Effects of Clay and Fire Clay Additives on the Porosity and Strength of Magnesia-Forsterite-Spinel Refractories

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Research Article

ABSTRACT

This study investigates the effects of adding clay and fire clay to magnesia refractories and on their physical properties, such as contraction, mechanical strength, bulk density, and apparent porosity. Domestic raw materials were used and samples were fired at 1350, 1450, and 1550ºC for 2 h. Adding clay exhibits no significant effect on density and porosity, whereas adding up to 40% fire clay has a significant effect on shrinkage with a maximum of 20%. The porosity measurements support a minimum at samples with 20% fire clay. Nevertheless, the effects of clay and fire clay on the strength of magnesia are unnoticeable. X-ray diffraction results show that, after firing, the main phase compositions of the samples with clay are periclase and forsterite. Adding fire clay leads to the formation of magnesite spinel, which can be attributed to the high Al_2O_3 content of fire clay. Scanning electron microscopy shows that no liquid phase was formed, thus indicating that the sintering mechanism can be a solid-state reaction that results in forsterite formation.

Keywords: Clay; Fire clay; Refractories

INTRODUCTION

Magnesite, which has a melting point of 2800ºC, is an excellent refractory material. However, when formed in a pure state, the cost of final product would be high. Sintering magnesite refractory materials with clay leads to other phases, such as spinel and forsterite. Forsterite melts at 1905ºC, which is suitable for manufacturing refractory products. Forsterite has a high thermal expansion of $11 \times 10^{-6}/°C$ and a hardness of approximately 9.1 to 9.9 (Moh's scale). Meanwhile, the thermal shock resistance of forsterite is tolerable, and its abrasion resistance is excellent. A working temperature of 1650ºC is recommended when using forsterite as a refractory material. In addition, forsterite has a reasonably good corrosion resistance against melted metals, such as iron, aluminium, lead, magnesium, and zinc. It is also unreactive to CO_2, CO gases, or water vapor. Magnesite exhibits the same behaviour against these gases; however, its thermal expansion coefficient ($14 \times 10^{-6}/°C$) is greater than that of forsterite [1]. Given the high cost of magnesia refractory products, using other low-cost materials, such as kaolin, talc, and serpentine, are recommended to produce sintered or chemically bonded magnesia bricks [2-4]. Other studies have investigated producing sintered forsterite–spinel aggregates by using other aluminosilicate minerals, such as sillimanite, kyanite, and andalusite with magnesia [5,6]. Khalil [7] investigated the formation of forsterite and spinel by adding Egyptian alum–waste to magnesia. Trindate et al. [8] produced forsterite, periclase, and spinel by using other sources, such as diopside, monticellite, and akermanite, during the firing process of dolomite-rich clay. The present study explores the possibility of reducing the cost of magnesia refractories by adding clay and fire clay. Its main objective is to investigate the result of adding clay and fire clay to magnesite and the effect of such procedure on the formation of magnesia–forsterite–spinel. This study also compares cold physical properties, such as strength and porosity.

MATERIALS AND METHODS

Clay code K53 from Khorasan Kaolin Co. and fire clay from Semirom in Iran were chosen as additives to magnesite. An X-Ray Diffraction (XRD) system (Siemens D-500 diffractometer with CuKα radiation) and a scanning electron microscope (SEM, Cambridge Stereoscan 360) were used to investigate the phase formation and structural characteristics, respectively, of the samples. The chemical composition of the raw materials was determined through X-ray fluorescence (XRF, ARL 8410 spectrometer with Rh radiation) measurements under normal conditions. Chemical and phase analyses were conducted via XRF (40 mA, 60 kV) and XRD (30 mA, 40 kV), respectively. The XRD results were analyzed with the aid of Xpert software. Particle-Size Distribution (PSD) and mechanical strength were determined by using a particle size analyzer (Fritsch Analysette 22) and a three-point bending strength test machine (Instron 1196), respectively. The raw materials were ground in an alumina jar mill and were passed through a 45 μm sieve to determine their chemical and phase compositions. Tables 1 and 2 present the results of the chemical and phase analyses of the raw materials.

