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Sintering and microstructure of spinel–forsterite bodies

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Abstract

Spinel–forsterite phase mixtures formed by the addition of different proportions of alumina to forsterite grog's mixes, containing 10–15% alumina, showed a good compromise of high density, cold crushing strength and microstructure after firing at 1450 and 1500 °C. Forsterite was first prepared from Egyptian talc and calcined magnesite at 1400 °C/2 h. Forsterite shows good density but the microstructure contains cracks along the grain boundaries affecting the mechanical properties. The sintering and mechanical properties are improved through the addition of alumina. Alumina reacts with equimolar MgO from forsterite to form $MgAl_2O_4$ spinel on sintering at 1450 °C/2 h. Forsterite occurs in either patches or euhedral rhombic grains. Spinel exists in different crystal habits; either in spots within forsterite patches, prismatic euhedral crystals or on rims of forsterite grains. Considerable amount of low melting enstatite phase was formed on 20% alumina addition as a result of the decrease in the MgO/SiO_2 of forsterite after the formation of spinel. Enstatite improves the sintering through enhancing the formation of glassy phase.

Keywords: D. Spinel; Spinel–forsterite; Alumina–forsterite; Forsterite; Enstatite

1. Introduction

Forsterite is a magnesium orthosilicate mineral with a high coefficient of thermal expansion and high melting point, 1910 °C. Forsterite is usually utilized in applications with high coefficient of thermal expansion. Typical applications are making substrates for high frequency electronics, ceramic–metal seals and high temperature bonding agent. In refractory fields, forsterite is considered as one of the most efficient materials for critical production stages of modern iron and steel industry, namely, steel making and casting or ladle metallurgy [1–5].

A wide scope for the development of forsterite ceramics was demonstrated over the last few decades to improve the physicomechanical properties, strength, dielectric constant, thermal expansion, thermal conductivity and mechanical performance. The properties are improved through addition of alumina, mullite, magnesium aluminate spinel and partially stabilized zirconia. Alumina–forsterite mixtures are the most preferred refractories that can be fired in an oxidizing atmosphere and withstand high temperature mechanical stress and holding time [6–8]. Forsterite together with high alumina refractory material is recommended for lining regenerator checkers without using a neutral chrome–magnesia layer [9]. The result is supported by the absence of contact interaction between high aluminosilicate and basic refractories at 1400–1500 °C.

The present work aims at the improvement of sintering and mechanical properties of forsterite through alumina addition. Alumina is expected to react with MgO resulting in MA spinel formation beside forsterite. The effect of spinel formation on the mechanical strength, phase composition and microstructure will be assessed.

2. Materials and methods

2.1. Raw materials

Fine Egyptian raw materials, namely, talc and calcined magnesite (<63 μm) with reactive alumina (Aldrich) were used to prepare spinel–forsterite phase mixtures. The chemical analysis of talc is given in Table 1.

2.2. Preparation of forsterite bodies

The stoichiometric composition of forsterite was satisfied using talc and calcined magnesite mixture. The mixture was carefully mixed in a ball mill for 1 h. Pellets

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of 1 cm diameter and 1 cm height were processed by uniaxial pressing at 100 MPa using 3% glycerin as a binder and then fired at 1400 °C/2 h at a rate of 5 °C/min. Phase composition of different samples was investigated using XRD diffractometer type Philips 1710 with Cu-target and Ni-filter.

2.3. Spinel–forsterite batches

Forsterite grog was prepared by crushing samples sintered at 1400 °C to less than 500 μm. Reactive alumina powder less than 100 μm was added to forsterite grog in different proportions in order to develop spinel–forsterite phase mixture. The compositions of the different mixes are demonstrated in Table 2. After mixing well, batches were uniaxially pressed at 100 MPa into 1cm diameter and 1 cm high pellets using 2% glycerin binder. Samples were sintered at different firing temperatures: 1450, 1500 and 1550 °C/2 h at a rate 5 °C/min.

