

Effect of nano iron oxide as an additive on phase and microstructural evolution of Mag-Chrome refractory matrix

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Abstract

Nano iron oxide, up to 8 wt.%, was added to Mag-Chrome refractory matrix through stirring in ultrasonic bath in an alcohol media. The phase and microstructure of samples heated up to 1650 °C were studied by XRD and SEM/EDS respectively.

It was found out that the formation of magnesioferrite spinel was encouraged at lower temperatures in the presence of nano iron oxide. The dissolution of iron oxide and ionic migration improved the sintering process in the matrix of the refractory. The presence of nano iron oxide also influenced the bonding structure in a way that direct bonding was enhanced while silicate bonding was hindered.

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1. Introduction

Mag-Chrome bricks have been playing a crucial role as a refractory material in various industries such as secondary metallurgy (AOD, VOD, etc.), non-ferrous furnaces (copper converter) and cement making (rotary kiln) due to their high temperature stability, low thermal expansion and outstanding erosion–corrosion performance at high temperatures.¹ Mag-Chrome refractories are basically categorized into silicate, direct and rebonded grades in terms of bonding between grains. Silicate bonds are mainly comprised of low melting compositions such as monticillite ($\text{CaO}\cdot\text{MgO}\cdot\text{SiO}_2$), merwinite ($3\text{CaO}\cdot\text{MgO}\cdot 2\text{SiO}_2$) and some amounts of dicalcium silicate and forsterite according to the molar ratio of CaO/SiO_2 . These silicate phases facilitate liquid phase sintering process but deteriorate thermo chemical and thermo mechanical properties of refractory in high temperature applications.^{2,3} Hence, developing direct bonded Mag-Chrome brick containing low amounts of silicate phase is of high importance based on their excellent properties at high temperatures.

In order to enhance direct bond formation between grains in Mag-Chrome refractories, SiO_2 content of the refractory is

to be less than 3 wt.%.¹ Such low content of silicate phases in the matrix, however, leads to high sintering temperature and high energy cost. One of the key factors in reducing the sintering temperature of direct bonded bricks as reported nearly four decades ago is lowering the dihedral angle between periclase and periclase–chromite grains. White claims that introducing some oxides such as ZrO_2 and TiO_2 into the refractory could decrease dihedral angle and lower the firing temperature by promoting direct bond between grains.² In this regard Halder and Ghosh have investigated the effect of TiO_2 and ZrO_2 addition in Mag-Chrome refractories respectively.^{4,5} They concluded that addition of TiO_2 and ZrO_2 improved the physical properties of Mag-Chrome refractories and enhanced direct bond formation. These additives, however, did not lower the sintering temperature significantly. Recently, Huizhong studied addition of nano Fe_2O_3 into the matrix of Mag-Chrome refractory and reported that the sintering temperature was reduced about 150 °C but he did not report any phase and microstructural evolutions.⁶

The aim of this work is to introduce nano iron oxide as an additive to Mag-Chrome refractories matrix and study the phase and microstructural developments during the sintering process.

2. Experimental

Commercial Chinese Dead Burnt magnesia and Iranian Chrome ore were taken as raw materials (Table 1). In order

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Table 1
Chemical analysis of magnesia and chromite.

Raw material	Chemical analysis (%)					
	Cr ₂ O ₃	MgO	CaO	Al ₂ O ₃	Fe ₂ O ₃	SiO ₂
Magnesia	–	97.36	1.1	–	0.94	0.59
Chromite	35.15	19.48	0.41	26.7	14.15	4.1

Table 2
Nano iron oxide specification supplied from Nanoamor Co.

Fe ₂ O ₃ (α)	Purity	APS	SSA	True density	Color
Specifications	+98%	20–50 nm	>50 m ² /g	5.24 g/cm ³	Red brown

to obtain a direct bonded magnesia–chromite system, a formulation containing 75 wt.% Chinese magnesia and 25 wt.% Iranian chrome ore was adopted. High grade nano iron oxide (α-Fe₂O₃) with average particle size of 20–50 nm was supplied from Nanoamor Co., USA (Table 2).

Two-hour simultaneous stirring and ultrasonication in methyl alcohol as dispersing media was applied to prepare a stable and uniform suspension of nano iron oxide. The refractory fine fraction composed of magnesia particles smaller than 100 μm was then added to the suspension and additional 30 min simultaneous stirring and ultrasonication were conducted to make a well distributed mixture of nano iron oxide and fine magnesia particles.

