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Sintering of magnesia refractories through the formation of periclase–forsterite–spinel phases

A.G.M. Othman *, N.M. Khalil

Ceramics Department, National Research Centre, Dokki, Cairo, Egypt

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Abstract

Effect of calcined kaolin additions on sinterability of dead-burned magnesia was studied through additions of Egyptian kaolin. Five batches containing powders of 100/0, 90/10, 80/20, 70/30 and 60/40 magnesia/kaolin, respectively, were mixed, dried and fired up to 1550 °C for 4 h. Their physical (bulk density and apparent porosity), mechanical (cold crushing strength) as well as refractory (thermal shock resistance and refractoriness under load) properties were tested according to the International Standard Specifications. The phase compositions of the fired batches were investigated using X-ray diffraction as well as scanning electron microscope to illustrate the effect of the different developed phases on the above properties compared with the main magnesia source itself. Generally, samples containing 10–20 wt.% kaolin are characterized by their high sintering, mechanical and refractory properties, so they are recommended for use as a lining for different parts of steel furnaces as well as heating zone of cement rotary kilns. Samples containing 30–40 wt.% kaolin with lower refractory properties can be used in the heat exchangers or as kiln furniture in ceramic industries.

Keywords: A. Sintering; D. Magnesia; D. Spinel; E. Refractory; Kaolin; Forsterite

1. Introduction

Magnesia is one of the widely used refractory materials for lining of steel and other industrial metallurgical furnaces. It is characterized by high refractoriness and good resistance to basic slags [1,2]. According to the high cost of magnesia and/or other magnesia refractory products as spinel and MgO–C, it is important to add suitable proportions of some other low cost materials as kaolin, talc, serpentine, . . ., etc., in order to produce sintered or chemically-bonded magnesia bricks without change its high efficiency and refractory properties. The addition of such materials enhances the formation of magnesium silicate phases as forsterite which contributes and enhances the sintering process of magnesia bodies. Also, forsterite is characterized with lower expansion, lower thermal conductivity, better volume stability as well as higher resistance to high-iron slags than magnesia. Beside forsterite, spinel is formed which leads to further enhancement in the refractoriness as well as slag and spalling resistance of magnesia bodies. Some research works were carried out in this direction to produce sintered magnesia by forming magnesia–forsterite–spinel bodies. Cunha-Duncan et al. [3,4] used sillimanite, kyanite and andalusite in addition to magnesia to produce sintered forsterite–spinel aggregates with fine microstructure by firing up to 1700 °C. Visloguzona et al. [5] and also Sergienko et al. [6] deduced that combination of periclase and forsterite refractories is useful in metallurgical units. The replacement of periclase nozzle by forsterite leads to an improvement in conditions of casting and less clogging of the nozzles. Khorashavin et al. [7] prepared fused forsterite–periclase bodies with high slag resistance by smelting dunite with addition of magnesite, brucite or sintered periclase. Petric [8] examined the forsterite and spinel formation reactions in the process of the isothermal sintering of magnesia obtained from sea-water. Also, they introduced some additives in order to determine the forsterite and spinel

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* Corresponding author.
E-mail address: agmothman@yahoo.com (A.G.M. Othman).

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formation conditions. Pereplitsyn et al. [9] produces forsterite–spinel bodies from carbon–ferrochrome slags and added up to 9 wt.% MgO to enhance the refractoriness of the product. Generally, these bodies can be used in furnace roofs, ceramic kilns as kiln furniture, glass furnaces (especially ports and regenerators), rotary kilns of cement industry and kiln for calcinations of lime, dolomite and magnesite.

The aim of this work is to prepare sintered periclase–forsterite–spinel refractory products with high refractory quality. This is reached by adding Egyptian calcined kaolin in proportions up to 40 wt.% to dead burned magnesite and study the sintering, mechanical and refractory properties of the prepared bodies and correlating them with their phase compositions and microstructure.

2. Materials and experimentals

2.1. Materials

Calcined kaolin from Teah area, Sinai, Egypt and Turkish dead burned magnesia were used as starting materials. They have been crushed, then finely ground in an alumina ball mill to pass completely through 70 μm sieve. Chemical analysis of these materials, determined with XRF method, is given in Table 1.