2.4. Characterization

The phase composition of the sintered samples was investigated using XRD technique. Bulk density and apparent porosity of the sintered samples were determined using ASTM C-20–74. Cold crushing strength was tested according to ASTM C-773–87. According to the results of sintering and mechanical properties, selected samples were etched using 10% HF for 20 s and followed by washing with distilled water. The microstructure of the etched samples was investigated using SEM type JSM 6400 operating at 25 kV.

3. Results

The XRD pattern in Fig. 1 displayed the formation of forsterite on firing at 1400 °C/1 h. All the peaks characterizing forsterite phase are detected. No peaks characterizing any other phase are detected. The result indicates complete interaction of MgO and talc at 1400 °C/1 h to form stoichiometric forsterite.

The phase compositions of the different mixes fired at 1450 °C/2 h are shown in Fig. 2. The peaks characterizing MA-spinel ($MgAl_2O_4$) are observed beside forsterite phase in all mixes. Alumina reacts with equimolar proportion of MgO from forsterite lattice through ion diffusion resulting in the decreasing of MgO/SiO_2 ratio (M/S). The decrease in M/S ratio leads to the formation of little amount of enstatite at the expense of forsterite. On increasing the content of alumina, the amount of spinel and enstatite increases. Little content of glassy phase exists as a result of the low impurities in the starting materials. No other phases are detected at 1500 and 1550 °C. The maturity of the processed ceramic bodies could be 1450 °C.

The results of bulk density for samples fired at different temperatures are shown in Fig. 3B. The density values for sintered samples increases with the increase in the content of alumina and /or the increase in temperature as a result of the formation of spinel phase. Density displays the same values for samples F_1, F_2 and F_3 sintered at 1500 and 1550 °C/2 h. Sample F_4 shows a remarkable increase at 1550 °C/2 h as a result to the formation of the low melting enstatite together with spinel that enhances the sintering. The results of apparent porosity are shown in Fig. 3A. The values of apparent porosity showed a sharp decrease on addition of 5% alumina. The apparent porosity is kept the same for sample F_2 and F_3 on firing at temperature 1500 °C or higher. The glassy phase fill in spaces among the recorded phases leading to dense matrix. No cracks are visible in the matrix [10].

The results of cold crushing strength for different mixes are shown in Fig. 4. The values of crushing strength for sintered samples increase in the content of alumina and/or the increase in temperature as a result of the formation of spinel phase. Crushing strength displays good values for samples F_2 and F_3 sintered at 1500 °C.

Table 1
Chemical analysis of talc grade 2

Oxides	SiO_2	MgO	Al_2O_3	CaO	Fe_2O_3	Na_2O	K_2O	L.O.I.
Wt.%	62.70	30.94	0.36	0.54	0.19	0.10	0.04	4.81

Table 2
Batch composition of the different mixes

	Mixes				
	F	F_1	F_2	F_3	F_4
Forsterite wt.%	100	95	90	85	80
Alumina wt.%	0	5	10	15	20

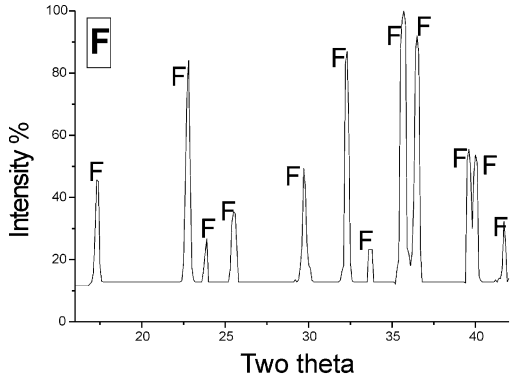

Fig. 1. XRD of forsterite sintered at 1400 °C/2 h.

