C

Fig. 5. SEM images of sintered samples at 1300°C and 1400°C with different TiO$_2$ additions

tered at the lowest and higher temperatures. When the images are examined, it is seen that increasing the sintering temperature decreases the pores and increases the grain size. In addition, it can be said that increasing the amount of TiO$_2$ improves sintering and reduces the pores. When we analyze the image of the sample that gave the best results in previous paragraphs (4 wt.% TiO$_2$ doped system sintered at 1400°C), the grain size is approximately 2-10 mm. Similarly, another study reported that spinel produced at a sintering temperature of 1600°C with the addition of 4 wt.% Dy$_2$O$_3$ had a grain size of approximately 8.5 mm [10]. EDS

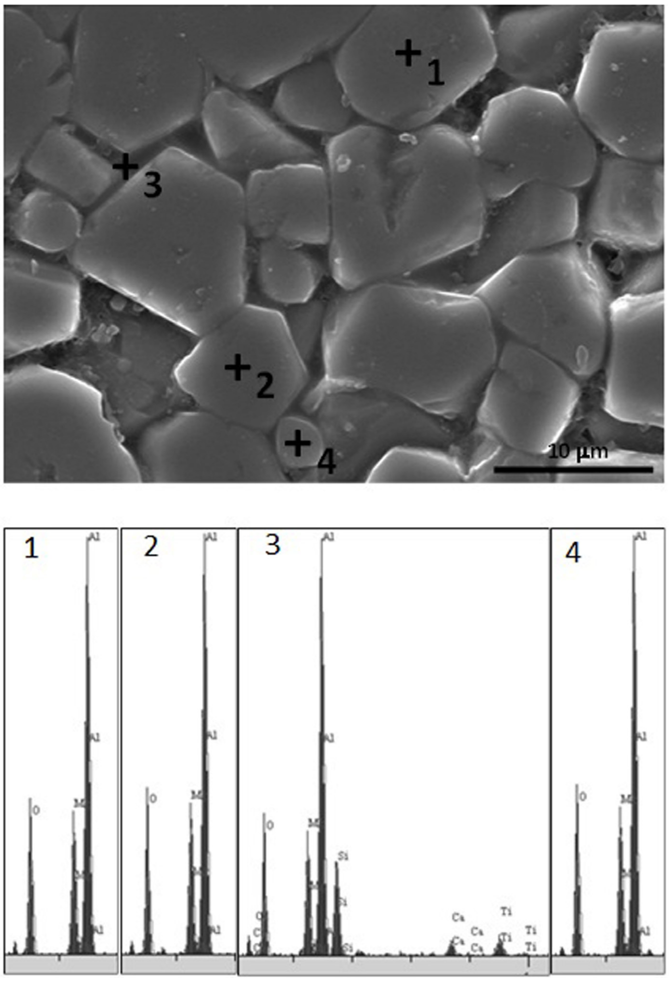


Fig. 6. EDS analysis of the sintered sample at 1400°C for 1 hour with 4 wt.% $TiO_2$ addition

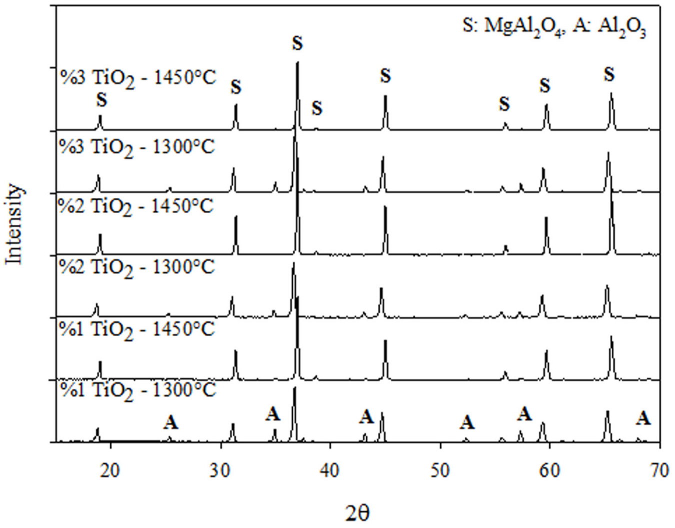


Fig. 7. XRD analysis of samples sintered at 1300°C and 1450°C for 1 hour

analysis of the sample with 4 wt.% $TiO_2$ addition sintered at 1400°C for 1 hour is shown in Fig. 6. Here, the presence of Mg, Al, and O elements in points 1, 2 and 4 indicate that these grains belong to magnesium aluminate ($MgAl_2O_4$). In addition to these elements, Si, Ca from magnesite waste, and Ti, which was added to the system, were also determined in intergranular region 3. This also proves the presence of oxide components which causes the production temperature to drop. Thus, the magnesite waste used as the starting raw material appears to be an advantageous material for producing magnesium aluminate faster and at low temperatures due to the oxide components therein, and the added $TiO_2$ is also effective.