The suspensions containing 2, 4, 6 and 8 wt.% nano iron oxide of the target batches were prepared and then other fractions, i.e. magnesia and chromite grains smaller than 1 mm were added to the mixture. The as-received suspensions experiencing simultaneous agitation at a temperature of 100 °C were dried on a magnetic stirrer. The dried powder containing 3 wt.% magnesium sulfate as binder was pressed in 31 mm diameter mold under a uniaxial pressure of 80 MPa. Samples were heated in an electric furnace at 1350, 1450, 1550 and 1650 °C with a soaking time of 2 h and subsequently were cooled in the furnace. Table 3 shows the codes of these samples in which Fx stands for iron oxide while x describes iron oxide content in samples respectively.

X-ray diffraction patterns of fired samples were obtained by Co Kα radiation in Philips Expert equipment. For microstructural analysis the samples were resin impregnated, polished and then studied in an SEM/EDS Cambridge model 360 machine. In order to monitor the expansion/shrinkage of the samples for sintering studies a Netzsch 402E/7 Dilatometer under flowing air was employed to achieve dilatometry results during firing process. The linear shrinkage change of the samples after firing was measured as well and compared with the dilatometry results.

Table 3
Samples coding used in this study.

Sample codes	F0	F2	F4	F6	F8
Iron oxide content (%)	0	2	4	6	8

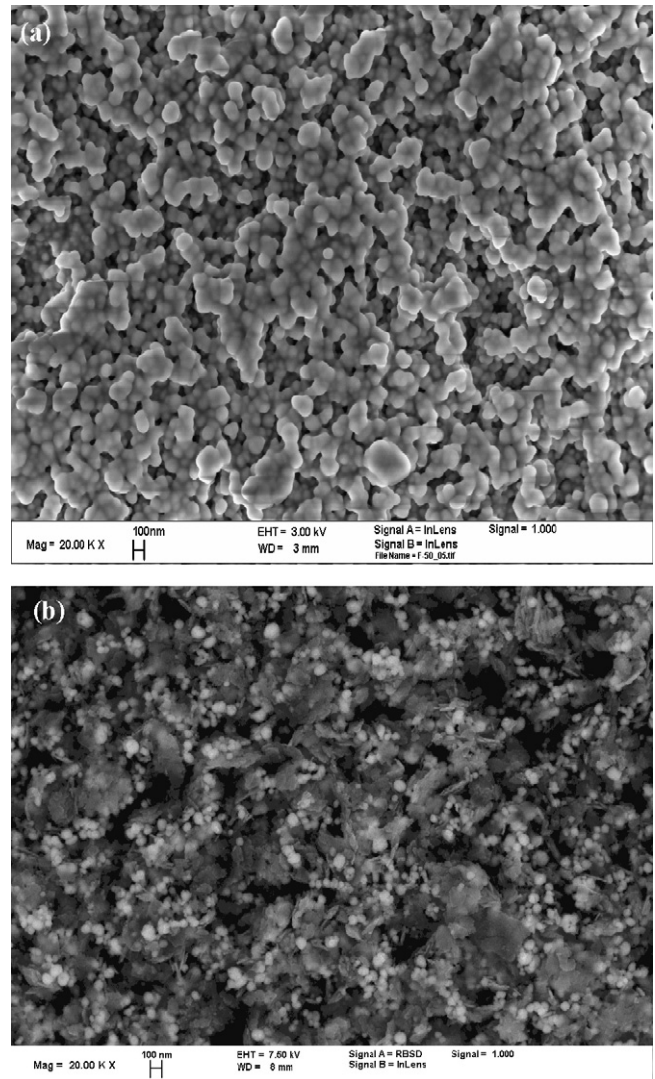


Fig. 1. SEM images of (a) nano iron oxide agglomerates and (b) nano iron oxide particles which are well dispersed between magnesia particles.

3. Results and discussion

In order to prepare a stable suspension carrying nano iron oxide powder, it is necessary to conduct a specific procedure to break the agglomerates. High surface tension of iron oxide particles leads to severe agglomeration and therefore we found that a liquid media such as methyl alcohol was required to disperse the particles in the suspension. However this media was found to be influential only if simultaneous ultrasonic stirring was adopted.^{7,8}

Fig. 1a and b shows the SEM images of nano iron oxide powder before and after ultrasonic stirring respectively. As it is seen the nano particles agglomerates are broken partially during the process. Two-hour stirring could break the agglomerates to 50–150 nm particles (Fig. 1b). Although the process was not successful in creating the primary particles of 20–50 nm (according to the specifications in Table 2) but it could be efficient for present work in which the refractory matrix particles are in the range of 10–100 μm.