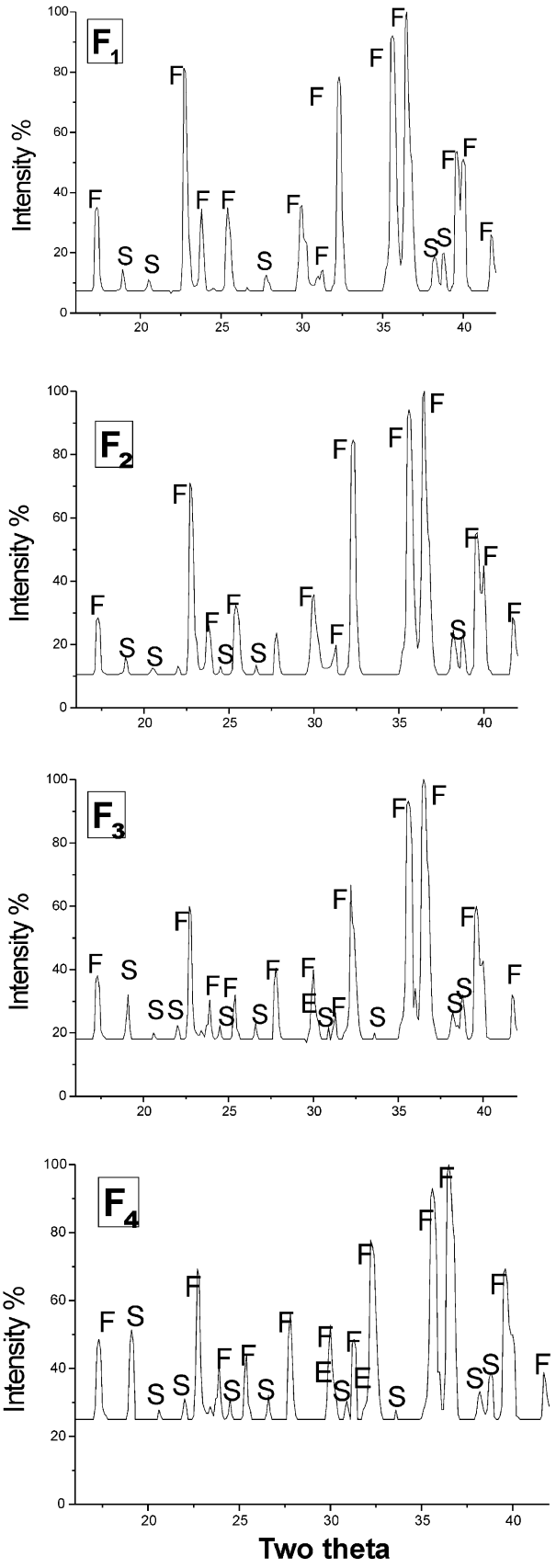

Fig. 2. XRD of different samples sintered at 1450 °C/2 h. F, forsterite; S, spinel; E, enstatite.

Higher temperature did not display a remarkable change. A remarkable increase in crushing strength at 1500 is due to the formation of the low melting enstatite. Forsterite, spinel and enstatite crystals interlocked together to form a dense body with little pores incorporated in the glassy matrix without cracks [11,12].

Ceramic and refractory properties are expected to increase with the development of spinel together with