The samples were prepared by first calcining the clay at 800ºC and then grounding it in an alumina ball mill. The fire clay and magnesite were also ground for 8 h to obtain a suitable PSD. The batches were first treated in a distilled water solution to enhance their mixing capacity. Then, they were mixed for 1 h and dried overnight in an oven at 120ºC.

The dried samples were used to make granules with 4% moisture for pressing. Bars with dimensions of 60 × 10 × 5 mm were uniaxially pressed at 100 MPa by using 10 g of each batch. Table 3 shows the constituents of the samples and their related sample numbers. The samples were fired at 1350, 1450, and 1550ºC in an electrical kiln at a rate of 5ºC/min and were soaked for 4 h at maximum temperature under atmospheric conditions. The shrinkage of the 27 samples (9

formulations fired at 3 different temperatures) was determined by directly measuring the length of the samples with a caliper. Meanwhile, their porosity was determined by using the Archimedes method as stipulated by BS 1902.

Table 1. Chemical analysis of raw materials in Wt%.

Oxides	Clay	Fireclay	Magnesite
MgO	0.05	7.3	97.3
Al_2O_3	15.2	43	0.26
SiO_2	75.5	46	1.3
CaO	0.28	0.29	0.33
Fe_2O_3	0.5	1.1	0.11
Na_2O	0.12	0.34	0.26
K_2O	2.5-3	0.28	-
TiO_2	0.56	1.5	-
L.O.I	3-May	-	-

Table 2. Phase compositions of starting materials.

Material	Composition
Clay	Silica, kaolinite, nakrite and illite
Fire clay	Mullite and crystobalite
Magnesite	Periclase

Table 3. The Wt% of starting materials in each sample mixture.

Code Nr.	1	2	3	4	5	6	7	8	9
Clay	0	5	10	15	20	0	0	0	0
Fire clay	0	0	0	0	0	10	20	30	40
Magnesite	100	95	90	85	80	90	80	70	60

RESULTS AND DISCUSSION

Phase analysis

The main phases of the samples after sintering consisted of periclase and forsterite. Figure 1 shows the XRD patterns of the fired sample No. 3 at three different temperatures and sample No. 6 at 1450ºC. Although some alumina occurred in the clay (ca.15% Al_2O_3, Table 1), the XRD patterns of samples 1 to 5 exhibited no phase that contained Al_2O_3.

 Thus aluminum oxide might have been solved in other phases as a solid solution. The second possibility is that the amount of crystalline phases having Al_2O_3 as a component is less than that could be detected in X-ray analysis. The presence of approximately 3% alkali and earth alkali metals in the clay mineral supports this view. Another important point is the absence of mullite phase in the XRD patterns of sintered samples 6 to 9. According to the calcia/silica molar

ratio (C/S<1), the aluminosilicate compounds were probably consumed during the evolution of forsterite and spinel phases [9].

