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Degradation of MgO–C refractories corroded by SiO_2–Fe_2O_3–V_2O_5–TiO_2–MnO–MgO slag

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Abstract

The properties and degradation of resin bonded MgO–C bricks corroded by SiO_2–Fe_2O_3–V_2O_5–TiO_2–MnO–MgO slag were investigated by dynamic induction slag test. Carbon oxidation by oxygen and/or reducing slag and corrosion of MgO grains attacked by corrosive vanadium containing slag are the main degradation mechanism. High temperature and long exposure time lead to more serious corrosion. Marangoni convection at the three phase boundary steel–slag–refractory is observed. Oxidation of carbon is observed which affords pores, cracks and voids for the vanadium containing slag corrosion and penetration. Periclase grains are seriously infiltrated by the slag, leading to the disintegration and the removal of MgO subgrains into the slag. Complex forsterite and spinel solid solution with FeO and MnO, sometimes V_2O_5 are confirmed by EDS. EDS also confirms the presence of corrosive low melting point species vanadate in the slag or as the result of reaction of slag and refractory components, which is deleterious to the slag resistance of the brick. Furthermore, diffused FeO content in periclase gradually decreases when going deeper into the refractory. However MnO is found difficult to diffuse into periclase.

Keywords: Corrosion mechanism; MgO–C bricks; Vanadium containing slag; Thermodynamatic simulation

1. Introduction

Resin bonded MgO–C bricks are widely used in the steelmaking industry, especially in basic oxygen furnace (BOF) and electrical arc furnace (EAF) due to its long campaign life [1–6]. Added flake graphite as carbon source is not easily wetted by steel slag which hinders the slag corrosion and overcome the weakness of periclase. Furthermore, high thermal conductivity of carbon improves the thermal shock resistance of the bricks. However, serious oxidation of carbon below 1400 °C results in porous structure and the deterioration of the properties of the bricks. So Al, Si, B_4C, Al–Si alloy and other antioxidants must be added in order to inhibit the oxidation resistance of carbon. [7–9]

Damage of MgO–C bricks is greatly dependent on operation conditions which vary from one factory to one factory. Corrosion of MgO–C brick by converter slag and steel slag has been studied by many researchers [1,10–13]. Lee summarized the corrosion mechanisms as following steps:

1) formation of decarburized layer due to the oxidation of graphite or other carbon sources by FeO and O_2 in the furnace environment.
2) Formation of transition layer and erosion layer due to the infiltration of slag into the decarburized layer.
3) Erosion of oxide grains by penetrated slag and the dissolution of oxide grains into slag and molten steel.
4) MgO–C reaction in converter and steel ladle at 1600–1700 °C.

It is must be noted that the as-mentioned stages can occur simultaneously. Kim et al. have observed a dense MgO layer formed at the slag/brick interface in laboratory scale in BOF

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Table 1
Chemical compositions of raw materials and vanadium containing slag (mass %).

	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	K_2O	Na_2O	TiO_2	MnO	V_2O_5	SiC	Cr_2O_3	IL
Electro fused periclase	0.11	0.14	0.4	97.9	0.78								
SiC	0.85	0.41	0.17	0.02	0.05						97.9		
Vanadium containing slag	15.5	2.78	31.22	4.66	1.7	0.16	0.12	12.6	8.32	19.29		3.58	8.32

condition, which suppresses the slag penetration, however, the dense MgO layer cannot be confirmed by post mortem analysis of the used MgO–C bricks [14].

Quon has indicated that MgO–C bricks are not suitable for VOD furnace due to the serious vaporization of gaseous Mg [15]. In this condition, oxygen pressure is insufficient to meet the demand of re-oxidization of gaseous Mg.

