Optimization of magnesia sintering parameters fabricated by spark plasma sintering method for infrared transparency

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Abstract
In this study, sintering of magnesia nanopowder was investigated using spark plasma sintering (SPS), and the effects of time and pressure on microstructure, physical properties, density, and infrared transparency were studied. Densification of magnesia nanopowder was examined at 1100 °C and the pressure of 40, 60, and 80 MPa, and at different times. Findings indicated that MgO ceramics’ density rapidly increased with increasing the sintering time up to 5 min, while it increased with a slow speed after 5 min. Analysis of grain growth rate at different times indicated that, in the initial stages of sintering, the process was done through a non-diffusional process and, in the final 15 min of the process, it was done through lattice diffusion. In addition, examining the yield stress of the sintered sample at 1100 °C and considering its conformity with the results of theoretical density showed that it underwent plastic deformation up to 15 min. In general, the results revealed that the main mechanism of magnesia sintering was plastic deformation. The highest infrared transmittance of 65% was obtained for the sample sintered at 1100 °C for 20 min at 80 MPa.

1. Introduction

Transparent ceramics for infrared windows need to have several properties, such as high transparency over a wide range of wavelengths, desirable mechanical properties, and low emission at high temperatures [1]. One of the transparent polycrystalline ceramics in the infrared range is magnesia. Magnesia has a high melting point of about 2850 °C, so it isn’t easy to apply the usual methods of high-quality magnesia single crystal growth on a large-scale [2]. Therefore, in order to produce magnesia optical ceramics, the only possible method is to use its polycrystalline form. Over the past decades, oxide-based nanoceramics have attracted considerable attention due to their unique physical and chemical properties [3, 4]. Among these materials, magnesium oxide can be considered as one of the most promising and remarkable metal oxides due to its special and extraordinary optical, electrical, thermal, mechanical, and chemical properties, as well as its high ionic nature [5]. Excellent physical properties along with low cost and environment-friendly magnesia have led to a wide range of applications of this compound [6]. Therefore, transparent polycrystalline magnesia can be used in various applications such as infrared windows and scintillators in military and optical industries [7].

Magnesia sintering and obtaining the theoretical density required for transparency is difficult due to the inability to precisely control the sintering process parameters and the initial powder’s properties. The task becomes more complicated when the relationships between the synthesis parameters, the sintering process, the structure, and the initial powder’s properties are not yet known and examined. The key to achieving the desired final properties is to understand the relationships between the available parameters and the reactions during sintering. Particle size, porosity, impurities, additives, and sintering process parameters such as pressure, temperature, time, heating rate, and how each of these would be applied can be factors determining the ceramic’s final properties [1].
Several studies have been carried out on magnesia sintering and mechanisms and its transparency [8–10]. Magnesia sintering via conventional sintering method required high temperature and longtime [11–13]. Pressureless methods with temperatures above 1400 °C have been used for magnesia sintering, which results in the activation of diffusional mechanisms. These methods can cause grain growth in the final product [12]. Grain growth can reduce mechanical and optical properties. On the other hand, research on magnesia sintering has been done using hot press and SPS methods. The findings have revealed that they have been used to achieve transparent magnesia at either high temperature or high pressure [8, 14]. It is noteworthy that the use of high temperature can lead to grain growth and high costs, and the use of high pressure requires special molds. In our previous study, the effect of sintering temperature was investigated; and findings indicated that, at high temperatures, magnesia sintering was controlled by a plastic deformation mechanism and that the best performance was obtained at a temperature of 1200 °C [15]. Therefore, studying magnesia sintering at low pressures and temperatures below 1200 °C can show the role of diffusional processes in magnesia sintering. Therefore, the aim of this study was to investigate time and pressure in magnesia sintering by the SPS method at 1100 °C.

2. Experimental method

2.1. Materials

Magnesia powder with a particle size of less than 100 nm (US-Nano) was used, with X-ray diffraction (XRD) pattern shown in figure 1. For the deagglomeration process, a planetary mill was used for 15 h at a rotational speed of 200 rpm in ethanol medium, an alumina chamber, and magnesia balls with the ball to powder ratio of 6:1. The milled powder was then dried in an oven at 80 °C for 10 h.

2.2. Method

For the aim of sintering the powder by spark plasma sintering method, 2 g of powder was used in each test after ball milling, after which the sintering operation was performed in graphite mold with an inner diameter of 20 mm, an outer diameter of 40 mm and a height of 40 mm. Graphite foil was used to prevent the powder from sticking to the mold. An optical pyrometer was used to detect the mold temperature by the device. Sintering in vacuum was performed at 1100 °C [15] for 5, 10, 15, 20, and 30 min at 80 MPa and at 20 and 40 MPa for 20 min. A schematic illustration of the different cycles is shown in figure 2. It is noteworthy that in all cycles with temperatures up to 800 °C, constant pressure of 10 MPa was applied and, after 300 s, both pressure and temperature reached their peak simultaneously, and the heating rate was 50 °C min⁻¹.