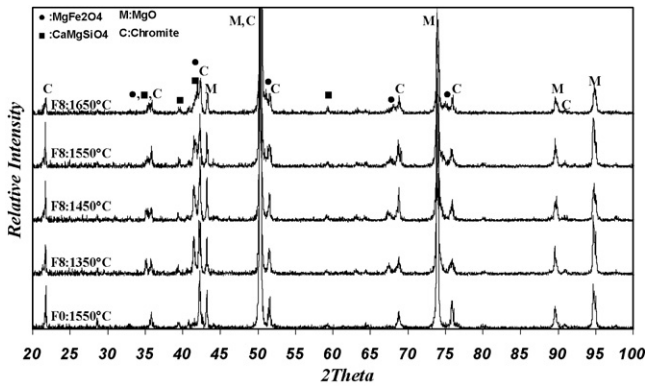


Fig. 2. XRD patterns of F0 heated at 1550 °C and F8 heated at 1350 °C, 1450 °C, 1550 °C and 1650 °C.

XRD patterns of F0 heated at 1550 °C and F8 heated at 1350 °C, 1450 °C, 1550 °C and 1650 °C are shown in Fig. 2. As it is seen the F0 sample fired at 1550 °C contains no traceable spinel phase and this phase was not observed in F0 heated at 1450 °C for 5 h either. In fact the only source of iron oxide to react with magnesia in F0 is chromite particle and occurrence of a direct bond as a result of solid state sintering could provide a channel for diffusion of Fe_2O_3 into MgO to form spinel. Therefore there is no significant direct bond between grains in F0 fired at temperatures lower than 1550 °C. XRD patterns of F8 indicate that magnesioferrite spinel peaks overlap with those of present phases such as chromite and monticillite and other spinel phases like FeFe_2O_4 and MgCr_2O_4 . However, formation of magnesioferrite spinel phase can be seconded with the evidence revealed from SEM photographs along with line scanning diagram. It seems that cation vacancies as point defects are created as the consequence of such dissolution in periclase encouraging solid state sintering between grains. The main silicate phase is shown to be monticillite in accordance with X-ray diffraction patterns (Fig. 2) and the intensity of the peaks proves that there is low amount of this phase in the matrix due to low SiO_2 content. According to Fig. 2 increasing the firing temperature does not promote formation of other phases in F8 and the matrix would consist of chromite, magnesia, moticillite and magnesioferrite.

Fig. 3 illustrates the dilatometry curves of F0, F4 and F8 indicating the expansion/shrinkage behavior of samples during heating process. All samples show similar behavior till 1000 °C due to similar thermal expansion coefficient of the samples. In spite of thermal expansion of samples, it is seen that by increasing the temperature a slight shrinkage is appeared as a result of sintering process in the system. This shrinkage happens at the approximate temperature of 1150 °C for F0 but introduction of nano iron oxide (F8) decreases the onset of sintering (starting of shrinkage) to 1100 °C according to Fig. 3. Hence it could be concluded that sintering process in nano bearing samples begins at lower temperature and proceeds with higher rate on the basis of shrinkage characteristics as indicated in Fig. 3.

Linear shrinkage of F0, F2, F4, F6 and F8 after firing process is shown in Fig. 4. Samples show different shrinkage behavior after firing process. F2 and F4 have higher shrinkage than F0 due to more sintering occurred in nano containing samples. F6 and F8 show less shrinkage after firing in comparison to other samples which is contrary to Fig. 3. As a matter of fact it seems that substantial amount of exsolved magnesioferrite spinel has precipitated over periclase grains which is followed by volume expansion. Comparing Fig. 3 and Fig. 4 shows that appreciable amount of spinel is formed by exsolution during cooling process which has faded away the sintering effect on volume shrinkage.

