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Optimization of sintering of Mg_2SiO_4 nanopowder prepared by polyacrylamide gel method

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Response surface methodology (RSM) was used to optimize the densification of Mg_2SiO_4 nanopowder prepared by Polyacrylamide gel method. The effects of monomer to salt molar ratio, calcination temperature and applied pressure on the densification of powders were investigated. The optimum operating conditions for densification were found to be monomer to salt molar ratio of 2.2, applied pressure of 563 MPa and calcination temperature of 784 °C. The obtained density under the optimum conditions determined by RSM was 98.1%.

Key words: Nanopowders, Densification, Chemical synthesis, Response Surface Methodology.

Introduction

Forsterite (Mg_2SiO_4) is an intermediate phase in the MgO-SiO_2 system. Forsterite is a member of the olivine family and it has a relatively high melting point of 1890 °C. It was used as a refractory material with high temperature applications [1]. In addition it has low thermal expansion, good chemical stability, and low electrical conductivity [2, 3].

Structure and properties of the sintered ceramics are strongly dependent on the homogeneity, particle size distribution, and phase purity of the initial powder. It is clear that the quality of ceramic powder changes with the preparation methods [4-6]. Several different methods have been employed to produce forsterite powder. These methods include solid state [7, 8], sol-gel processing [9], mechanical milling [10] and so on. Among chemical methods, polyacrylamide gel process is a fast, cheap, reproducible and easily scaled up chemical route for obtaining fine powders [11, 12]. In this work forsterite nanopowder was prepared by polyacrylamide gel method. After production of the powder via this method, it is important to determine the optimum conditions to have the best densification. The traditional optimization methods, which usually examine a single factor at a time, used for optimization of multi-variable systems are not only time consuming but also may result in wrong conclusions. In addition, it is not possible to detect the frequent interactions between two or more factors [13]. Recently, response surface methodology (RSM) has been widely used for the processes optimization and prediction of the interaction between process variables. Application of RSM method on optimization of sintering of forsterite nanopowder has not reported in literature. Thus, this work aimed to investigate and optimize the sintering of forsterite nanopowder prepared by a polyacrylamide gel method using the RSM.

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Experimental Procedure

Materials and methods

The Mg_2SiO_4 nanopowders were prepared using polyacrylamide gel method. Magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$, Merck) and tetra ethyl ortho-silicate (TEOS, Merck) were used as starting precursors. The TEOS was dissolved in 1 M HNO_3 and reflux for 6 h. $Mg(NO_3)_2 \cdot 6H_2O$ were added to this solution and stirred for 2 h at room temperature. Acrylamide (AM) and N,N'-methylene bis acrylamide (MBAM) monomers as polymerization agents were added in the prepared solution. The free-radical crosslinking copolymerization of AM and MBAM was initiated by adding N,N,N',N'-tetramethyl ethylene diamide (TEMED) and ammonium persulfate (APS) to the mixture. In this state, a transparent gel was rapidly obtained. The gel was dried at 80 °C for 48 h and calcined at different temperatures. In order to reduce the amount of agglomerates, the nanopowders were planetary milled for 1 h. The powders were pressed into compacts with different applied pressures. The compacts were then sintered in a tube furnace under air atmosphere at 1450 °C for 3 h with a heating rate of 6 °C/min.

Characterization

The crystalline structure of the powder was determined by X-ray diffraction using a Philips X-pert model with Cu Kα radiation. Thermogravimetric analyses (TG) were used with STA equipment (PL

Thermal Sciences STA 1500, U.K.). The microstructure of the powder was observed by transmission electron microscopy (TEM; CM200-Phillips, Netherlands). The densities of the sintered specimens were measured by the Archimedes method.