Guo et al. have reported the interaction of Al_2O_3-rich slag with MgO–C bricks during VOD refining and found a porous MgO layer at the hot face of the used brick and a spinel layer at the slag/brick interface. From their study, MgO–C bricks can be used in some certain cases. They also studied the degradation of MgO–C brick by MnO-rich stainless steel slags. [16–18]

MgO–C bricks are still used in other furnaces. At Panzhihua Iron and Steel Company P R China, in which, vanadium titanium magnetite ore is chosen as the main resource of iron making, rather than common iron ore [19–20]. During the iron making process, most of the element vanadium entered into molten iron and the titanium was left in blast furnace slag. The vanadium in molten iron will be extracted in a new added converter. The slag containing vanadium oxides and titanium oxides has considerable effects on the following hot metal pretreatment, converter steelmaking, and secondary refining. For example, the campaign life of the MgO–C bricks in vanadium containing converter is far lower than that in steelmaking converter, which cannot fulfill the normal production.

Liu et al. have studied the corrosion resistance of MgO–C bricks to smelting reduction slag containing 0.2–2.0 wt% titania by rotary immersion and stationary immersion in an electric resistance furnace [20]. Carbon can be oxidized by TiO_2 and the deterioration layer containing Ti and TiC. The corrosion reaction is quite different from that without titania.

Xu Yuan et al. have reported that Al_2O_3–C and MgO–C bricks were seriously attacked by slag containing TiO_2 from 2.4–21.7 wt% [21]. However, when the TiO_2 surpasses 30%, the corrosion slows down.

Ao Jinqing et al. have invested the corrosion process of MgO–C bricks by slag containing titania and vanadium oxides by immersion test in an induction furnace [22]. The slag containing vanadium oxides shows more serious corrosion than without vanadium oxides and TiO_2 and VO_x can oxidize the carbon and facilitate the infiltration of the slag. Formed TiC and VC_x will reoxidize at high oxygen partial pressure. Furthermore, low melting point phases maybe formed in the system.

Chen indicated that slag containing TiO_2 and V_2O_5 has lower surface tension and viscosity and has a considerable effect on properties and slag resistance of MgO–CaO materials [23].

Table 2
Chemical compositions and physical properties of developed MgO–C bricks (mass %).

Chemical composition (mass%)	**Physical properties**
75MgO	Apparent porosity: 2.4%
15C+SiC	Bulk density: 2.99 g/cm^3
$1SiO_2$	Cold crushing strength after dried at 200 °C: 49.7 Mpa
$5Al_2O_3$	Bending strength at 1200 °C for 0.5 h:22 Mpa
1CaO	Bending strength at 1400 for 0.5 h: 18.7 Mpa
$<1Fe_2O_3$	PLC after heated at 1400 °C for 3 h: 0.1%

Wen et al. studied melting properties of two converter slag containing vanadium and titanium oxides [24]. One contains 3.22% V_2O_5 and 1.75% TiO_2, another contains 1.38 wt% V_2O_5 and 0.59% TiO_2. They found that the melting temperature of the slag is <1400 °C far lower than the common converter slag. The slag containing TiO_2 and V_2O_5 is more corrosive than common slag.

Han Bingqiang et al. have studied the interaction of Al_2O_3–SiC–C brick with vanadium containing desulfurization slag [25]. FeO and V_xO have strong penetrating ability. MgO and spinel can dissolve some FeO, and the latter also can dissolve some V_2O_5 and TiO_2.

In a vanadium recovering converter, the vanadium containing slag belongs to SiO_2–Fe_2O_3–V_2O_5–TiO_2–MnO–MgO–Cr_2O_3 system, which is quite different form common slag system. For example, the typical slag contains more than 18 wt% V_2O_5 and 12 wt% TiO_2. CaO and Al_2O_3 content keep in a low level. There is a little study on the properties of such slag. The corrosion mechanism of such slag to refractories is also seldom. The suitable material selection is still controversial and need further study.

In the present paper, properties of new type MgO–C brick are developed and the degradation of the as-prepared MgO–C bricks to SiO_2–Fe_2O_3–V_2O_5–TiO_2–MnO–MgO–Cr_2O_3 slag is discussed.

2. Experimental procedures

2.1. Sample preparation

Three grades electro fused magnesia 5–3 mm, 3–1 mm and 1–0 mm, ≤ 0.088 mm, ≤ 0.088 mm SiC and -198 grade graphite flake (Fad: 87.24; Vad: 0.54; Aad; 12.24) were used as main raw materials. Si powder was used as antioxidant and