The phase evolution is described on the basis of the diffusion of iron ions through chromite toward periclase grains due to chemical gradient of iron oxide in neighboring particles. Walter et al. reported that the Fe^{2+} oxidizes to Fe^{3+} at 300 °C and is reduced to Fe^{2+} at temperatures lower than 1400 °C.⁹ Such oxidation–reduction processes are reversible and could cause drastic volume changes in the refractory. High dissolution of iron oxide into periclase grains (around 60 wt.% at 1600 °C) and monticillite is reported by White and this could result in direct bonding between chromite and periclase grains in Mag-Chrome refractories.² Counter diffusion of iron and magnesium ions between chromite and periclase at high temperatures could lead to formation of magnesioiwustite ($(\text{Mg},\text{Fe})\text{O}$) which is oxidized to magnesioferrite ($(\text{Mg},\text{Fe})_2\text{O}_4$) appearing as white dots on periclase grains.⁹

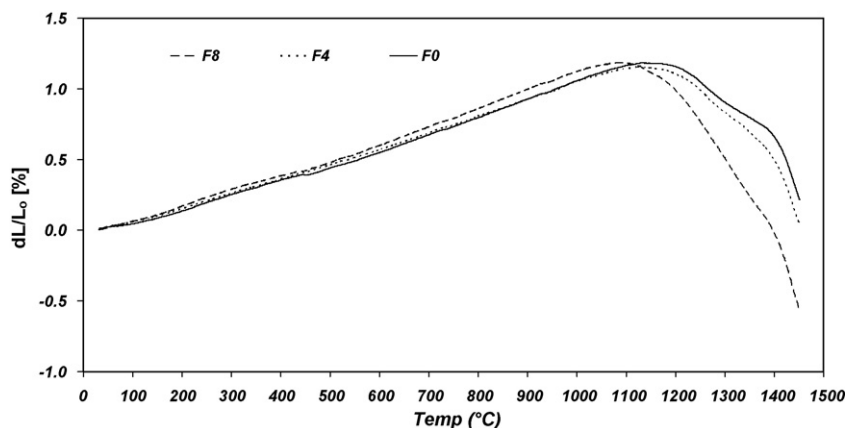


Fig. 3. Dilatometry curves of F0, F4 and F8.

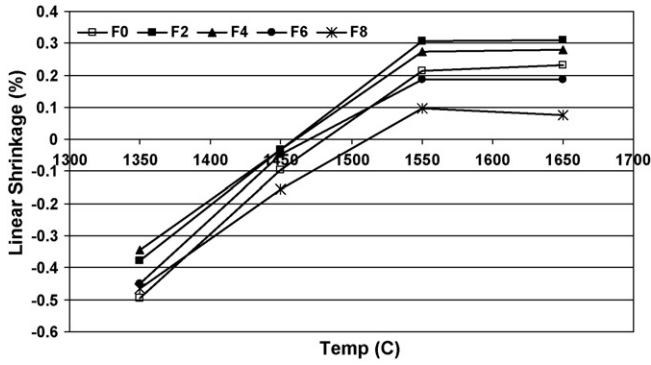
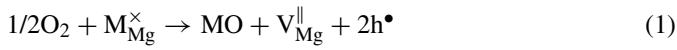
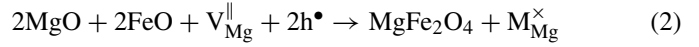


Fig. 4. Linear shrinkage of F0, F2, F4, F6 and F8 after firing process.

Hence tracing magnesioferrite phase could be a sign of direct bond formation between grains. Luecke suggested that this reaction begins at the surface where oxygen partial pressure is high enough to form wustite or magnesia including cation vacancy and electron hole according to following equation:¹⁰



Counter diffusion of cations and electron holes through the grain is the consequence of above reaction introducing chemical gradient of cations. Diffusion of electron holes and cation vacancies to the interior part of the grain results in formation of magnesioferrite spinel and a free cation which diffuses to the surface afterwards according to Eq. (2):



Therefore lower shrinkage of samples containing higher amounts of nano iron oxide is probably because of more spinel formation on magnesia grains during cooling process.

In Fig. 5a SEM image of F0 fired at 1550 °C shows that there is no direct bonding between chromite and magnesia grains because of low firing temperature and short soaking time (2 h). In addition, no white dots indicating exsolution of magnesioferrite phase is seen on the periclase grains.

