A STUDY ON SPINEL FORMATION AND SINTERING BEHAVIOR OF Al_2O_3-MgO SYSTEM FOR INDUCTION FURNACE LININGS

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Keywords: Spinel Formation, Refractory, Steel, Induction Furnace, Neutral Lining

Abstract

Alumina (Al_2O_3) is the most fashionable material for producing neutral linings of induction furnaces used in steel industry. This type of lining has very high melting temperature, high strength, high hardness, and relatively high resistance to slag attack. In induction furnace applications chemical durability, thermal shock resistance, and mechanical strength of Al_2O_3 based neutral linings can be improved by direct addition of pre-reacted spinel ($MgAl_2O_4$), or by adding fine MgO to form an *in situ* spinel phase. When using *in situ* spinel forming alumina based neutral linings factors such as control of spinel formation kinetics, distribution of the spinel phase in the microstructure, and sintering kinetics in the Al_2O_3-MgO system are critical issues. Accordingly, the objective of this research was to study the spinel $MgAl_2O_4$ formation behavior and the sintering of alumina based Al_2O_3-MgO type induction furnace ramming materials in terms of the controllable variables like particle size distribution in the ramming mix, sintering temperature, and sintering time.

1. Introduction

In steel industry, refractories gain importance for many reasons, including product quality, energy saving, and cost effectiveness. About 75 percent of world refractory production is consumed in iron and steelmaking. In recent years, induction furnaces have become indispensible tools of melting units for the steel industry owing to their high efficiency, low energy consumption, easy operational control, and compatibility with a vast variety of scrap types [1-3]. In induction furnaces the most preferred refractory lining type is dry vibrating mixes. This is due to their ease of application, low cost of lining production, and absence of junction points [4].

SiO_2, MgO and Al_2O_3 based Dry vibrating mixes for linings of induction furnaces may be based on silica, magnesite or alumina. Due to high working temperature and slag chemistry, SiO_2 based and MgO based refractories not favorable in steel melting induction furnaces [4]. In contrast, alumina based neutral linings featuring *in situ* $MgAl_2O_4$ spinel forming capability have become materials of choice due to their high thermal shock resistance, high corrosion resistance, longer service life, and high chemical stability in both acidic and basic media [5,6].

$MgAl_2O_4$ spinel is called as mullite of 21st century because of its outstanding chemical, thermal, and mechanical properties [7]. It maintains its lattice structure even at elevated temperatures. In alumina based refractories differences between thermal expansion coefficients of alumina and spinel creates microcracks in microstructure. The microcrack network imparts a toughening mechanism and improves mechanical properties of the refractory body [8]. The *in situ* spinel formed in the alumina ramming mix at service temperature has a defective structure with a tendency of forming substitutional solid solutions while in contact with molten steelmaking slag [9]. When Fe^{2+} and Mn^{2+} cations migrate into A-site of spinel they form (Mg, Mn, Fe)O(Al, Fe)$_2$O$_3$. Also Ca^{2+} cations in the slag react with excess Al_2O_3 for forming Hibonite (CA_6). Depletion of MnO, FeO and CaO causes increment in relative SiO_2 content of the slag which limits the slag penetration and thereby reduces slag corrosion [9, 10]. Although spinel is known to exhibit superior properties in refractory bodies the knowledge on the formation of *in situ* spinel and sintering behavior of alumina based Al_2O_3-MgO dry vibrating mixes is still far from being complete. Preliminary studies on Al_2O_3-MgO refractory systems have concentrated on Al_2O_3-MgO castables or on ceramic systems with fine particle size [11, 12].

The success of neutral ramming mixes in steel melting induction furnaces depends critically on the formation of *in situ* spinel during service. A better understanding of spinel formation and sintering kinetics is essential for designing Alumina based Al_2O_3-MgO spinel forming dry vibrating mixes for induction furnace linings with improved thermal, chemical, and mechanical properties compared to those in the commercially available products. The objective of this study is to examine the effect of particle size range, sintering time and sintering temperature on spinel formation and sintering behavior of these particulate refractories.

2. Experimental Procedure

Fused Al_2O_3 and sinter MgO with particle size 0-5 mm and <100 μm were used as raw materials. Particle size range of the raw materials resemble those in commercial dry vibrating mixes. Particle size range in experimental mixes, designated as K1, K2, K3 and K4, was defined as shown in Table 1.