Design of experiments

Response surface methodology was used to estimate the relationship between a set of controllable experimental factors and observed results. The most common experimental design used in RSM is the Central Composite Design (CCD) which has equal predictability in all directions from the center [14]. According to CCD, the number of designed experiments obtained as

$$N = 2^K+2K+n_0$$

In this equation, k is the number of variable parameters and n_0 is the number of center points. Practically, 2^K and 2K are numbers of points that make up corners and centers of a cube, respectively. Based on CCD, three to five points are recommended for n_0, however, $n_0 = 3$ has been selected in this research. In this study, three chosen independent process variables and five levels ($\pm\alpha$, ± 1, 0) (where $\alpha = 2^{3/4} = 1.682$), were used to design the experiments. The processing variables involved in the study are shown in Table 1. "Design Expert" software (Trial Version 7.1, Stat-Ease Inc., Minneapolis, Minnesota, USA) was applied to analyze the densification process as well as to obtain optimum parameters data that are indicated in Table 2.

Table 1. Coded and actual levels of variables considered for design.

Factors	Levels				
	−1.682	−1	0	+1	+1.682
(A) Monomer to salt molar ratio	0.2	0.97	2.1	3.23	4
(B) Calcination temperature (°C)	200	362	600	837	1000
(C) Pressure of press (MPa)	100	282	550	817	1000

Results and Discussion

Fig. 1 shows X-ray diffraction patterns of the powders. As can be seen, the powder heat treated at 80 °C up to 600 °C seems to be amorphous. Forsterite was detected in the powder heat treated at 800 °C. By increasing the heat treatment temperature up to 900 °C the intensity of peaks increases which shows growing of the nanocrystallites.

Fig. 2 shows the TEM image of the nanopowders prepared by polyacrylamide gel method heat treated at 800 °C. The particles are in the range of 30-60 nm and irregular in shape. In the polyacrylamide gel process, gelation of the solution is achieved by the formation of an organic polymer network. This organic network-cage could cause an increase in the distance between cations [15]. Therefore, nanopowders with weak agglomerates

Table 2. Design layout using the "Design-Expert" software and experimental results.

Samples	Factors			Responses
	Monomer to salt molar ratio	Calcination temperature (°C)	Pressure of press (MPa)	Density (%)
S_1	−1	−1	−1	72.9
S_2	1	−1	−1	80.3
S_3	−1	1	−1	92
S_4	1	1	−1	94
S_5	−1	−1	1	74.4
S_6	1	−1	1	87.5
S_7	−1	1	1	93
S_8	1	1	1	96
S_9	−1.682	0	0	91.3
S_{10}	1.682	0	0	95.4
S_{11}	0	−1.682	0	77.1
S_{12}	0	1.682	0	94.1
S_{13}	0	0	−1.682	85.6
S_{14}	0	0	1.682	96.5
S_{15}	0	0	0	94.8
S_{16}	0	0	0	95.1
S_{17}	0	0	0	94.8

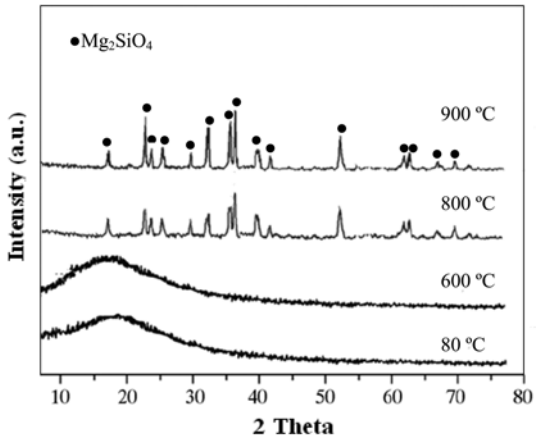

Fig. 1. The XRD patterns of samples heat treated at various temperatures for 3 h.