2.3. Characterizations

Morphology and grain size of the spark plasma sintered MgO samples were investigated using a field emission scanning electron microscope (FESEM, VEGA/ TESCAN Mira). In order to analyze the obtained images, Digimizer software (Digimizer v4.1.1.0, MedCalc Software, Belgium) was used. Furthermore, particle size was calculated employing a coefficient of 1.56 [16]. Philips Xpert X-ray diffraction device with 30 mA working
current and 40 kV voltage was used (Cu Kα radiation $\lambda = 1.54059 \text{ Å}$). Fourier transform infrared (FTIR) spectra of the spark plasma sintered MgO bodies were measured in the range of 2–10 μm by an FTIR-8400S spectrometer. Finally, the sintered samples’ density was determined via the Archimedes method according to ASTM C373-88 standard using equation 1.

$$\rho = \frac{D}{M - S}$$  \hspace{1cm} (1)

where $D$ is the dry weight of the sample, $M$ is the saturation weight, and $S$ is the suspended weight of the samples in water.

3. Results and discussion

3.1. Raw material characterization

FESEM image of magnesia nanopowder after 15 h milling in ethanol medium is shown in figure 3. Powder particles do not have a specific morphology, and, in this respect, they are almost uniform. As can be seen in the related figures, the powder particles have an almost uniform distribution. As the particle size decreases, the adhesion force increases, which is related to gravity. Due to the predominance of gravitational force in smaller particles, they will have lower densities. This is true for powders with the same particle size distribution and equal amounts of pores [17]. The milled powder’s particle size distribution, which passed through a sieve with
230 mesh, was also obtained. As it is evident, the milled powder has an almost uniform distribution, and the average particle size ($d_{50}$) is about 98 nm, and the 50% cumulative particle size ($d_{50}$) is about 90 nm. The particle size distribution is in the range of 100 nm, which is a suitable distribution for use in the manufacturing of bodies through the sintering method.

### 3.2. Sintering time

Figure 4 shows the fracture surfaces of sintered magnesia specimens at 1100 °C and 80 MPa at different times. Figure 4(a) is the fracture surface of the sample sintered for 5 min. According to the obtained image, it is clear that the microstructure is almost uniform and that the formed necks have grown. The pores can be seen to have accumulated at the grain boundaries and are concentrated at almost multiple points where the grains meet, while the open pores can be seen in the images. Figure 4(b) shows the fracture surface of the sample sintered for 10 min with uniform distribution of grains. However, the porosities in the structure are visible. The fracture surface of some grains has an intragranular fracture mode which can be due to increased grain strength [18]. Comparing the two samples sintered for 5 and 10 min (figures 4(a) and (b)), it is obvious that as the sintering time increases, the pores become smaller, and the grains accumulate at the corners of the multiple junctions. With increasing sintering time to 15 min (figure 4(c)), the grain size has not changed significantly compared to 10 min. This is while the porosities are significantly closed. There are also signs of intragranular fracture at the whole surface, indicating the particles’ plastic deformation during the sintering process. Due to the sample’s porosity, the pressure on the aggregates intensifies, and the pressure exceeds the yield stress of magnesia. Magnesia has deformed plastic. As a result, plastic deformation in grain boundaries is more and has increased the grain strength. Figure 4(d) shows the fracture surface of the sintered sample in 20 min. Obviously, the grain size has increased along the sintering time, and almost all the pores have been removed. During the sintering process, by moving the pores to multiple points between the grains and trapping them, especially in processes such as SPS, which use pressure in the process to compact the structure, the pores are removed, and density is increased. Increasing the sintering time has also increased the rate of grain growth [18]. With further increase of the sintering time up to 30 min (figure 4(e)), the grain size did not increase significantly compared to the sintered sample in 20 min. The microstructure is almost uniform, and pores are present at the junctions of the grains. Also, the accumulation of pores in the grains has increased, and they have joined together so as to form larger pores. Due to the high energy level of grain, increased grain boundary mobility and the joining of very small pores can occur at higher temperatures. Density reduction with increasing sintering temperature has also been reported in some other researches [19]. In this sample, the lamination fracture mode due to plastic deformation is seen.