Name of Compositions	Particle Size of Al_2O_3	Particle Size of MgO
K1	0-5 mm	< 100 μm
K2	< 100 μm	0-5 mm
K3	1-3 mm	1-3 mm
K4	< 100 μm	< 100 μm

Table 1. Compositions and particle size range of raw materials.

Flow chart of the experimental procedure is shown in Fig. 1. According to the flow chart experimental compositions were mixed with stoichiometric molar ratio of Al_2O_3 to MgO in a rotating high density polyethylene (HDPE) bottle, then pressed uniaxially under 150 bar into the form of cylinders measuring 50 mm in diameter and 50 mm in height. The cylindrical compacts were sintered at temperatures in the range 1350 °C to 1700 °C. The longest dwell time at the peak sintering temperature was 4 hours. Samples fired at 1550, 1650, and 1700 °C were withdrawn from the furnace at 1 hr intervals. The sintering operation was carried out in a programmable muffle furnace heated by $MoSi_2$ elements.

The dimensions of the samples were measured before and after sintering for determining the permanent linear change (PLC) in dimensions of the sintered bodies. PLC in neutral ramming mixes is an important index, because in addition to dimensional change it provides clue on sintering behavior and sintering depth. Phases in the sintered specimens were determined by powder XRD techniques, using an X-ray difractometer (Rigaku Rint 2200) with Cu - Kα radiation.

Spinel transformation rates were calculated according to Eqn. (1) which is an internal standard method based on ratio of highest intensity peaks of the components periclase (200), corundum (113), and spinel (311) in their XRD patterns [13].

$$\frac{\mathrm{Spinel}_{(311)}}{\mathrm{Spinel}_{(311)}+\mathrm{Corundum}_{(113)}+\mathrm{Periclase}_{(200)}} \times 100 \qquad (1)$$

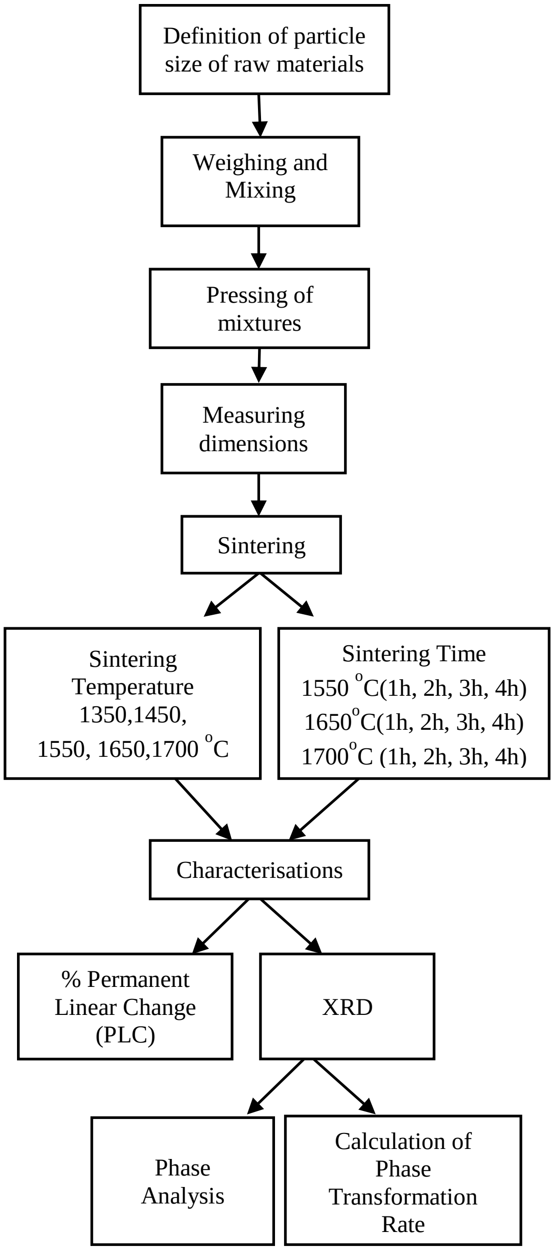

Fig. 1. Summary of experimental procedure

3. Results and Discussion

3.1. Spinel Conversion Rate

Spinel conversion rate is important in understanding the spinel formation mechanism. The spinel conversion rates of experimental compositions are shown in Fig. 2. It can be seen that K4 has the highest spinel conversion rate at all temperatures. K1 follows as the the second highest in conversion rate, while K2 and K3 exhibit the least conversion rates. The conversion rates of the latter two compositions are very close to each other for all sintering temperatures.