XRD analysis of products with different additive amounts sintered at 1300°C and 1450°C are given in Fig. 7. Here, only the products sintered at the lowest and highest temperatures were selected and compared since the phase analyses at the other temperatures were also similar. Magnesium aluminate conversion was not fully achieved at the sintering temperature of 1300°C in all additive added products. In other words, the temperature was not enough. It can be seen that increasing the sintering temperature to 1450°C was not sufficient to complete the conversion in samples with 1 wt.% and 2 wt.% $TiO_2$ addition. That is, unconverted $Al_2O_3$ phase was determined in the structure. However, it can be said that increasing the amount of additive improves the conversion as seen in the 3 wt.% $TiO_2$ doped product. Therefore, it is thought that increased $TiO_2$ addition has a lowering effect on magnesium aluminate production temperature.

Fig. 8 shows XRD analysis of products with 4 wt.% $TiO_2$ addition sintered at different temperatures. As can be seen, spinel formation is fully achieved at 1400°C. Considering the XRD analyses given in Fig. 7, increasing $TiO_2$ amount to 4% by weight has a positive effect on magnesium aluminate conversion. Although conversion could not be fully achieved with lower additive ratios even at 1450°C, production at 1400°C was achieved in the 4% doped system. Therefore, 4 wt.% $TiO_2$ added system at a sintering temperature of 1400°C where the best results were obtained according to density, apparent porosity and microhardness measurements was determined as optimum conditions to produce magnesium aluminate from magnesite waste and alumina.

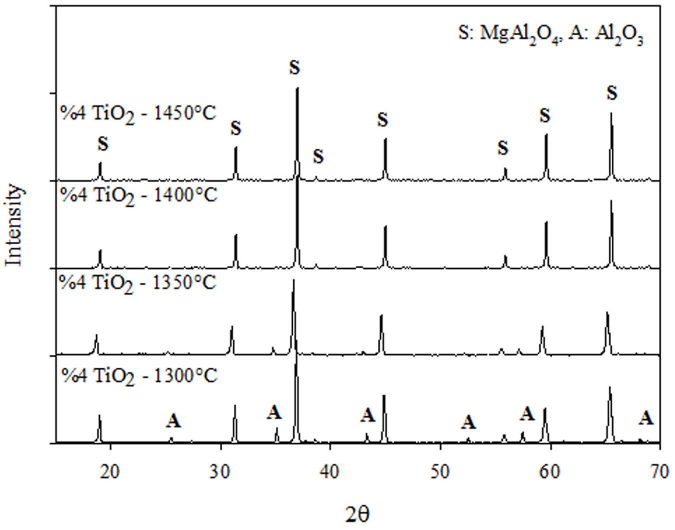


Fig. 8. XRD analysis of samples containing 4 wt.% $TiO_2$ sintered at different temperatures for 1 hour

In another study [15], properties of magnesium aluminate spinel with $MgCl_2$, LiF, $AlCl_3$ and $MnO_2$ additions sintered at a temperature range of 1200-1600°C were investigated. According to the results, the highest density and lowest porosity values were obtained at 1600°C and the values obtained were similar to the results of the present study. In addition, when XRD analyses were compared, it was found that full formation was achieved at 1600°C whereas full spinel formation was achieved at 1400°C in the present study with $TiO_2$ addition. Therefore, when this result is compared with the literature, it is seen that production occurs at lower temperature. This can be explained by the fact that the various oxides present in the starting raw material and the $TiO_2$ added externally to the system form liquid phase sintering between the grains, facilitating sintering and promoting densification at lower temperatures. Similar to the present study, Mohan and Sarkar produced magnesium aluminate spinel with the addition of $ZrO_2$ at a sintering temperature of 1600°C [16]. They argue that the presence of $Zr^{+4}$ ion impedes grain boundary movements and grain growth and provides a more uniform and denser microstructure. Caliman et al. [17] investigated the effects of lithium oxide addition to spinel and they observed to segregate of lithium to both surface and grain boundary regions.

## 4. Conclusıons

In this study, magnesium aluminate spinel production with magnesite waste, alumina, and $TiO_2$ additive was studied in order to recycle magnesite waste which is an industrial waste. As the result, the highest density value was determined as 3.05 $gr/cm^3$ with 4% $TiO_2$ doped sample at a sintering temperature of 1400°C. Consistent with the density value, the lowest apparent porosity was obtained after sintering the 0.3% and 4% $TiO_2$ doped sample at 1400°C. The highest hardness value was determined as 1510 HV with the 4% $TiO_2$ doped sample at a sintering temperature of 1400°C. SEM analysis revealed that increasing sintering temperature reduced the pores and increasing $TiO_2$ additive amount facilitated sintering. In addition, a grain size of approximately 2-10 mm was determined in the 4% $TiO_2$ doped sample sintered at 1400°C. According to XRD analysis, increasing the sintering temperature and $TiO_2$ additive promotes magnesium aluminate conversion.

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