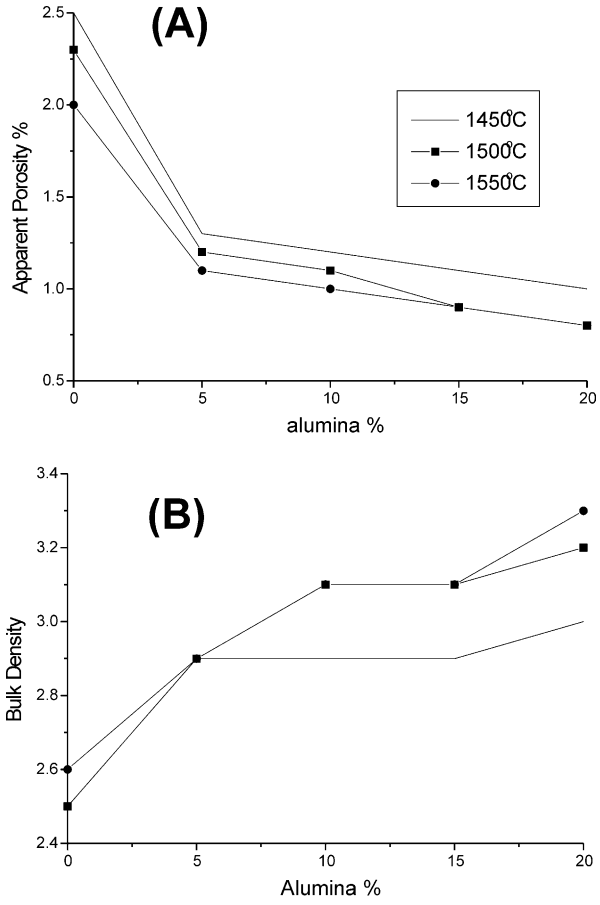

Fig. 3. Effect of alumina % on the densification properties: (A) apparent porosity; (B) bulk density.

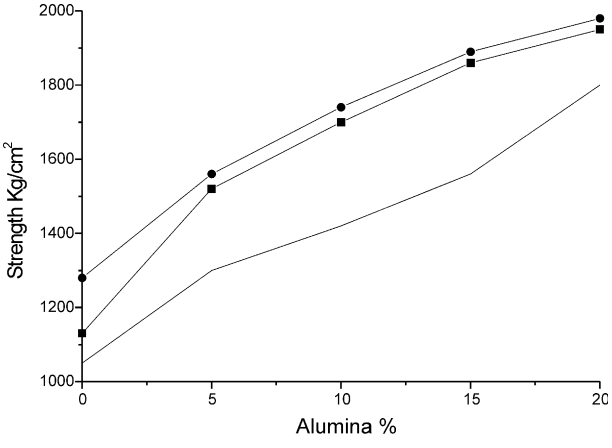

Fig. 4. Effect of alumina content on cold crushing strength.