Figure 1. XRD patterns of fired samples (code No.3 and 6) at different temperatures. **Note**: (P: Periclase, F: Forsterite, SP: Spinel).
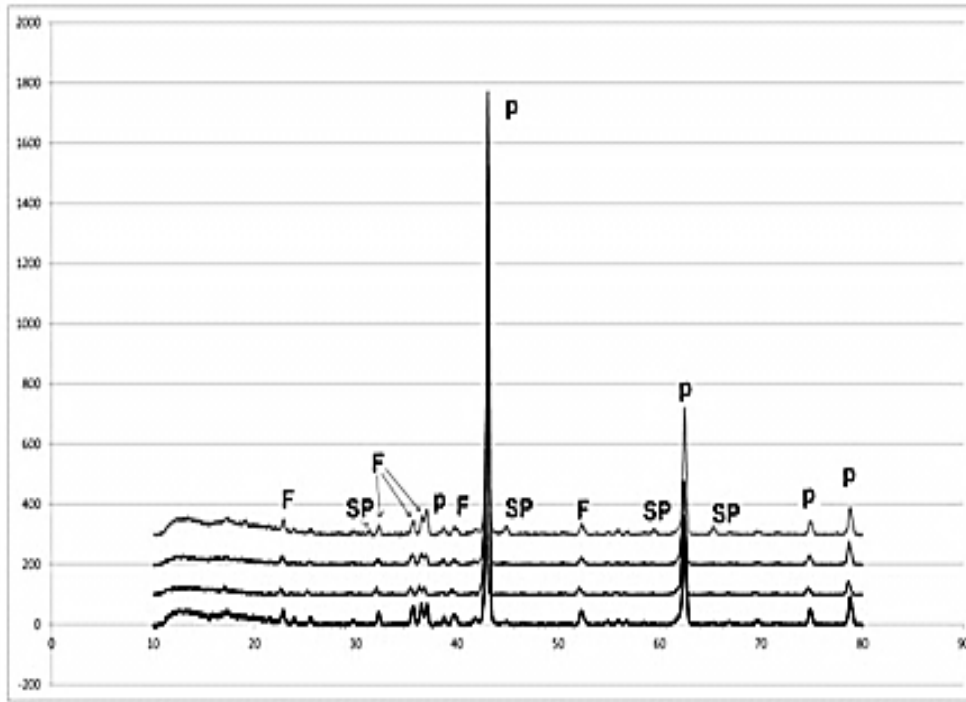

Figure 1 shows that spinel does not exist in the samples with clay as additive and is only formed in sample 6, the additive of which is fire clay. The semi-quantitative analysis of the samples fired at 1350°C reveals that the major phase of the samples is periclase, which is as expected.

Porosity, bulk density, and shrinkage

Figure 2 shows the variation of porosity as a function of clay content at different firing temperatures.

Figure 2. Variation of porosity of sintered samples as a function of temperature and clay content. **Note:** --◆-- 1350, —■— 1450, —▲—1550.
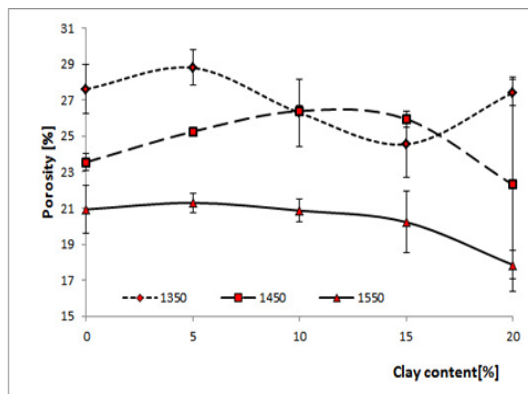
The standard deviation of the samples suggests that nearly no change in porosity occurs when clay is added to magnesia. By contrast, adding fire clay clearly leads to a change in the porosity of magnesia at a minimum of 20% (Figure 3).

Figure 3. Variation of porosity of sintered samples as a function of temperature and fire clay content. **Note:** ‑‑◆‑‑ 1350, ‑‑■‑‑ 1450, ‑‑▲‑‑ 1550.
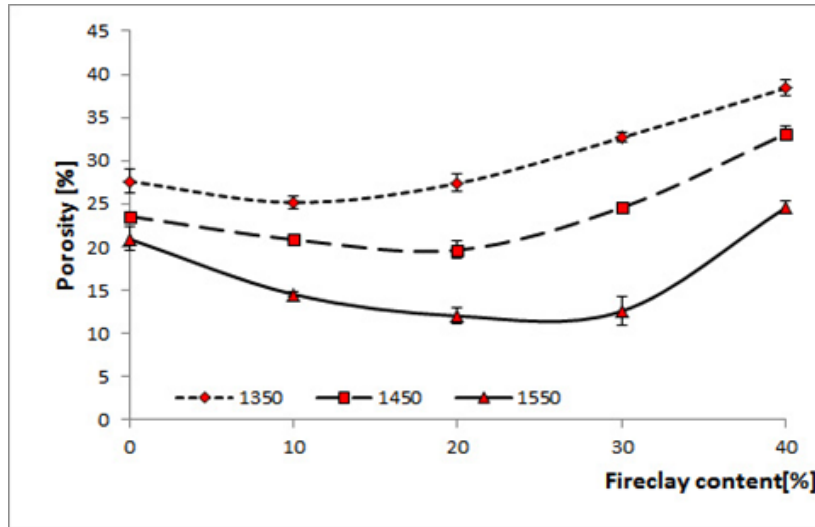
As expected, sintering at increasingly high temperatures decreases the porosity of both clay- and fire clay-containing samples.