2.2. Experimentals

Five batches containing powders of 100/0, 90/10, 80/20, 70/30 and 60/40 magnesia/kaolin, respectively, were well mixed, then formed into briquettes using a starch solution as a binder. After drying for 24 h at 110 °C, the samples were subjected to firing up to 1500 °C for 3 h soaking time. The fired samples were investigated through their phase compositions using X-ray diffraction technique. The Philips PW 1710 diffractometer using Ni-filtered Cu radiation operating at 30 mA and 40 kV was used. Different physical (bulk density and apparent porosity), mechanical (cold crushing strength) as well as refractory (thermal shock resistance, and refractoriness under load) properties were tested according to the International Standard Specification [10]. The microstructure of some selected samples was investigated using a Philips XL30 scanning electron microscope. The surfaces of dense samples were gradually polished using subsequent grades of SiC papers and diamond pastes. The polished surfaces were then cleaned under water by ultrasonic waves before coating under vacuum with a thin layer of gold for SEM investigation.

Table 1
Chemical analysis of the starting materials

Oxide	Calcined kaolin (wt.%)	Dead burnt magnesia (wt.%)
SiO_2	55.55	1.65
Fe_2O_3	1.26	0.86
Al_2O_3	40.27	0.36
TiO_2	2.58	0.01
CaO	0.22	2.30
MgO	0.11	94.81

3. Results and discussion

Table 2 shows the phase composition of the samples fired up to 1550 °C and soaking for 3 h as calculated from their chemical compositions [11]. It will be seen that, samples containing 10–40 wt.% kaolin exhibit lower calcia/silica (C/S) molar ratio (<0.5) that means they lye in the field of monticellite (CMS) and forsterite (M_2S) as silicate phases. The percentage of CMS decreases gradually, while, the amount of M_2S increases sharply on increasing the content of kaolin added to magnesia. Sample M1 is composed mainly of periclase mineral (≈94%) in addition to some low melting silicate phases as merwenite (C_3MS_2), dicalcium silicate (C_2S) and M_2S beside very low contents of magnesium aluminate spinel (MA) and magnesium ferrite (MF) solid solution according to C/S; 1.49 molar ratio. With kaolin additions, most of periclase reacted with Al_2O_3 to form spinel in addition to forsterite mineral. The amounts of spinel and forsterite increases from M1 up to M5 at the expense of MgO. The results of calculated phase compositions are in a good agreement with those of XRD patterns of the fired samples shown in Fig. 1 which illustrates the phase compositions of the fired samples. The main phases detected are periclase, spinel, monticellite and forsterite. The number and intensity of the peak lines of CMS decreases from M2 to M5 on contrast to forsterite which shows increases on its intensity and lines from M1 to M5 especially in M4 and M5 samples which contains 38 and 50% forsterite as calculated in Table 2. Most of periclase reacted with Al_2O_3 to form MA phase. This phase increases from M2 and reaches its maximum value at M5 (23%) with sharp detected lines. On the other hand, periclase was detected in M1 as a major phase with few lines of silicate phases as C_3MS_2 which reflects the purity of this sample.

According to the above results, the study was extended to discuss the role of C/S on sintering, refractory and mechanical properties of the fired samples. Figs. 2 and 3 exhibit the effect of C/S molar ratio on densification parameters as bulk density (B.D.) and apparent porosity (A.P.) as well as mechanical properties as cold crushing strength (CCS).

Table 2
Phase compositions of the fired mixes

Sample	Calculated phase composition (wt.%)								
	C/S ratio	C_3MS_2	C_2S	CMS	M_2S	MF	MT	MA	M
M1	1.49	2.69	1.41	–	0.41	1.0	–	0.57	93.88
M2	0.32	–	–	5.82	11.23	1.12	0.41	6.05	75.37
M3	0.16	–	–	5.24	24.30	1.18	0.79	11.62	86.87
M4	0.07	–	–	3.40	38.55	1.20	1.15	17.17	38.00
M5	0.067	–	–	4.60	50.51	1.20	1.55	22.72	19.87

