Improvement in microstructure and properties of MgO-C refractory by addition of Fe

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Abstract. In order to achieve self-repairing of MgO-C refractory in oxidizing atmosphere at high temperatures, Fe powder, serving as both antioxidant and direct-bond former, was introduced into this refractory. The effect of Fe addition on the microstructure, properties and oxidation resistance was investigated. The coexistence of $(Mg,Fe)O_{ss}$ and $Mg(Fe_{1.2}Al_{0.8})O_4$ was identified for the Fe-containing MgO–C refractory after graphite was oxidized, by which a network was formed in the matrix. As a consequence, both densification and direct-bond in the oxidized layer were greatly enhanced compared with the conventional MgO-C refractory, solving the issue of strength degradation during high temperature oxidation. An excellent oxidation resistance was obtained owing to the above improvements.

1. Introduction

It is well known that MgO–C refractory played important role in the steelmaking industry by using as the linings of converters, electric arc furnaces and steel ladles. The excellent thermal shock and slag corrosion resistance owing to the presence of graphite is the key reason for the success of this refractory [1]. However, a major disadvantage regarding the incorporation of graphite is its high oxidation potential at high temperatures, accompanied by the formation of a porous structure and decrease of mechanical strength. To solve this issue, many technologies, such as introduction of antioxidants [2-4], graphite surface modification [5] and attachment of anti-oxidation coating [6], were developed. Besides, the structure stability of the decarburized layer is also of utmost importance to the oxidation resistance, which has been confirmed by the successful application of slag-splashing technology in converters. On the other hand, the presence of a decarburized layer with considerable thickness can also decrease the contact area between graphite and liquid, slowing down or even stopping the carbon pick-up in molten steel. However, very few studies have focused on this point.

Fe_xO is an effective sintering aid to enhance the densification and mechanical properties of MgO based ceramics and/or refractories [7]. Similarly, improvement in structure and properties of the porous layer can be achieved if Fe^{2+}/Fe^{3+} were present. Moreover, other benefits such as anti-oxidation and toughening effects could be attained if metal Fe is introduced into MgO–C refractory. To date, the role of Fe in the properties of MgO–C refractory is still unknown. In this work, therefore, Fe-containing MgO–C refractories were prepared, and their microstructure, oxidation resistance and mechanical properties were studied by comparing with the conventional one.

2. Experimental procedures

2.1. Preparation

High purity fused magnesia, flake graphite and aluminum powder were used as the raw materials in this work, and the liquid phenol resin was used as binder. An initial mixture was prepared based on the composition of the refractories used as the linings of steelmaking converters, as shown in Table 1. Then 4, 8 and 12 wt% high purity Fe powders were added into this mixture, respectively. The final products were prepared by the following procedure: mixing (30 min) – aging (25 ^{o}C for 12 h) – pressing (250 MPa to cylindrical samples) – curing (200 ^{o}C for 24 h) – firing (1500 ℃ for 3 h in air atmosphere).

Table 1. Chemical composition of the designed MgO–C refractories.

Samples	MT14-0	MT14-4	MT14-8	MT14-12
Fused magnesia	86	86	86	86
Graphite	14	14	14	14
Phenolic resin[a]	4	4	4	4
Aluminum[a]	2	2	2	2
Fe powder[a]	0	4	8	12

[a] with external addition.

2.2. Characterization and analysis

The bulk density and apparent porosity were measured by Archimedes principle according to GB/T 2997-2015 standard. The cold crushing strength was evaluated by hydraulic universal test machine (Model YEW-2000). 6 valid samples were used for each test. The phase assemblage in different layers was identified by X-ray diffraction (XRD; X'pert PRO, PANalytical, Netherlands). Microstructure observation as well as chemical analysis in different zones was performed by field-emission scanning electron microscopy (FE-SEM; Model Ultra Plus, Carl Zeiss, Germany) attached with energy dispersive X-ray analyzer (EDX).

3. Results and Discussion

Figure 1 shows the typical cross-section photographs of the four refractories after firing at 1500 ^{o}C in air for 3 h. Two distinct regions, i.e. unoxidized layer and oxidized layer (or decarburized layer), with clear reaction interface were observed for all the samples. For the MT14-0 sample, the thickness of the decarburized layer was around 4 mm after oxidizing. This value decreased apparently with increase of Fe content, which was only 2 mm after 12 wt% Fe was introduced into this refractory. Smooth cut surfaces also were observed for the Fe-containing refractory, indicating that the bonding strength of the decarburized layer was greatly improved by Fe addition.