Given that the porosity of the fired mixtures with clay does not markedly change, the slight decrease in density caused by adding clay (Figure 4) may be attributed to the differences in density of clay and magnesite.

Figure 4. Variations of bulk density of sintered samples as a function of temperature and clay content. **Note:** ‑‑◆‑‑ 1350, ‑‑■‑‑ 1450, ‑‑▲‑‑ 1550.
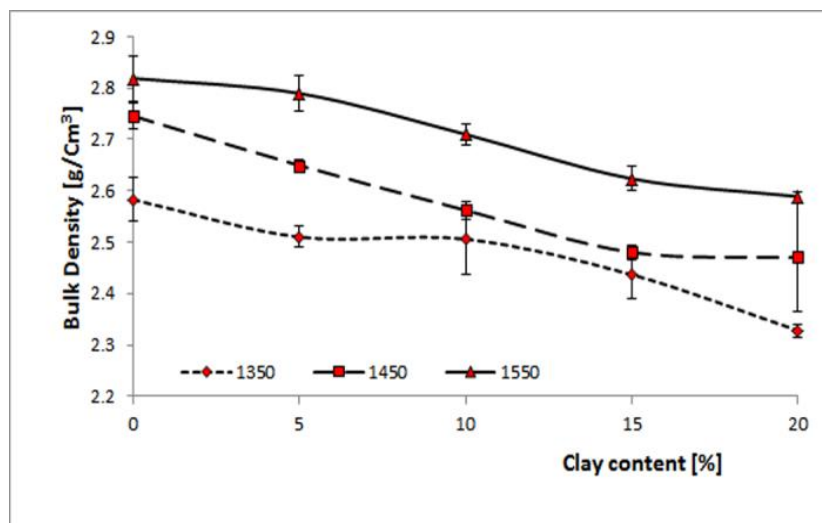
This attribution is supported by the nearly constant shrinkage of the samples with various amounts of clay, as shown in Figure 5.

Figure 5. The change of shrinkage as a function of temperature and clay content. **Note:** ‑‑◆‑‑ 1350, ‑■‑ 1450, ‑▲‑ 1550.
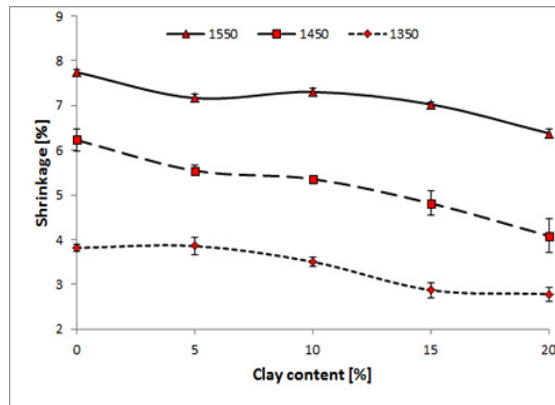
The minimum porosity of the fire clay-containing samples, as shown in Figure 3, can be attributed to the increased compaction of the ingredients. Nevertheless, a slight maximum, as shown in Figure 6, is in good agreement with the variation in shrinkage, as shown in Figure 7. That is, the changes in properties shown in Figures 3, 6, and 7 supports one another. The effect of temperature on shrinkage is also as expected, and firing at increasingly high temperatures causes the samples to shrink further (Figures 6 and 7).