No exsolution proves that no diffusion of iron ions from chromite into periclase has taken place to promote direct bonding. Adding 2%wt. nano iron oxide has brought about emergence

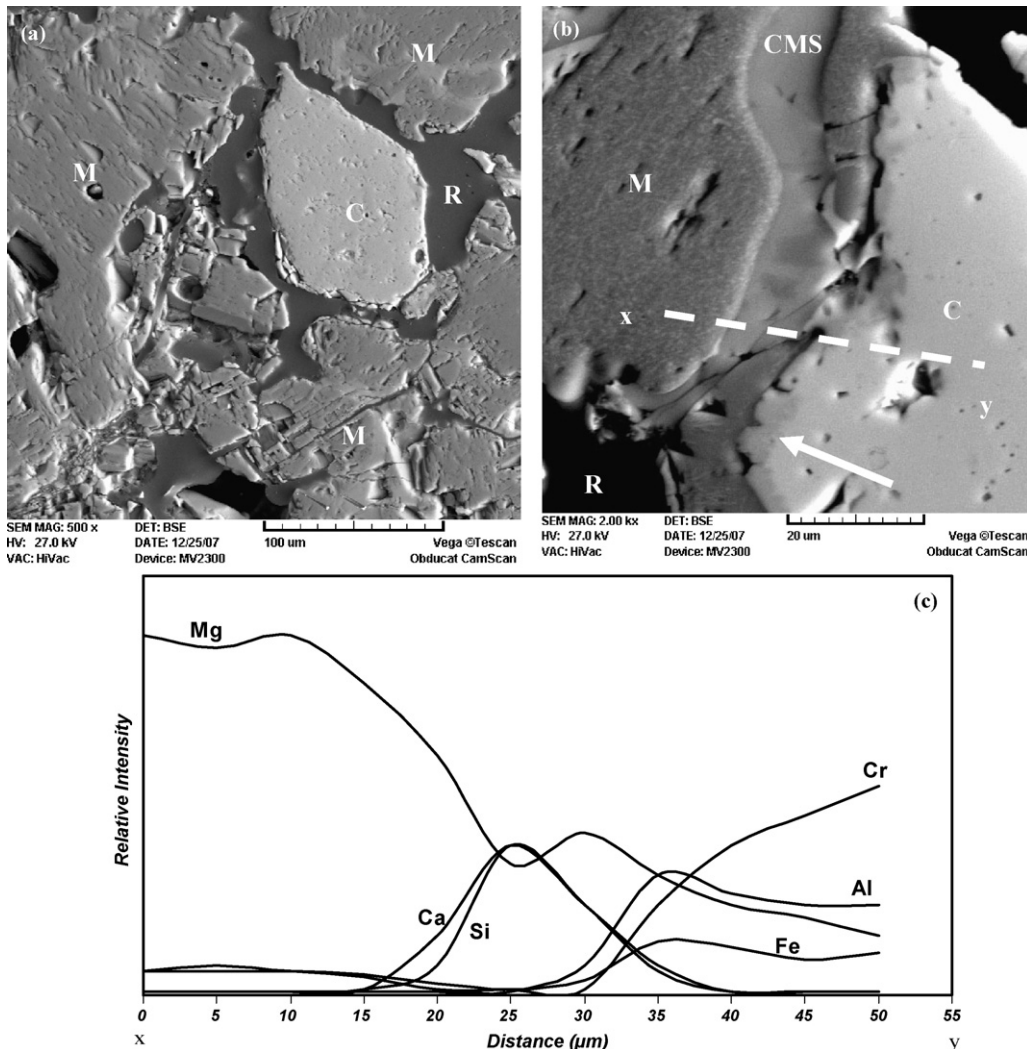


Fig. 5. SEM micrograph of (a) F0, (b) F2 heated at 1550 °C (M: magnesia, C: chromite, CMS: monticillite and R: resin) and (c) Line Scanning of elements along the dashed line in (b).