These results show that particles size of components has a major effect on spinel conversion rate. When we compare the conversion rates of K1 and K2 it can be seen that particle size of MgO is predominant. With fine MgO the rate is higher. As MgO gets coarser the effect of particle size of Al_2O_3 on conversion kinetics becomes lesser.

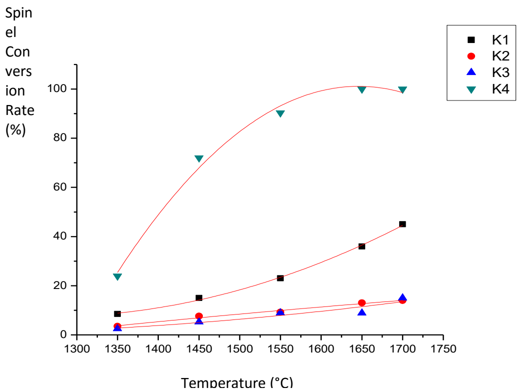

Fig. 2. Spinel conversion rate of compositions according to temperature

These results show that the Wagner mechanism [14], which explains spinel formation mechanism in fine MgO + Al_2O_3 particulate mixtures, works for the dry vibrating mixes used in the present study.

3.2. Permanent Linear Change

PLC represents a combination of dimensional variations due to sintering shrinkage and volume expansion encountered during spinel formation. Because of differences in density of MgO, Al_2O_3, and $MgAl_2O_4$ phase the thermal synthesis of spinel is associated with a volume expansion [15]. The magnitude of this expansion is governed by the particle size of the components MgO and Al_2O_3. Thus, PLC can be controlled and monitored by adjustments in particle size distributions.

PLC determination is important for understanding the thermo-mechanical behavior of neutral ramming mixes in the induction furnace. The results of calculations on PLC values of sintered bodies in the present study are shown in Fig. 3.

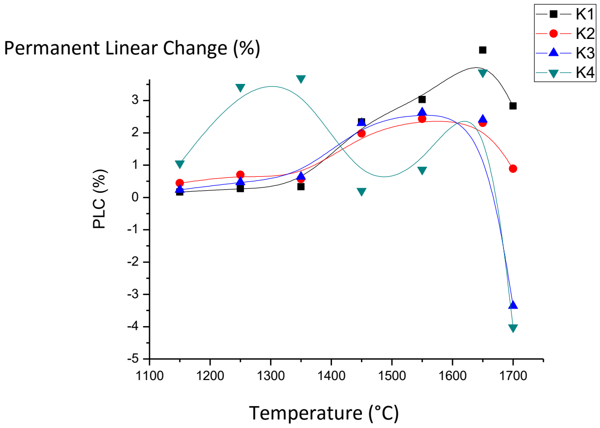

Fig 3. PLC values of compositions according to temperature

In case of experimental mix K1, until 1650°C volume expansion due to spinel formation is dominant mechanism on PLC behavior, above this temperature K1 starts to shrink, because the dominant mechanism shifts to densification instead of volume expansion. When K2 is compared with K1, the expansion is lesser, and the sintering shrinkage starts at 1550°C. Hence, when Al_2O_3 particles are coarse the spinel formation becomes slower and densification mechanism of sintering becomes effective on PLC at lower temperature.

The details of the PLC behavior were studied at temperatures 1500, 1650 1700°C for sintering times at peak temperature between 1 to 4 hours. The results of PLC determinations obtained under these conditions are shown in Fig. 4, Fig. 5, and Fig 6, at 1500°C , 1650 °C , and 1700 °C, respectively.

Fig. 4 shows that at 1550°C, in K4 which has both Al_2O_3 and MgO particles in fine fraction, the PLC exhibits a maxima at hours of firing, therefore at this temperature initially the spinel formation mechanism is dominant. In fact, within 2 hours all reactants are transformed totally into spinel phase. Following the maxima in PLC, the sintering shrinkage takes over. At 1550 °C, the compositions K1, K2, and K3 show relatively moderate PLC values. Interestingly, however, these mixes maintain their PLC at longer retention times at temperature.