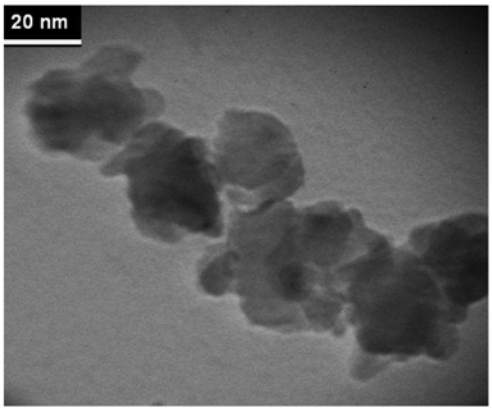

Fig. 2. TEM image of the powders heat treated at 800 ºC.

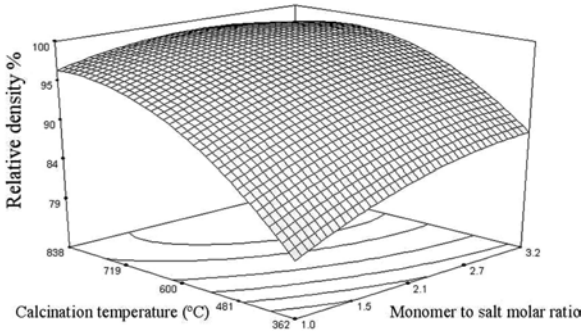

Fig. 3. 3D surface plot showing the effects of calcination temperature and monomer to salt molar ratio on density.

can be formed.

To investigate the interactive effects of two factors on the response value, three dimensional surface plots (3D plots) were drawn by considering two variables at a time while keeping another one at the central level. Fig. 3 shows the effects of calcination temperature and monomer to salt molar ratio on density. The density increased when the calcination temperature changed from 360 to 760 ºC and then it decreased. It may be due to removal of volatile components which create a lot of pores in the samples during the sintering. For

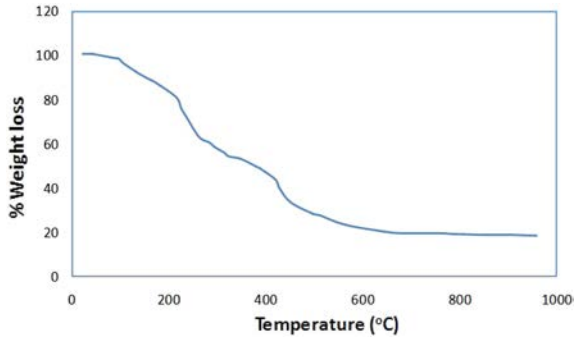

Fig. 4. TG curve of the dried gel.

better investigation, TG analysis was taken from the samples (Fig 4). The first weight loss between 30 and 170 ºC was attributed to the removal of physically adsorbed water. The second weight loss (between 200 and 700 ºC) was attributed to the decomposition of hydroxyl groups and polymeric network. The total weight loss was about 83% up to 700 ºC. As can be seen this huge weight loss can leave a lot of pores in the pressed samples and leads to an increase in the distance between the particles which may cause a reduction in the final density. Increasing the calcination temperature above this limit resulted in a decrease of the density, which may be due to the reduction of the specific surface area of the powders. By increasing monomer to salt molar ratio, the density increases and then decreases. The polyacrylamide gel method takes advantage of the polymerization of acrylamide, which is initiated by free radicals afforded by N,N,N',N'-tetramethyl ethylene diamide and ammonium persulfate. The polyacrylamide grows into a complex web of interconnected branches [15]. This polymeric network leads to an increasing in the distance between metal cations. Therefore weaker interactions among particles occur during synthesis, lead to a powder with smaller particle size and weaker agglomerates. It was found that dry pressing of nanopowders can cause a green body microstructure with two types of pores. The first one is micrometers pores between agglomerates and the other one is nanometric pores within the agglomerate itself [6]. During densification, nanometric pores shrink, but removal of the micrometers pores between agglomerates requires higher temperatures and often degrades densification. According to the above discussion it can be concluded that the powders with weaker and fewer agglomerates result in higher density after sintering. One way to reduce agglomeration is to use polymeric materials between the particles.