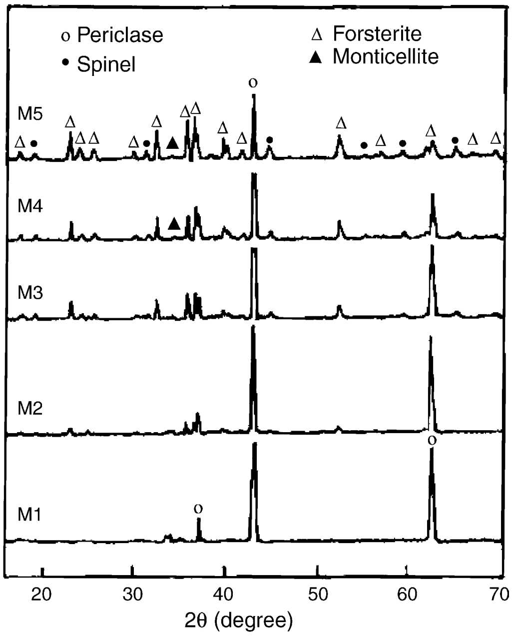

Fig. 1. XRD patterns of the fired samples.

As shown in Fig. 2, on increasing the amount of added kaolin from M2 to M5, the C/S decreases and the value of B.D. and CCS increases up to M3 and then decreases from M4 to M5 with decreasing of A.P. from M1 to M3 and increasing from M4 to M5.When C/S molar ratio decreases gradually from M1 to M5 the amount of M_2S increases at the expense of CMS leading to increasing the amount of liquid-phase content which contributes on the sintering process up to M3. On the other hand, increasing the amount of liquid-phase deteriorates the B.D. and increasing A.P. sharply as illustrated in Fig. 2 according to the bloating which takes place by the liquid-phase on the surface as well as in the bulk of the fired samples leading also to a decrease in the value of CCS for M4 and M5 (Fig. 3) on contrast to samples M1 to M3 which exhibits high cold crushing strength.

Table 3 shows the refractory properties of the samples fired up to 1550 °C/2 h as refractoriness under load (RUL) and thermal shock resistance (TSR). All samples exhibit beginning of subsidence ranging from 1510 °C (in the case of M1) up to 1410 °C (in sample M5). The value of RUL decreases gradually with decreasing C/S molar ratio in which the amount of liquid-phase developed on firing these samples up to 1550 °C increases according the formation of CMS and M_2S phases. These phases contributes on densification process but deteriorates the refractoriness under load of the tested samples. On the other hand, all these tested samples exhibit good TSR value (>30 Cycle). The improvement in the refractory properties is correlated with the developed phases (forsterite and MA spinel in addition to periclase) that characterized with high refractoriness and low reversible thermal expansion that assist improvement of refractoriness under load and thermal shock resistance [3]. Fig. 4 shows photomicrographs of some selected samples (M1, M3 and M5). This figure shows the improvement of sinterability of the matrix with kaolin additions. The sintering behavior of magnesia is determined by the type and quantity of the accompanying mineral phases. Basically, the presence of secondary components with low melting phases such as CMS would be welcomed as an aid of sintering. But their presence also lowers the softening points and hence the application limit. Sample M1 is composed mainly of the rounded and subrounded crystals characterizing periclase mineral. These periclase crystals are directly bonded together but leaving some open pores in some locations at the grain boundaries. Also, some inclusions of magnesioferrite (white) was detected. In sample M3 containing 20 wt.% kaolin (Fig. 4c and d), the rhombic crystals characterizing forsterite mineral with different sizes and containing some white inclusions of calcia–magnesia–silicate and ferrite phases are observed. Also, some euhedral crystals characterizing magnesium aluminate spinel are appeared. Both forsterite and spinel crystals are distributed together with some glassy phases within the periclase matrix resulting in a dense and compact microstructure. This

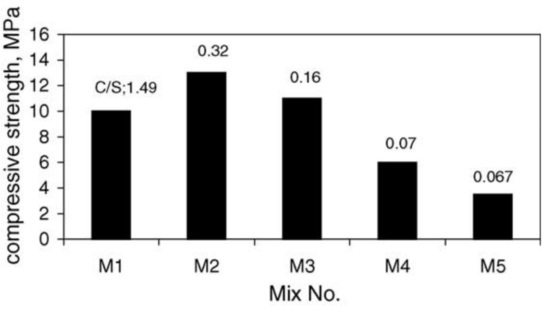

Fig. 2. Effect of C/S ratio on the sintering parameters of the fired samples.

