Sintering of magnesia: effect of additives

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Abstract. Effect of different additives, namely Cr_2O_3 , Fe_2O_3 and TiO_2 , up to 2 wt% was studied on the sintering and microstructural developments of the chemically pure magnesia using the pressureless sintering technique between 1500 and 1600°C. Sintering was evaluated by per cent densification and microstructural developments were studied by electron microscopy and elemental distribution of the additives in the sintered products was also investigated for their distribution in the matrix. Cr_2O_3 and TiO_2 were found to deteriorate the densification associated with grain growth. Fe_2O_3 was found to improve the densification and well-compacted grain distribution was observed in the microstructure.

Keywords. Magnesia; additives; sintering; densification; microstructure.

1. Introduction

Densification/sintering of a material is of high interest for ceramists due to increased density values and associated strength at temperatures without the generation of a considerable amount of the liquid phase.¹ The term sintering, as used in ceramics, refers to the process by which an assembly of discrete particles is transformed into a single porous solid mass by the application of heat without liquefaction.² At the microscopic level, the driving forces for sintering in the capillary pressure are associated with surface curve where particles come into contact. The neck formation between particles has a saddle curvature characterized by two radius of curvature x , the diameter of the neck and γ , which is small and negative. The capillary pressure is $\Delta p = \gamma (1/\gamma + 1/x)$ and is negative (γ = surface energy). Summed over powder compact, the capillary pressure gives a modest net compressive pressure in sintering.³

In ceramics, magnesia is a valuable material, mostly useful as a refractory with a high resistivity against alkali metals and basic environments. Magnesia is important refractory material for cement rotary kilns, steel ladle, converters and furnaces, due to the higher softening temperature of MgO (2800°C) and also because of its chemical stability in a basic environment.⁴ However, they do have shortcomings such as lower thermal shock resistance as well as higher thermal conductivity, which limits their applications.¹ To improve corrosion, especially infiltration resistance, the effect of different additives, such as SiO_2 , Cr_2O_3 , Al_2O_3 , TiO_2 , MgCl_2 , WO_3 and ZrO_2 were studied since long.^{1,5–12} Even small additions (less than 1%) of other materials have a marked effect

on the grain growth, densification, and other properties.¹³ The method of preparation of magnesia¹⁴ was reported to be important for sintering and calcination of magnesium carbonate resulting in magnesia was found to be easily sintered at temperature as low as 1650°C. Very high relative density ($\sim 98.8\%$) of sintered magnesia was reported¹⁵ with restrained grain growth at 1740 K by using ultra-high heating rate (above 1700 K min⁻¹) under an applied pressure of up to 170 MPa. Grain growth of the nanocrystalline MgO was reported to be controlled by the mechanism of evaporation–condensation rather than surface diffusion. Applied pressure was reported¹⁶ to have a result of increasing densification while restraining grain growth, and the higher sintering temperature was reported to result in larger grain size as well as lower density. Pure magnesia with a relative density of 99.1% nanocrystalline ceramics was obtained at 1620 K and 170 MPa, and simultaneously grain growth was almost quietly restrained.

Literature shows the effect of various additives on densification of magnesia. For example, Weyl¹⁷ discussed the behaviour of foreign ions in a crystal lattice and Tacvorian¹⁸ studied the problem that arises due to the phase diagram and liquid phase formation from the macroscopic point of view. Nelson and Culter¹⁰ studied the effect of many additives in the range of 1–16%. Additions of Ti^{4+} , Al^{3+} , Cr^{3+} , Mn^{2+} and Fe^{3+} were found to be successful in decreasing the sintering temperature of magnesia due to non-stoichiometry of periclase caused by crystal lattice defects.^{19,20} The addition of ZrO_2 in MgO was reported²¹ to enhance the densification and the main reasons proposed were the conversion of monoclinic ZrO_2 to its cubic phase ZrO_2 . Also, excess ZrO_2 was reported to react with MgO to form $\text{Mg}_{0.13}\text{Zr}_{0.87}\text{O}_{1.87}$, which activated lattice and promoted the diffusion of ions during the sintering process. In addition, liquid phase sintering was also one of the main reasons for promoting the sintering of

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magnesia. Dense MgO was prepared by adding TiO₂ due to cation vacancy formation as follows:²²