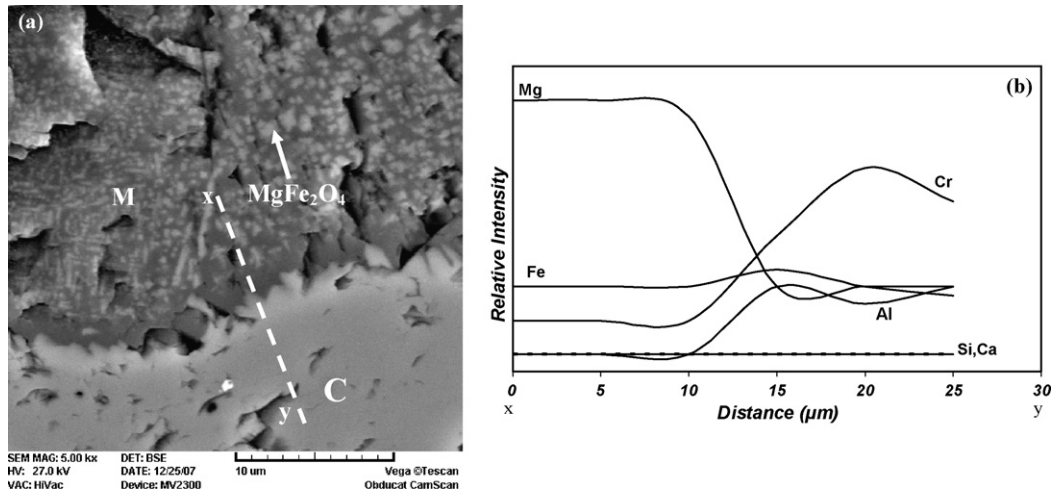


Fig. 6. (a) SEM micrograph of F6 heated at 1550 °C (M: magnesia, C: chromite) and (b) Line Scanning of elements along the dashed line.

of spinel exsolution on periclase (white dots on the grain) as illustrated in Fig. 5b.

In Fig. 5b, the arrow shows the reaction layer in chromite as a result of diffusion of ions to the boundary. Chromite is a complex spinel solid solution phase composed of different spinels such as MgAl_2O_4 , MgCr_2O_4 , FeCr_2O_4 and different silicate phases like serpentine ($3\text{MgO}\cdot 2\text{SiO}_2$), piroxine ($(\text{Mg},\text{Fe})\text{SiO}_3$) and pelagioclase ($(\text{Ca},\text{Na})\text{Al}_2\text{Si}_2\text{O}_8$) based on the CaO/SiO_2 ratio.² Menezes et al. showed that concentration of iron ions towards the exterior of the chromite grain would vary up to 800 °C due to the solid state diffusion process and is followed by the diffusion of other ions, i.e. magnesium, chromium and aluminum at higher temperatures forming the reaction layer at the grain boundary.^{11,12}

Silicon and calcium are concentrated in the middle phase between magnesia and chromite based on line scanning of Fig. 5b illustrated in Fig. 5c. It shows that silica and calcia as primary impurities in magnesia and chromite particles have diffused thoroughly away at this temperature creating monticillite phase in the matrix.

The other interesting point to be mentioned here regarding Fig. 5c is the presence of some amounts of iron oxide in periclase which could stem from both nano powder additive dissolution in magnesia and probably diffusion of iron ions from chromite to CMS and then into the periclase as well. Iron oxide has high solubility in CMS but it shows a higher trend towards periclase.² On the other hand, dissolution of iron ions into periclase could encourage counter diffusion of magnesium cations and enhance direct bond formation. Increasing the heating temperature could decrease the viscosity of CMS leading to better distribution and formation of narrower film of this silicate phase in the matrix between grains. Narrower films of CMS could bring about shorter distance between grains for counter diffusion of ions and then further the prospects of direct bond formation as described later. Chromium and aluminum migrate to the reaction layer as well but the amount is not appreciable in comparison to iron and magnesium (Fig. 5c).

Adding 6 wt% nano iron oxide has developed direct bond between magnesia and chromite in F6 as indicated in Fig. 6a.

Solid state sintering between magnesia and chromite is accompanied by significant diffusion of iron oxide into periclase encouraging precipitation of magnesioferrite spinel from periclase. As a matter of fact applying nano additives into refractories could effectively improve the properties effectively owing to high surface activity of nano powders and promote better solid state sintering at lower temperatures. High solubility of iron oxide (Fe_2O_3) into periclase (around 60 wt.% at 1500 °C) because of near ionic radius of iron and magnesium (Mg^{2+} : 0.65 Å, Fe^{3+} : 0.6 Å)¹³ leads to formation of cationic vacancies in magnesia according to the following equation:



One of the main mechanisms involved in formation of direct bonds between periclase and periclase–chromite grains is described based on the diffusion of iron oxide into magnesia grains resulting in high atomic mobility because of cation vacancies. White has reported that the dihedral angle between periclase grains could be declined to less than 20° by adding about 10 wt.% iron oxide.² Introduction of nano particles must be basically more effective in decreasing dihedral angle and encouraging direct bonds in comparison to micron particles as it is obvious from microstructural observation in Fig. 6a. Line Scanning of F6 across the grains proves well distribution of iron in magnesia and chromite as well as the low contents of silicon and calcium in both grains (Fig. 6b). Although further investigations of interfaces by TEM to understand the mechanism is recommended but even with the present X-ray line scanning we have a good insight of the dominant process.