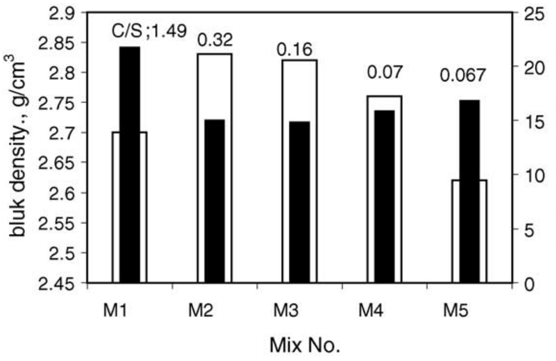

Fig. 3. Effect of C/S ratio on the mechanical strength of the fired samples.

Table 3
Thermal shock resistance and refractoriness under load of the fired mixes

Sample	TSR, number of cycles (RT, 1000 °C)	RUL;Ta (°C)
M1	>30	1510
M2	>30	1490
M3	>30	1460
M4	>30	1445
M5	>30	1410

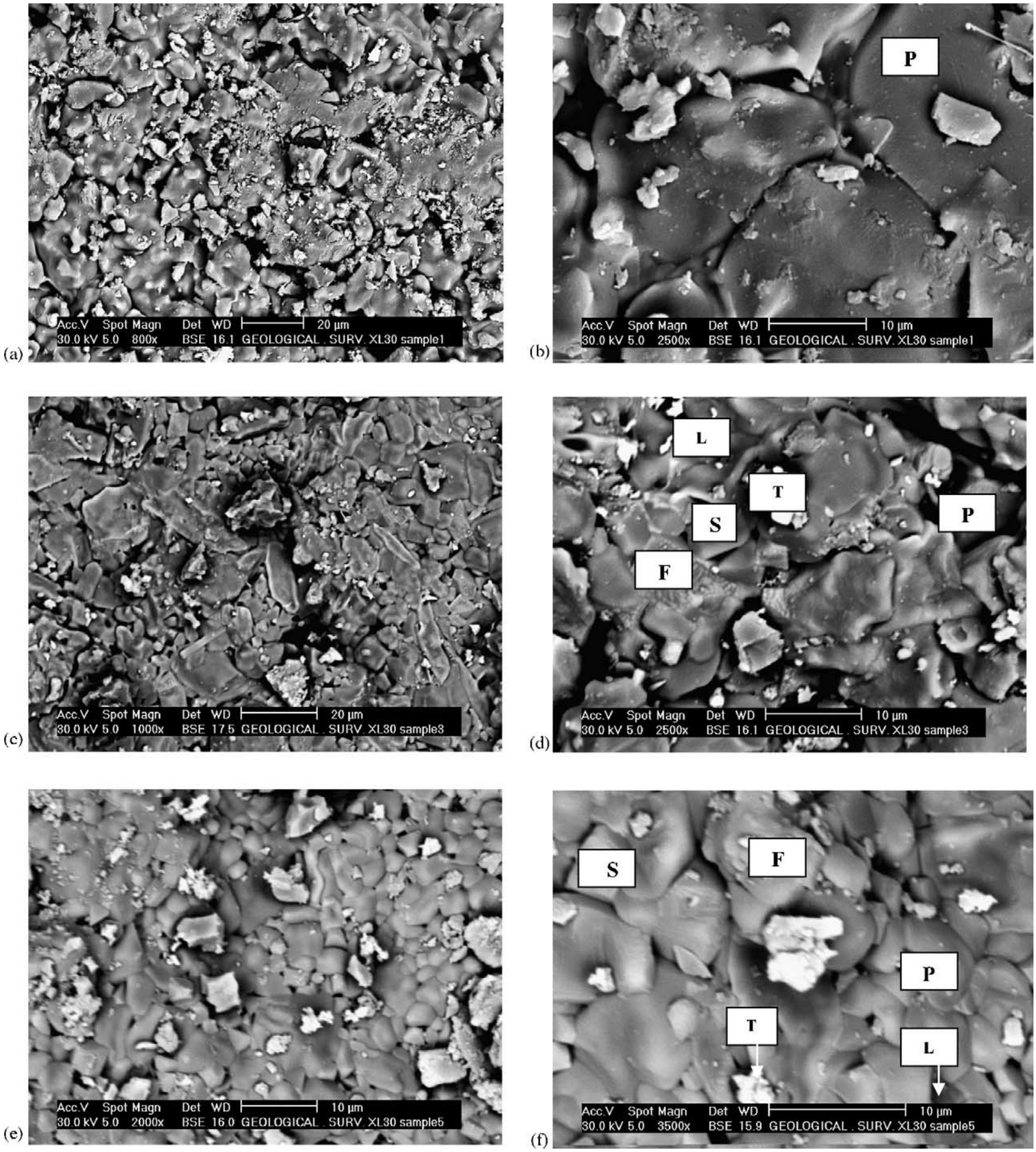

Fig. 4. SEM photomicrograph of the fired M1, M3 and M5 samples. P: periclase, S: spinel, F: forsterite, L: silicate phases, T: magnesioferrite.

phenomena is correlated with the presence of kaolin and becomes more obvious with its higher contents in the original (green) mix (sample M5) as shown in Fig. 4e and f. It is the aim of the sinter production to eliminate the foreign oxides as far as possible or to transform them by other additives into a highly refractory form such as forsterite and magnesium aluminate spinel that assist improvement of mechanical and refractory properties [12,13]. Generally, samples M2 and M3 of sintered magnesia briquettes are recommended to be used for lining different parts of steel furnaces, as well as, heating zone of cement rotary kilns, while, M4 and M5 can be used, according to their low refractory properties in comparison with M2 and M3, as heat exchangers or as kiln furniture in ceramic industry.

4. Conclusion

Well sintered magnesia bodies could be prepared through addition of up to 40 wt.% kaolin to magnesia. Materials containing of 10–20 wt.% kaolin are characterized with high sintering, good mechanical as well as high refractory properties. These products are recommended for use as a lining for different parts of steel furnaces as well as heating zone of cement rotary kilns. Samples containing 30–40 wt.% kaolin having limited refractory properties can be used in the heat exchangers or as kiln furniture in ceramic industries.