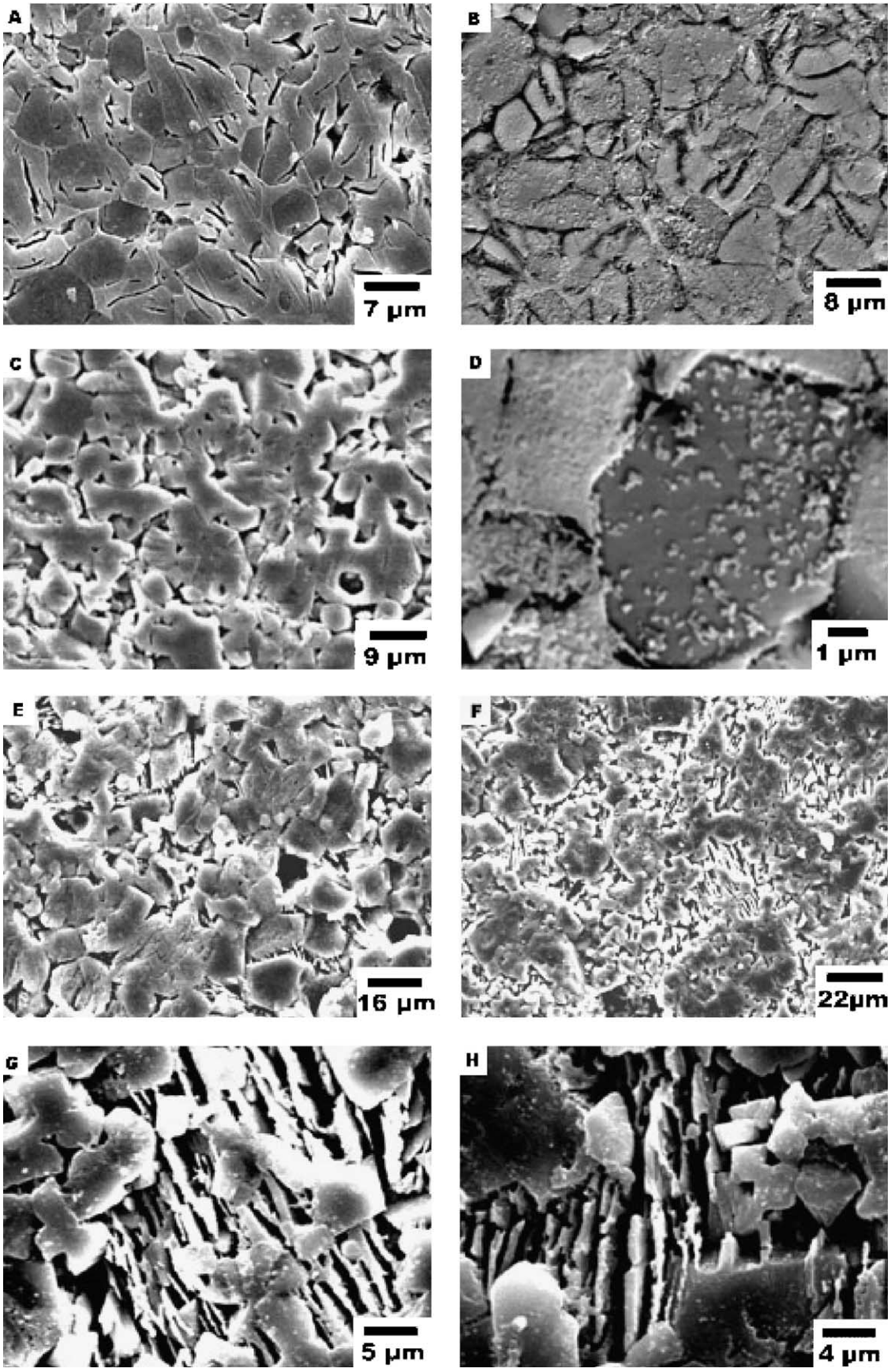

Fig. 5. SEM of the different mixes: (A, B) mix F; (C, D) mix F_2; (E–H) F_4.

the forsterite in the glassy matrix. MA- spinel is characterized by low coefficient of thermal expansion leading to the improvement of the thermal shock resistance. As the amount of alumina content increase, MA-spinel amount increases resulting in raising the temperature of application. On the other hand, the amount of low melting enstatite increases with the increase in the amount of spinel. Over the full range of alumina added, the amount of low melting enstatite is still not very high to deteriorate the refractory properties. A good compromise of sintering properties, phase composition, mechanical and refractory properties and microstructural characteristics are achieved by samples containing 10–15% alumina.

The microstructural parameters are the most controlling factors for the different ceramic and refractory properties. The results of microstructure are demonstrated in Fig. 5. Forsterite patches with grain size 10–30 μm are shown in sample F fired at 1500 °C as shown in Fig. 5A and B. Cracks with sharp edged pores are present along boundaries. Other euhedral rhombic shape grains with about 8μm size are present with patches The addition of 10% alumina results in the formation of spinel with low thermal expansion relative to forsterite. Spinel is distributed in different forms either in spots within forsterite patches, small grains with about 1–2 μm in grain boundary intersection and on the rims of forsterite patches as shown in Fig. 5C and D. On the increase of alumina up to 20%, spinel in prismatic forms increases connecting the forsterite patches as shown in Fig. 5E and F. Euhedral spinel grains are demonstrated in Fig. 5 G and H.

4. Conclusion

1. Well-sintered forsterite with good mechanical properties was prepared using Egyptian talc and calcined magnesite on firing at 1400 °C.
2. $MgAl_2O_4$ spinel phase was formed by the reaction of the added alumina with equimolar forsterite MgO through diffusion.
3. Spinel exists either in spots within forsterite, on the rims of forsterite or prismatic crystals connecting the boundaries of forsterite patches.
4. The formation of spinel strongly improves bulk density and cold crushing strength.
5. Low melting enstatite phase was formed as a result of the decrease in the MgO/SiO_2 of forsterite after the formation of spinel.
6. A good compromise of phase composition, bulk density, and cold crushing strength together with the good microstructure is achieved through the addition of 10–15% alumina.
7. Mixes containing higher than 15% alumina leads to formation of undesirable content of low melting enstatite that may deteriorate the mechanical and refractory properties.

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