A prominent adequate grain growth is observed due to the addition of TiO₂ on densification and at relatively low

temperatures <1500°C and TiO₂ content up to 5 wt%.¹² Even (0.5%) of TiO₂ is favourable to enhance the densification of magnesia even at 1300°C.¹¹ The addition of TiO₂, exceeding solid solubility limit, results in the intergranular and intragranular magnesium titanate (Mg₂TiO₄) formation, which promotes magnesia grain growth.^{20,23} The addition of TiO₂ was also reported²⁴ to decrease the activation energy of MgO grain growth, accelerated the growth rate of MgO grains, and markedly promoted the sintering of MgO, prepared from MgCl₂·6H₂O. The principal mechanism of TiO₂ promoting the sintering of MgO was that TiO₂ solubilized in MgO to form unequivalence substitutional solid solutions and cation vacancies that were favourable to cation diffusion.

Table 1. Ionic radius of various cations (pico-metre).^{26,27}

Mg ²⁺	Ti ⁴⁺	Fe ³⁺	Cr ³⁺
72	61	64.5	62

Figure 1. Particle size distribution of (a) MgO, (b) TiO₂, (c) Cr₂O₃ and (d) Fe₂O₃ particles.

Reduction in the size of the Cr_2O_3 additive was found to be more efficient and beneficial for densification of magnesia.²⁵ According to the phase analysis, higher dissolution of Cr_2O_3 in the $\text{MgO-Cr}_2\text{O}_3$ system was also responsible for the faster densification.²⁵ The addition of iron in magnesia also promotes low-temperature densification that appears to be proportional to the degree of solid solution and arising vacancies.⁷

In the present work, densification and microstructural characterization of magnesia is studied at pressureless sintering condition in the presence of different additives like Cr_2O_3 , Fe_2O_3 and TiO_2 . The additives were chosen to have very

close cationic radius compared to that of magnesium ion, which may help in faster solid solution formation. Table 1

Figure 2. Process flow diagram.

Figure 3. Variation in density and standard deviation of density values of pure MgO composition against temperature.

Figure 4. (a and b) Scanning electron photomicrograph of fractured surface of pure magnesia batch sintered at 1600°C (no additive).

Figure 5. Variation in density and standard deviation of density values of MgO containing TiO_2 additives.

provides the ionic radius of various cations used in the study.^{26,27}

2. Experimental

High-purity chemical grade magnesia (LobaChemie, India, AR grade, purity >99) was taken for the study. Different additives namely, TiO_2 , Cr_2O_3 and Fe_2O_3 (LobaChemie, India, Purity >97%) were used at 1 and 2 wt%. The particle size distributions of MgO as well as the additives, TiO_2 , Cr_2O_3 and Fe_2O_3 , are given in figure 1a–d, respectively. All

Figure 6. Scanning electron photomicrograph of the fractured surface of 2 wt% TiO_2 containing magnesia batch sintered at 1600°C .

the different batches were wet mixed in isopropanol medium using a magnetic stirrer and then dried at 110°C . After this, all the different batches were pressed into pellets of 20 mm diameter in a uni-axial hydraulic press at 100 MPa using 6% PVA solution (4 wt% concentration) as green binder. Pressed samples were then oven dried at 110°C and sintered at 1500, 1550 and 1600°C with soaking time of 2 h. Fired products were then characterized for densification and microstructural studies.

Densification studies were conducted by the conventional liquid displacement method using the Archimedes principle in vacuum process with xylene as a liquid medium. Per cent theoretical (relative) density was calculated as a ratio of measured bulk density value with the theoretical density value. Each individual data represented in the study is an average of five individual samples and the variations of the individual values are represented as the standard deviation of the density values in the same densification plots. Particle size distribution of the starting materials was carried out in computer-controlled particle size analyser, Malvern Master Sizer (UK). Microstructural studies and elemental distribution were investigated in a field-emission scanning electron microscope (FEI, USA, make) attached with EDXA facility (Oxford, UK). The flow diagram of the process is given in figure 2.

3. Result and discussion

Particle size distribution of high pure chemical grade magnesia and other additives are shown in figure 1. Magnesia

Figure 7. Elemental mapping photomicrograph of 2 wt% TiO_2 containing MgO sintered at 1600°C .

Figure 8. Variation in density and standard deviation of density values of MgO containing Cr₂O₃ additives.