Fig. 6b also indicates that very little amount of chromium and aluminum diffuses through the boundary to periclase due to the high difference between their ionic radii (Cr^{3+} : 0.75 Å, Al^{3+} : 0.45 Å) and different crystal structure.

Both F2 and F6 heated at 1650 °C indicate appropriate direct bond between magnesia and chromite grains (see Fig. 7) including appreciable amount of exsolved magnesioferrite spinel on periclase grains in F6 as illustrated in Fig. 7b. The arrows in Fig. 8 show the reaction layer formed in the boundary of chromite

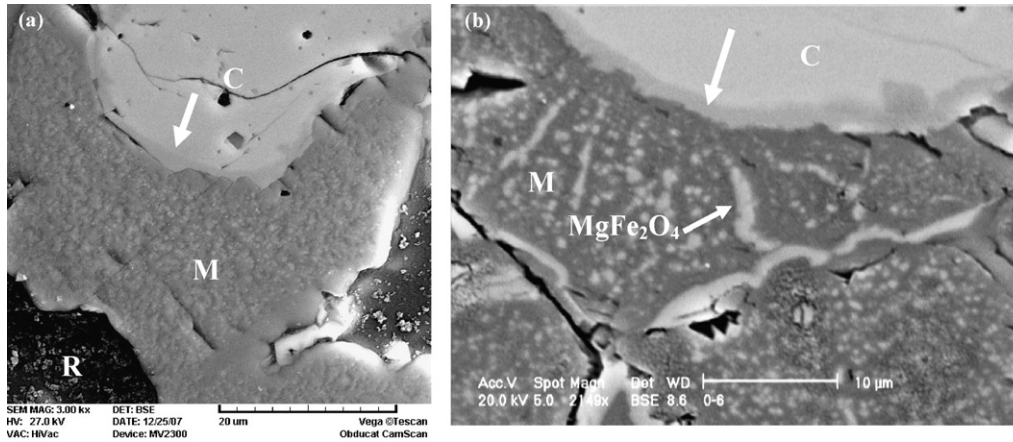


Fig. 7. SEM micrographs of (a) F2 and (b) F6 heated at 1650 °C (M: magnesia, C: chromite, R: resin).

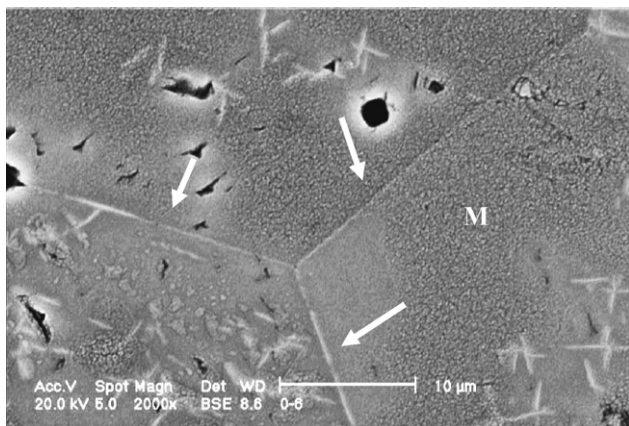


Fig. 8. SEM micrograph of a triple junction between three periclase grains in F6 heated at 1650 °C.

containing diffusing ions through the grain because of chemical gradient toward the periclase.

A triple junction between magnesia grains which have reached the lowest state of surface energy in F6 heated at 1650 °C is indicated in Fig. 8. The arrows show the white lines between grains indicating spinel bonds which play an effective role in lowering the dihedral angle between magnesia grains.

4. Conclusion

Nano iron oxide addition enhanced the formation of magnesioferrite spinel at lower temperatures. Also substantial amount of spinel was found to precipitate during cooling process. Solid state sintering was promoted by accelerated counter diffusion of Mg and Fe ions between chromite and magnesia particles as well.

Nano iron oxide additive encouraged the formation of direct bonding in refractory matrix. This phenomenon was observed to be accompanied by decreasing the viscosity of liquid silicate phases resulting in improved solid state sintering.

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