Fig. 5 shows the effects of applied pressure and calcination temperature on the density while the monomer to salt molar ratio kept at the central level. It can be seen that the density increased as applied pressure and calcination temperature increased and then decreased. The compaction mechanism of brittle

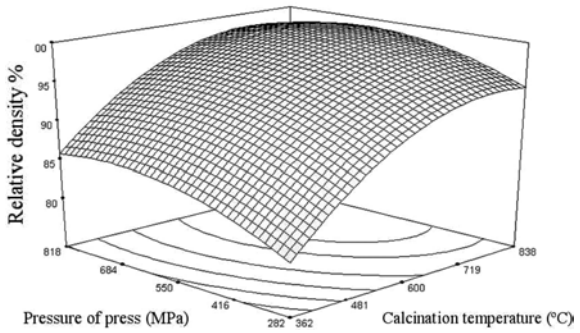

Fig. 5. 3D surface plot showing the effects of pressure of press and calcination temperature on density.

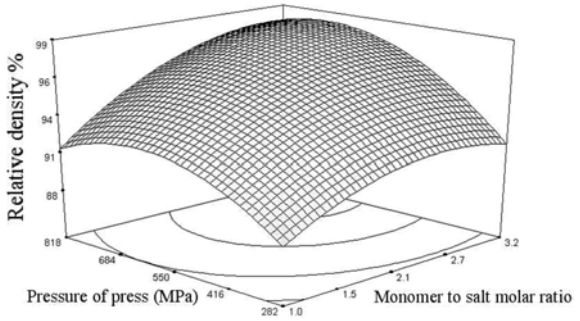

Fig. 6. 3D surface plot showing the effects of pressure of press and monomer to salt molar ratio on density.

powders in a rigid die is usually considered in three stages including; (I) sliding and rearrangement of the particles; (II) fragmentation of brittle solids and (III) elastic deformation of bulk compacted powders [16]. When the applied pressure increases, the movement of the particles and crushing of the agglomerates can cause an increase in the green density which results in higher final density. The samples calcined at low temperatures are sensitive to under- and over-pressing. The material crystallization and the elimination of water and volatile component from the samples may be responsible for these sensitivities. The densification curve of the powders calcined at 362 °C has a maximum in the region between 500 and 600 MPa. By increasing the calcination temperature, the optimal pressure region shifts to higher pressures. The sinterability of powders calcined above 700 °C has low pressure dependence at high pressures. The results show that under the experimental conditions examined, calcination temperature has a greater effect on density than the applied pressure.

Figure 6 shows the effects of pressure of press and monomer to salt molar ratio on density. The effect of applied pressure on density is similar to that in the Fig. 5. As can be seen, an increase in monomer to salt molar ratio up to 2 reduces the applied pressure for an equal density which is due to improving the quality of synthesized powders and green density. The density decreased with further increase of monomer to salt molar ratio. It may be due to removal of organic residuals which create porosity during sintering. Comprehensively considering the three process variables, with the help of regression equation, the maximum density of 98.4% could be obtained, and the independent variables were as follow: monomer to salt molar ratio 2.2, calcination temperature 712 °C and pressure of pressure 563 MPa. The density of sample under the optimum conditions was about 98.1%. This result confirmed the optimum conditions predicted by RSM method.

Conclusions

Nanosized forsterite was synthesized via a polyacrylamide gel method. Response surface methodology involving an experimental design was used to optimize the monomer to salt molar ratio, applied pressure and calcination temperature for densification of forsterite. The obtained results demonstrated the usefulness of response surface methodology in predicting of the synthesis parameters as well as the interactive effects of manipulating process variables. The optimum operating conditions determined were a monomer to salt molar ratio of 2.2, applied pressure of 563 MPa and calcination temperature of 712 °C.

Acknowledgments

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