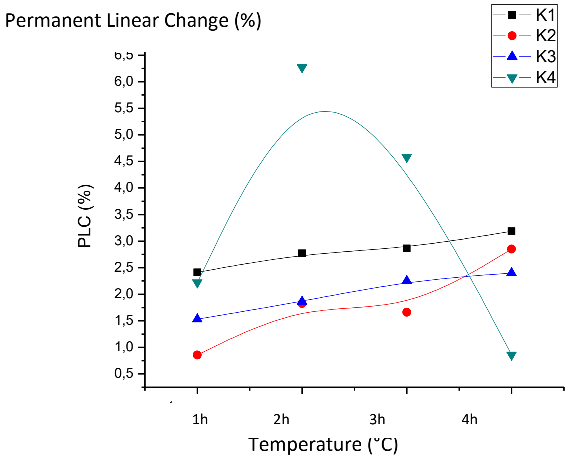

Fig 4. PLC values for 1550°C

Fig. 5 shows that when firing temperature is raised to 1650°C the spinel conversion rate in the mixture designated as K4 becomes very high, therefore spinelization occurs within a very short period followed by sintering shrinkage. Thus, negative PLC values are encountered due to the dominant mechanism of densification. In the early stages of thermal exposure, the mixes K1, K2, and K3 all develop certain amount of spinel phase within a period shorter than 1 hour. This is because of the fact that, in the early stages, the spinel formation is faster than densification. Pass this period, the spinel formation in mixture K1 continues with rising PLC. The other mixtures attain a stable PLC which may indicate that the spinel formation and densification rates are almost equal

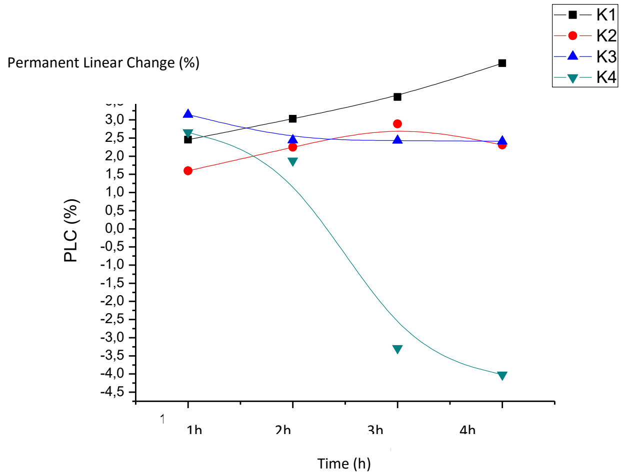

Fig 5. PLC values for 1650°C

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Fig. 6 shows that, at 1700°C, for K4 the volume change behavior is same as the one observed at 1650°C. The remaining mixes attain a higher level of spinelization in the early stages. Later in the firing process, in all mixtures densification becomes dominant over spinel conversion so that shrinkage, at a low overall rate, occurs at all holding times.

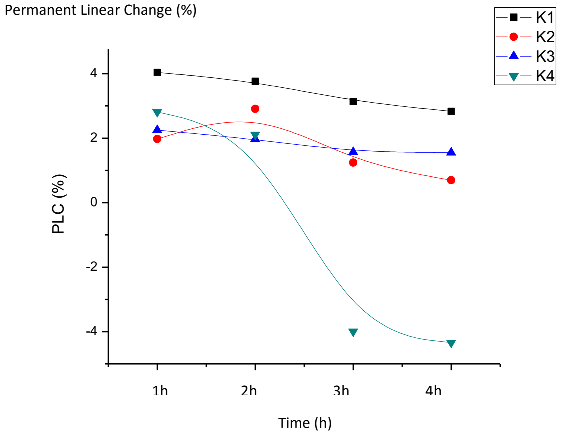

Fig 6. PLC values for 1700°C

4. Conclusion

The focus of the present study was examining the effect of parameters like particle size, firing temperature, and firing time on the spinelization and sintering kinetics of stoichiometric particulate mixtures of MgO and Al_2O_3. The results are important for the design of neutral ramming mixes of induction furnace linings. It is known that in neutral type dry vibrating mixes spinel formation and sintering are two competing mechanisms. Spinelization is important because it provides the bonds necessary for strength development in the lining. Shrinkage determines the level of microstructure development. Present study revealed that MgO particle size plays a key role in the spinelization and sintering processes. The rates of these may be kept under control by adjusting the temperature. Thus linings with different internal structures may be produced.

These investigations provide fundamental knowledge for producing alumina based spinel forming induction furnace linings with controllable mechanical, chemical and thermal properties.

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