Figure 9. Scanning electron photomicrograph of the fractured surface of 1 wt% Cr₂O₃ containing magnesia batch sintered at 1600°C.

is a high pure (>99%) fine powder with an average particle size of 450 nm (figure 1a). The additives used in the study are also highly pure and fine, having average particle size in the range of 300–600 nm, details of the particle size distribution are provided in figure 1b–d. Figure 3 shows the densification behaviour of pure magnesia containing no additive. Densification plot shows that the increase in temperature results in increased density values. Variations of the density values of individual samples were very less as indicated by the standard deviation of density values (figure 3). Microstructural photographs (figure 4) show well-compacted grains with little amount of porosity, mostly as intragranular nature. Well-compacted cubic and cuboid-shaped periclase (MgO) crystals are also observed at higher magnification, indicating a high purity nature of the samples.

Figure 10. Scanning electron photomicrograph of the fractured surface of 2 wt% Cr₂O₃ containing magnesia batch sintered at 1600°C.

3.1 Effect of TiO₂ addition

The addition of TiO₂ was found to deteriorate the densification behaviour of magnesia. Higher amount of additive deteriorates in greater extent (figure 5). The addition of TiO₂ might have reacted with magnesia to form intergranular magnesium titanate (Mg₂TiO₄) and assists the grain growth,^{18,20} which has resulted in lower densification. Variation in the density values of each compositions were also minimum as observed from the standard deviation values (figure 5). Microstructure of the 1600°C sintered product containing 2 wt% TiO₂ shows (figure 6) non-uniform grains distributed in a scattered manner, indicating considerable growth for few grains. A porous structure is observed with large extent of intragranular porosity. Less compact grains with porosities in between has resulted in poor densification of the batch. Elemental distribution of the components is shown in figure 7. It shows well-distributed presence of Ti ions in the matrix of sintered MgO and Ti is mainly present in between the MgO grains.

3.2 Effect of Cr₂O₃ addition

The addition of 1 wt% Cr₂O₃ has resulted in (figure 8) an increase in density values compared to no additive batch, but further addition was found to reduce the density values. Secondary phase, like magnesium chromate formation at the grain boundaries, might have helped in increasing the densification.¹⁹ Well, compact grains with uniform grain structure were observed for 1 wt% Cr₂O₃ containing batch sintered at 1600°C (figure 9). But an increase in Cr₂O₃ content to 2 wt% has resulted in some abnormal grain growth in the compacts, showing non-uniform size of grains and they are distributed in a scattered manner (figure 10). This non-uniform growth of some grains has negatively affected the density values. Standard deviation values (figure 5) of density of different compositions were low indicating minimum variation. Elemental distribution study shows (figure 11)

Figure 11. Elemental mapping photomicrograph of 2 wt% Cr_2O_3 containing MgO sintered at 1600°C .

Figure 12. Variation in density and standard deviation of density values of MgO containing Fe_2O_3 additives.

nearly uniform and well distribution of additive Cr ions all through the MgO matrix, and Cr ions are mainly present in between the MgO grains.

3.3 Effect of Fe_2O_3 addition

The addition of Fe_2O_3 up to 2 wt% in MgO showed a continuous increase in density values (figure 12). The formation of magnesium ferrite at the grain boundaries might have helped in increasing the sintering and densification of magnesia, as also observed by Chaudhuri and others.²² Dense and compact microstructure was observed for the 1600°C sintered 2 wt% Fe_2O_3 containing batch (figure 13). Little amount of intragranular porosity is also observed. In elemental distribution, Fe ion was found to be well distributed in the MgO

Figure 13. Scanning electron photomicrograph of the fractured surface of 2 wt% Fe_2O_3 containing magnesia batch sintered at 1600°C .

matrix, mainly in between the MgO grains (figure 14). Again the standard deviation values (figure 5) of density of different compositions were also found to be low.

4. Conclusion

Density of the pure magnesia was found to increase with the increase in the sintering temperature and a maximum density value of 3.4 g cm^{-3} , i.e., is near about 93.972% of theoretical density was obtained at 1600°C . Fe_2O_3 was found to improve the densification with very well compact and nearly uniform grain structure. TiO_2 was found to deteriorate densification

Figure 14. Elemental mapping photomicrograph of 2 wt% Fe_2O_3 containing MgO sintered at 1600°C .

due to grain growth. The addition of Cr_2O_3 at 1 wt% has improved densification but at higher amount, grain growth was observed with a reduced densification. Elemental distribution shows nearly uniform distribution of the additive ions all through the magnesia matrix. Again the standard deviation of density value was found to be very minimum (<0.03) which confirms minimum variation of the density values of individual samples in each composition.

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