Figure 2 shows the XRD patterns of the oxidized layers for different samples. The major diffraction peaks were periclase (MgO) and spinel ($MgAl_2O_4$) for the MT14-0 sample after the graphite was oxidized. Besides these phases, another spinel of $Mg(Fe_{1.2}Al_{0.8})O_4$ was identified when 4 wt% Fe powder was added into the refractory. The peak intensity of this new phase increased obviously with increasing Fe content, while an opposite trend was observed for that of $MgAl_2O_4$. These changes were caused by the following reactions: Fe powder began to oxidize after the oxidation of carbon, after which the produced FeO and Fe_2O_3 both can react with periclase based on the MgO-Fe_xO system, forming $(Mg,Fe)O_{ss}$ and $MgFe_2O_4$, respectively [8]. Both $MgFe_2O_4$ and $MgAl_2O_4$ belong to the minerals of spinel [9], and thus isostructural $Mg(Fe_{1.2}Al_{0.8})O_4$ can be obtained by substituting Al^{3+} for Fe^{3+}. Moreover, the ionic radius of Fe^{3+} (0.55 Å) is similar to Al^{3+} (0.53 Å), which favours the formation of continuous solid solution. As a consequence, only MgO and $Mg(Fe_{1.2}Al_{0.8})O_4$ were detected for the Fe-containing refractories with higher Fe content.
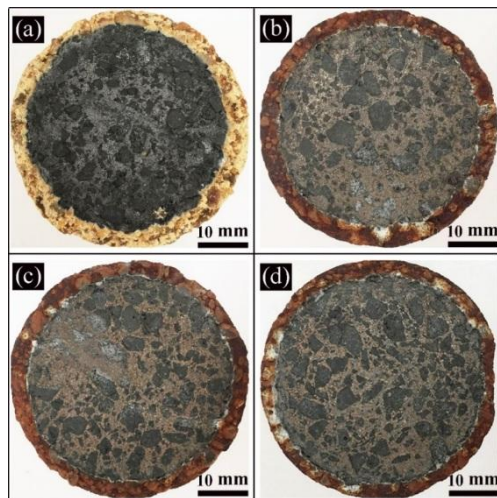
Figure 1. Photographs of the refractories after firing at 1500 ^{o}C for 3 h: (a) MT14-0, (b) MT14-4, (c) MT14-8, (d) MT14-12.
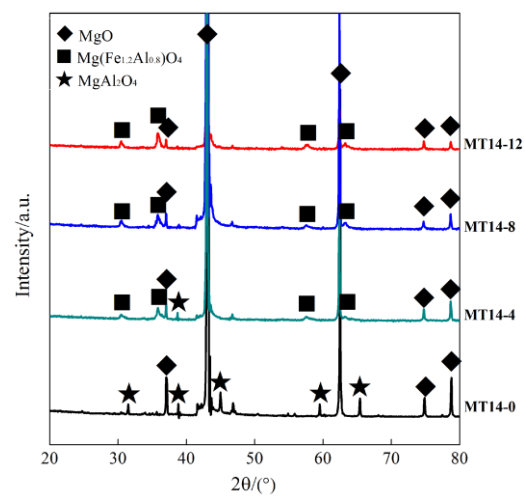

Figure 2. XRD patterns of the oxidized layers for different samples fired in air at 1500 ^{o}C for 3 h

Figure 3 displayed the representative microphotographs of the two samples after firing at 1500 ^{o}C for 3 h. High porosity and big pores (50-200 μm) were clearly observed in the matrix structure of the sample MT14-0, and interconnected pores were left after graphite was oxidized. What is worse, the direct-bond between neighbouring grains was rather poor. However, the pore sizes were obviously decreased and the direct-bond was greatly improved after Fe powder was introduced, as shown in Figure 3(b). On the one hand, the large formation of magnesio-wustite $(Mg,Fe)O_{ss}$ by replacing Mg^{2+} with Fe^{2+} enhanced the sintering of the magnesia matrix [9], as shown on the right of Figure 3(b). On the other hand, owing to the formation of $Mg(Fe_{1.2}Al_{0.8})O_4$ network by the interdiffusion of Fe^{3+} and Al^{3+}, as shown in Figure 4, the isolated periclase grains can be effectively rebonded. Undoubtedly, both bonding strength and oxidation resistance can be greatly enhanced by the formation of the complicated network and the tortuous pores.
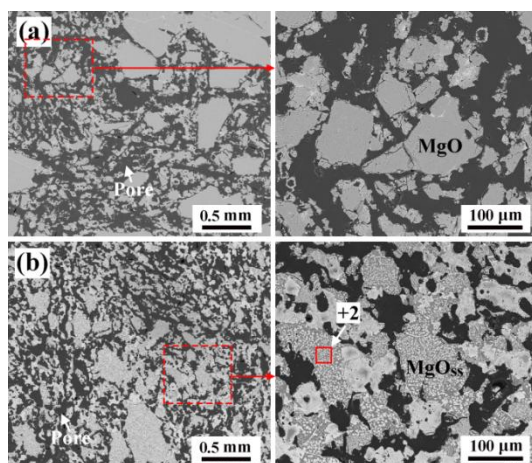