Figure 5 also shows a macroscopic image of the sample sintered at different times. As can be seen, the sample sintered for 5 min has no visual transparency. This condition can be due to compaction and reduced porosity during sintering. As the density increases and the porosity decreases, it increases the light transmission [20]. As can be seen with increasing time, the visual transparency increased to a specific time, and then the transparency decreased. Figure 6 shows the transparency in the infrared region of sintered samples at different times at 80 MPa after polishing. It was observed that with increasing sintering time up to 20 min, the infrared wave transmission rate increased and reached a value of about 65%. Moreover, further increase in sintering time resulted in reduced transparency. Generally, large absorption peaks can be seen in the wavelengths of 2.73 to about 3 μm and also in the range of 6 to 6.24 μm, which belong to the hydroxyl group adsorbed on the surface or structural water in the brucite formed on the surface of the bodies [21]. Also, the reduction in the transparency rate at wavelengths about 7 μm can be due to the presence of structural water in the brucite created on the samples’ surface. This increase in transparency can be related to the density and porosity of the samples.

Figure 7(a) shows the relative density of sintered magnesia samples at 1100 °C at various times of 5 to 30 min, along with their grain size at 80 MPa. As can be observed, the grain size initially grew with a gentle slope at 5 to 15 min intervals. At 15 to 20 min, the growth rate increased and continued to grow with a lower slope. Regarding the samples’ density, a sudden increase in density occurred up to 5 min, after which the increase in density was gradual and very small. However, there was no significant increase in density after 15 min, and only grain size growth occurred. The final density at 20 and 30 min was 98.50 and 98.29% of the theoretical density, respectively. As can be seen, the density of the samples reduces after 20 min. It was reported that the coalescence of small pores in the grain boundaries might be the reason for this reduction in the final stage of sintering [19, 22]. At 15 min, the density was 97.30% of the theoretical density. In general, in the production of transparent bodies, there is a tendency to produce parts with a finer structure. The finer the microstructure, the more granularity there is, increasing the strength and distributing the defects along the boundaries and would be less than a barrier to the light passage, especially at smaller wavelengths [20, 23].

In order to further investigate the process of magnesia using spark plasma sintering, densification rate at different times versus time was plotted in figure 7(b). It was observed that, in the early times, the density rate was
very high and decreased over time. It is noteworthy that the density rate dropped rapidly up to 10 min, but after that, the density rate decrease was very small. This indicated the difference between the mechanism of densification and grain growth in the initial times and the times above 15 min. To investigate this issue, equation 2 [13] and the logarithmic plot of grain growth versus time, a coefficient can be found and used, representing the sintering mechanism.

\[
\ln \left( D^n - D_0^n \right) = \ln(K_0t) - Q/RT
\]

where \( D \) is the grain size, \( D_0 \) is the initial grain size, \( n \) is the grain growth capacity depending on the grain growth mechanism, \( R \) is the gas constant, \( T \) is the absolute temperature, \( K_0 \) is the constant, and \( t \) is the time. By drawing a

Figure 4. FESEM images of the fracture surface of sintered magnesia at 80 MPa for: (a) 5, (b) 10, (c) 15, (d) 20 and (e) 30 min.
diagram in figure 8, in this figure, two fitted lines with different slopes were obtained, from the slope of which the amount of grain growth power was obtained. This value was about 1.25 for up to 15 min and about 3 for 15 to 30 min. Number 3 indicates the process of diffusion through lattice diffusion [12], while with regard to the number obtained in lower times, nothing has so far been reported. This number indicates a non-diffusional process that could be plastic deformation. Plastic deformation has been mentioned in many sources as an effective magnesia sintering mechanism [9, 24]. This can be due to the fact that as the temperature increases, the resistance to plastic deformation, i.e., the yield stress, decreases. The relationships obtained by Artes et al [25] were used to investigate the temperature at which magnesia underwent plastic deformation. Figure 9 shows the critical pressure at different densities at 1100 °C as well as the effective pressure at different densities. It can be observed that after the density of 97% at a pressure of 80 MPa, the sintered sample leaves the plastic deformation range. By matching this density with the data obtained from density measurements, it can be said that there has been no plastic deformation sample since 15 min. The coefficients obtained in the figure also confirm that plastic deformation has been the main deformation mechanism until 15 min when the density has reached 97%. The mechanism has changed to diffusional processes with a slow speed.