References

[1] A.G.M. Othman, Effect of talc and bauxite on sintering, microstructure and refractory properties of Egyptian dolomitic magnesite, Br. Ceram. Trans. 102 (6) (2003) 265–271.

[2] G. Routschka (Ed.), Pocketmanual of Refractory Materials, Vulkan Verlag, Essen, 1997.

[3] F.N. Cunha-Duncan, et al. Synthetic spinel–forsterite refractory aggregate from the sillimanite minerals, Miner. Metall. Process. 20 (3) (2003) 143–152.

[4] F.N. Cunha-Duncan, C. Bradt-Richard, synthesis of magnesium aluminate spinels from bauxite and magnesia, J. Am. Ceram. Soc. 85 (12) (2002) 2995–3003.

[5] E.A. Visloguzova, et al. Experience in utilization of forsterite refractories, Metallurgy (2) (2002) 46–47.

[6] V.S. Sergienko, et al. Service of refractories in the slide gate of 250-ton steel teeming ladles, Refractories 27 (11–12) (1986) 705–708.

[7] L.B. Khoroshavin, et al. Fused forsterite–periclase refractories, Ogneupory-i-Tekhnicheskaya-Keramika (6) (2002) 53–55.

[8] N. Petric, et al. Thermodynamic analysis of results obtained by examination of the forsterite and spinel formation reactions in the process of magnesium oxide sintering, Ind. Eng. Chem. Res. 28 (3) (1989) 298–302.

[9] V.A. Perepelitsyh, et al. Petrochemical calculations in the production of forsterite–spinel refractories from carbon–ferrochrome slags, Refractories 27 (9–10) (1986) 568–572.

[10] ASTM Standards, Section 15, vol. 15.01, 2001.

[11] J. White, in: A.M. Alper (Ed.), High Temperature Oxides, vol. 1, Academic Press, New York, 1970, p. 77.

[12] N.M. Khalil, Refractory aspects of Egyptian alum waste material, Ceram. Int. 26 (2001) 695–700.

[13] E. Mustafa, N.M. Khalil, A.G. Othman, Sintering and microstructure of spinel–forsterite bodies, Ceram. Int. 28 (2002) 663–667.