Figure 3. Microstructure comparison of the two samples after oxidation: (a) MT14-0, (b) MT14-8. +2: $(Mg,Fe)O_{ss}$.
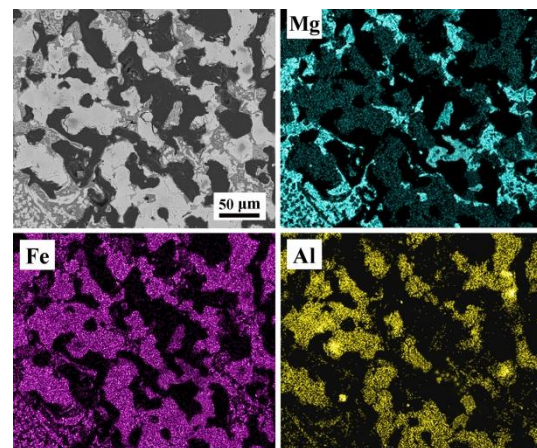

Figure 4. Map scanning results in the matirx of the sample MT14-8 after firing at 1500 ^{o}C for 3 h.

Figures 5 and 6 show the effects of Fe addition on the physical and mechanical properties, respectively. For the apparent porosity, it was about 5% after curing for all the refractories, which is accordant with the theoretical values [10]. The porosity then rose to ~10% after coking at 1500 ^{o}C due to the pyrolysis of the phenol resin. After firing in oxidizing atmosphere, this value further increased to around 16%

for the sample MT14-0, which is consistent with the microstructure observation, as shown in Figure 3(a). Nevertheless, the increase of porosity after oxidation was much less pronounced for the Fe-containing samples. The volume expansion owing to Fe oxidation and $Mg(Fe_{1.2}Al_{0.8})O_4$ formation and effective sintering owing to solid solution formation were the key reasons for this change. Similar change rule was observed for the cold crushing strength. It can be seen that about 45% strength was lost after firing at 1500 ^{o}C for the conventional MgO–C refractory. However, the strength was kept in a constant value for the samples MT14-8 and MT14-12, suggesting that the self-repairing was effectively achieved for the porous and weak decarburized layer by addition of Fe powder. The main reasons for this improvement can be described as follows: (i) the increase of densification (ii) the promotion in sintering by accelerating the ions migration; (iii) the enhancement of direct-bond owing to the formation of $Mg(Fe_{1.2}Al_{0.8})O_4$ network.
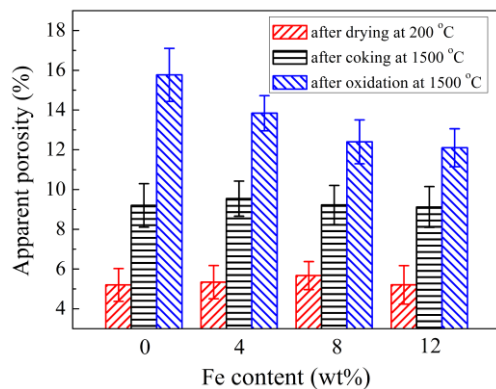

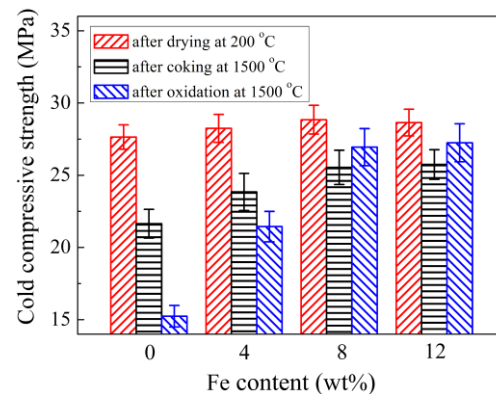**Figure 5.** Effect of Fe addition on the apparent porosity.

Figure 6. Effect of Fe addition on the cold crushing strength.

4. Conclusions
The microstructure, physical and mechanical properties, and oxidation resistance of Fe-containing MgO–C refractory were studied by comparing the conventional one. Based on the above results and discussion, the following conclusions can be obtained:

(1) $(Mg,Fe)O_{ss}$ and $Mg(Fe_{1.2}Al_{0.8})O_4$ were formed for the Fe-containing refractory by the reaction between the produced FeO and Fe_2O_3, periclase and $MgAl_2O_4$ in the oxidized area, by which the neighbouring matrix particles were firmly connected.

(2) Porous structure with poor direct-bond was observed for the conventional MgO–C refractory. However, the densification and bonding degree were greatly improved after Fe powder was introduced by the formation of network structure in the matrix.

(3) The oxidation resistance of MgO–C refractory was greatly improved by addition of Fe. The key factors were revealed as follows: (1) the improvement in densification; (2) the increase in the diffusion resistance of gases by the $Mg(Fe_{1.2}Al_{0.8})O_4$ network.

(4) The issue of strength degradation during high temperature oxidation for the MgO–C refractory was solved by addition of Fe powder. This is of great importance to the stability of the decarburized layer, thus further inhibiting the oxidation of graphite.

5. References
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