Figure 6. Variations of bulk density of sintered samples as a function of temperature and fire clay contents. **Note:** ‑‑◆‑‑ 1350, ‑■‑ 1450, ‑▲‑ 1550.
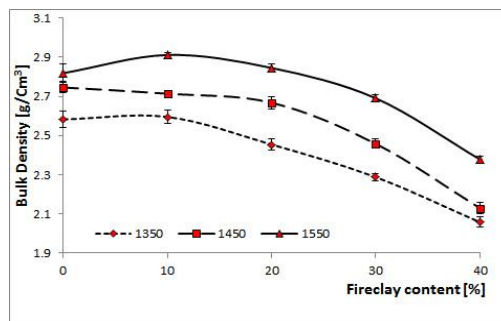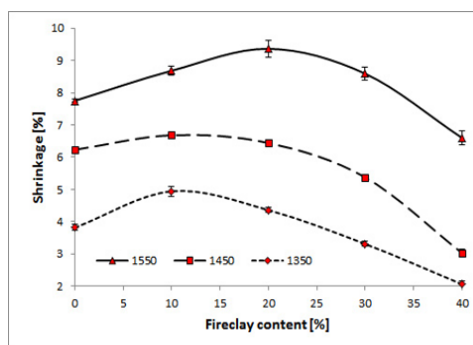

Figure 7. The change of shrinkage as a function of temperature and fire clay content. **Note:** ‑‑◆‑‑ 1350, ‑■‑ 1450, ‑▲‑ 1550.

Strength

The strength measurement of the samples reveals no absolute increasing or decreasing trend resulting from changing the clay and fire clay percentages at different temperatures, as shown in Figures 8 and 9, respectively. For a given composition, an increase in temperature leads to an increase in the mechanical strength of both fire clay and clay samples. This phenomenon may be attributed to a decrease in the porosity or an increase in the binding of grain samples. An increase in mechanical strength is generally observed at an increasingly high temperature from 1350°C to 1550°C.

Figure 8. The changes of strength of fired samples as a function of clay contents. **Note:** --◆-- 1350, —■— 1450, —▲— 1550.
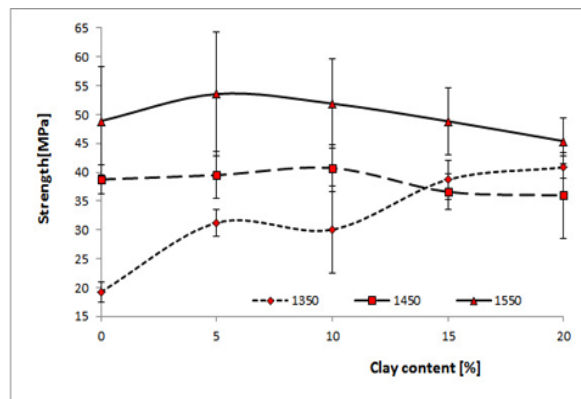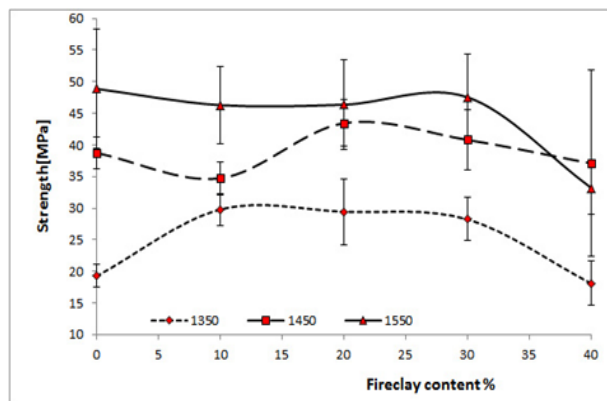

Figure 9. The changes of mechanical strength of fired samples as a function of clay and fire clay contents. **Note:** --◆-- 1350, —■— 1450, —▲— 1550.

Structural observation

Figure 10 shows the microstructure of the samples with 10% clay additive sintered at a temperature of 1350°C to 1550°C. The growth of crystals is observed at increasingly high firing temperatures. Necks are increasingly formed, thus confirming the increase in strength at increasingly high temperatures. The formation of a liquid phase is not evident in the SEM images, thus supporting the hypothesis that the major mechanism of sintering is solid-state reactions.