3.3. Sintering pressure
Figure 10(a) shows the microstructure of the sample sintered at a pressure of 40 MPa. As can be seen, the microstructure is full of porosity and cavities between the grains, and a large amount of porosity is observed, indicating the lack of successful sintering of magnesia at this pressure. The grain sizes are almost uniform, and the cavities are evenly distributed between the grains. Magnesia seeds are almost in the form of 14 spatial facets. In some parts of this sample, intragranular fractures are observed, which are much less observed than samples with higher pressure (sintered sample at a pressure of 60 MPa). This can be due to the lower pressure applied and the reduction of stress on the grains, especially the grain boundaries. But even at low pressures, when the sample density is not high, the stress applied to the grain joints increases and affected some of the grains. Figure 10(b) shows the microstructure of the sintered sample’s refracted surface at a pressure of 60 MPa. As can be seen, similar to the sintered sample at 40 MPa, much porosity is observed in the sample, and the porosity is distributed among the grains, but the volume fraction of the porosity is less than the sample of 60 MPa. In this sample, 14-sided shapes and intragranular fracture in the grain are also visible. However, in this sample, the grain size is
Figure 7. (a) Grain size and relative density of sintered magnesia at different times and (b) Density rate versus sintering time at 80 MPa.

Figure 8. Ln diagram of grain size at different times for magnesia sintering at 80 MPa.
slightly larger than the sintered sample grains at a pressure of 60 MPa. These larger grains were probably due to lower sample pressure and the grain’s freer growth under lower pressure.

In examining magnesia sintering with different pressures of 40, 60, and 80 MPa, its density and grain size have been obtained, which is shown in Figure 11. In the grain size distribution diagram of the 60 MPa sample in Figure 10(b), it can be seen that the grain size is in the range of 3 to 6.5 μm. The average particle size is about 3.6 μm, and their cumulative 50% size is about 3.5 μm. However, according to the image obtained from this sample and its grain size and comparison with the sintered sample at 80 MPa, it can be seen that the grain growth is very slow, and it can be proposed that the main mechanism for the sintering and grain growth in these samples is plastic deformation. The grain size distribution of a sample of 40 MPa is 2.5 to 6 μm. The average particle size is about 3.9 micrometers, and the cumulative size of 50% is about 4 μm. This indicates that increasing the pressure can, to some extent, prevent grain growth and reduce grain growth. However, if the pressure increases to more than the yield stress, it can cause sintering and grain growth by changing the misalignment and plastic deformation [24]. It was observed that the obtained density increases with increasing the pressure. But at pressures of 40 and 60 MPa, densities of 93.35% and 95.8% were obtained, respectively. As mentioned earlier, the grain size obtained for the 60 MPa pressure was slightly less than the 40 MPa pressure, which was probably
related to the higher pressure, and some measurement errors can also be considered. The density rate in terms of pressure was investigated using equation \(3\) [14], and the results are shown in figure 11(b).

\[
\frac{1}{\rho} \frac{d\rho}{dt} = \frac{d\varepsilon}{dt} = AD\mu b / kT \left( \frac{b}{G} \right)^m \left( \frac{gPa}{\mu} \right)^n
\]  

Figure 11. (a) Grain size and relative density of sintered magnesia in 20 min at different pressures and (b) Densification rate versus pressure for sintered magnesia in 20 min.

where \(\rho\) is the relative density, \(A\) is the numerical constant, \(b\) is the Burgers vector, \(\mu\) is the shear modulus, \(G\) is the grain size, \(D\) is the diffusion coefficient, \(k\) is the Boltzmann constant, \(T\) is the temperature, and \(m\) and \(n\) are the powers dependent on the particle deformation mechanism. According to the obtained coefficient, which is about 1, it can be said that sintering has been done at 1100 °C, and densification was governed by grain boundary diffusional mechanism.

4. Conclusions

In this study, the sintering of magnesia nanopowder was investigated using spark plasma sintering as well as the effect of time and pressure on microstructure, physical properties, and infrared transparency. The most important results can be presented as follows:

Examination of grain growth and density of sintered samples at different times revealed that firstly the density increase occurred quickly and, after 5 min, the density increased slowly. It was observed that the density rate decreased rapidly for up to 10 min and then the density rate slowly decreased. A closer study of grain growth rate showed that, in the early stages of sintering, the process was done through a non-diffusional process and, in the final 15 min the process, it was done through lattice diffusion. Examination of the yield stress of the sintered sample at 1100 °C and its conformity with the results of the theoretical density showed that it underwent plastic deformation for up to 15 min and then it left the yield stress limit after 15 min. Pressure analysis showed that
with decreasing the sintering pressure, the density of samples decreased. Therefore, the main mechanism in magnesia sintering was plastic deformation. Examination of the compaction rate versus pressure indicated that the diffusion was carried out through grain boundaries in sintering at low pressures.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Conflicts of interest

The authors declare that they have no competing interests.

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