Figure 10. Microstructure of samples with 10% clay additives sintered at various temperatures, A: 1350ºC, B: 1450ºC, C: 1550ºC.
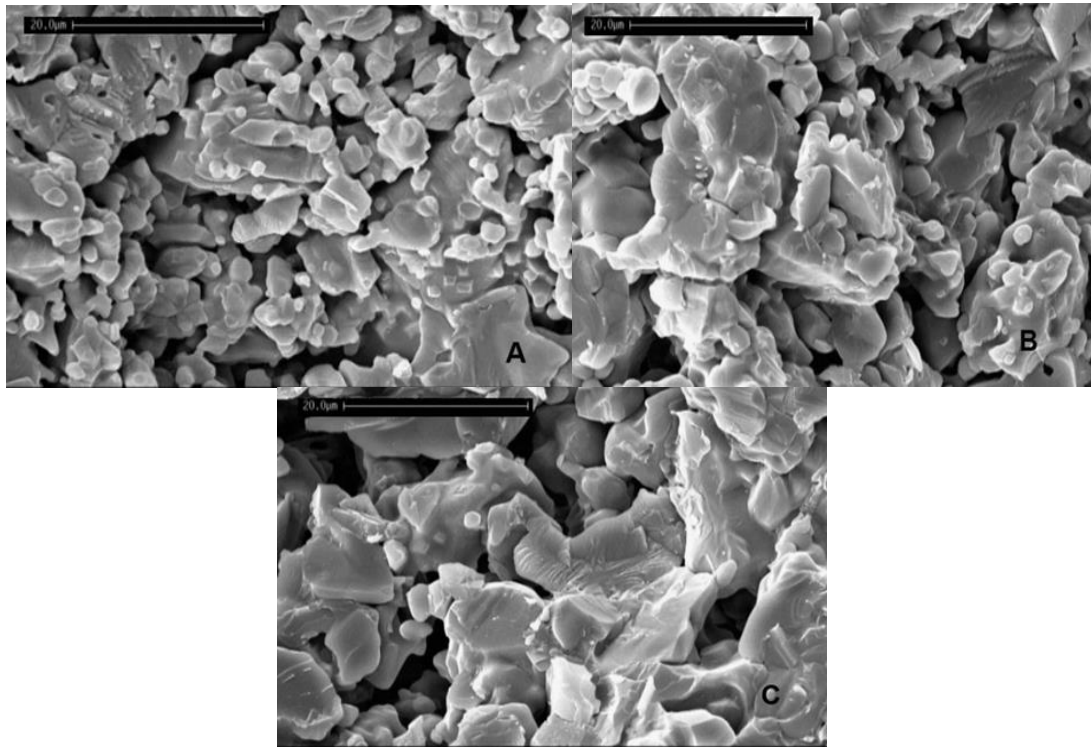
CONCLUSIONS

Given the experimental results of this study, the following conclusions can be drawn.

➢ Phase analysis shows that adding fire clay to magnesite causes the formation of forsterite and spinel, whereas adding clay primarily leads to the evolution of forsterite.

➢ The results of the mechanical testing of the sintered samples show that increasing the amounts of clay or fire clay additives to magnesite does not significantly affect mechanical strength; by contrast, an increase in temperature also increases strength.

➢ Sintering the samples at increasingly high temperatures increases contraction and decreases porosity.

➢ Although a slight change in particle sizes is observed, increased bonding occurs among the particles, which may account for the high strength of the samples fired at high temperatures.

➢ The selected clay and fire clay can be used as suitable additives to reduce the cost of magnesite. However, further investigation is necessary to scrutinize the effects of these additives on the function of magnesite refractories at high temperatures.

➢ Determining the optimal amount of fire clay or clay based on the cost of the final product is impossible. The significant difference between the costs of magnesite and the additives used decreases product cost. Based on cold properties, adding these additives leads to benefits; however, the final decision making is possible only after

testing Refractoriness Under Load (RUL) and other high-temperature properties, and thus, some industrial applications can be suggested accordingly.

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