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Towards slag-resistant, anti-clogging and chrome-free castable for gas purging

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ABSTRACT

In this study, a chrome-free refractory slot plug was prepared by adding micro-magnesia powder to alumina-magnesia castable. The currently used alumina-chrome castables and improved alumina-magnesia castables were used to investigate slag infiltration and corrosion of plugs with slots of different widths at different temperatures. In addition, dynamic and thermodynamic calculations were performed to determine the causes of slag infiltration and clogging. The results showed that the slag-infiltration depths in the slots of the alumina-chrome castable were significantly higher than those in the slots of the alumina-magnesia castable. In addition, increasing the slot width, soaking time, and temperature all led to increases in the depth of slag infiltration in the slots of the purging plugs. Owing to the wettability of $(Al,Cr)_2O_3$ with respect to the molten slag being poor, the molten slag exhibited low viscosity and infiltrated deep into the slots of the alumina-chrome castable. However, as the slag infiltrated further into the slots, the dissolution of $(Al,Cr)_2O_3$ led to the formation of extensive high-melting-point phases, which existed deep in the slots and resulted in significant blockage of the purging plugs. The addition of micro-magnesia to the alumina-chrome castable resulted in the formation of a homogeneously distributed spinel with fine grains, which could absorb the FeO_x present in the slag and increased the slag viscosity. As a result, the slag-infiltration rate was reduced significantly. The slag in the slots exhibited an invariant point at a temperature lower than 1600 °C. Therefore, its oxygen burning should be easy, leading to the higher service life of such castables than that of alumina-chrome ones.

1. Introduction

As a common process, in secondary metallurgy gas stirring is applied for chemical and thermal homogenization, efficient dissolution of alloys as well as for acceleration of liquid-liquid and liquid-gas reactions, such as deoxidization and desulfurization [1,2]. Normally, argon gas is used for bottom blowing, which forms many bubbles after entering the steel bath through the purging plugs. It has a pivotal impact on the quality of the steel, so that the purging plug is a key unit concerning the stirring process [2]. Therefore, the required plug should have a higher blow-off rate, robust security and long durability. In order to improve the service life of purging plugs, their thermal shock resistance and slag resistance need to be improved.

Current purging plugs are mainly made of alumina-chrome and alumina-magnesia castables. Alumina-chrome castables exhibit excellent slag resistance; however, due to the potential leaching of Cr^{6+} into the environment, recent environmental initiatives are a driving force for the development of chrome-free refractory types [3,4]. Alumina-magnesia castables have been considered as a potential replacement of alumina-chrome castables [5]. Several studies have reported the thermal shock resistance and slag resistance of alumina-magnesia castables [6–16], and it is widely accepted that the thermal shock resistance and slag resistance can be modulated by microstructural control over the alumina-magnesia castable matrix [17]. Additives, micropowder and porous aggregates, such as TiO_2 [6,7], SiO_2 [8,9], ZrO_2 [10,11], porous corundum-spinel aggregates [12], and micro-porous corundum aggregates [13] were introduced to alumina-magnesia castables to improve their performance. In our previous work, the micro-magnesia containing particles of a smaller size and higher surface energy was introduced to replace magnesia powder in alumina-magnesia castables. It facilitates the formation of homogeneously distributed spinel with fine grain sizes, resulting in improved slag resistance and thermal shock resistance [18]. Slot plug is widely used for gas stirring of ladle refining and go through molten steel

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acceptance, ladle refining, steel casting, deslagging, and oxygen burning process in service of steelmaking. Especially in the late steel casting process, molten slag probably contact the slot plug and infiltrate into the slots because of no gas blowing, which could result in serious blockage. So oxygen burning and gas bottom blowing process need to clean the blockages and guarantee the blow-off rate. In this situation, ultra-high temperature and strong oxidation, as well as increased gas rushing pressure can lead to impaired plug. The purging plug bear the large axial stress, can easily lead to premature crack and damage [19–22]. Therefore, it is important to learn more about slag nodulation of slot plug, and avoid oxygen burning over long time.

Hence, in this study, currently used alumina-chrome castables and improved alumina-magnesia castables were used to investigate slag infiltration and corrosion of plugs with slots of different widths at different temperatures. In addition, dynamic and thermodynamic calculations were performed to determine the causes of slag infiltration and nodulation.

2. Experimental

The low-cement Cr_2O_3 containing Al_2O_3-MgO castable (LCKC) and designed no-cement Cr_2O_3 free Al_2O_3-MgO castable (NCFC) were prepared by using tabular alumina (Jiangsu Jingxin High-temperature Materials Co., Ltd., Jiangsu, China) as coarse aggregates, and fused alumina (Jiangsu Jingxin High-temperature Materials Co., Ltd., Jiangsu, China), reactive alumina (Kaifeng Special Refractory Co., Ltd., Henan, China), calcium aluminate cement (Secar71, Kerneos, Tianjin, China), microsilica (940, Elkem Silicon Materials, Shanghai, China), and micro-magnesia as matrix. The micro-magnesia was prepared by using fused magnesia powder as raw materials, which was grinded in Planetary ball mill for 2 h with 0.1 wt% organic grinding aids [23]. Table 1 presents the castables' composition.

After weighted, the raw material were mixed with 0.1 wt% dispersant FS 10 (BASF Construction Polymers GmbH, Trostberg, Germany) and 4.5 wt% water in a mixer, and then cast into 300 mm × 200 mm × 150 mm by vibration. Having been cured at room temperature for 24 h, the samples were heated at 110 °C for 24 h, and then heated at 1600 °C for 3 h, furnace cooled. Finally the sintered samples were processed by wire cutting in order to simulate the slag infiltration and corrosion of purging plugs with different slots in the situation of the late process of continuous casting in steelmaking plants. Fig. 1 shows the schematic of the experiment samples and procedure of the slag resistance experiments. The samples, of which the slag hole located in the upside center and dimensions were 200 mm (length) × 100 mm (width) × 50 mm (depth), were applied to melt the 500 g slag (Wuhan Iron and Steel (Group) Corporation, Hubei, China). The slag resistance experiments were carried out adopting the static crucible method, the sample was put in a corundum sagger to avoid slag leakage. The main chemical composition of the slag is listed in Table 2. After heated at 1600 °C, 1630 °C and 1670 °C for 3 h, 6 h, and 9 h, respectively, samples were cut open along the center line to observe the status of the infiltration and corrosion. The slag infiltration depths of the samples were measured and averaged by slide caliper and feelers. The microstructures and composition of the samples were characterized by scanning electron microscopy (SEM, JSM-6610, JEOL, Tokyo, Japan) and a linked X-ray energy dispersive spectroscopy (EDX, QUANTAX, Bruker, Berlin, Germany).

Table 1
Composition of the two castables.

Raw material	Particle size	LCKC wt%	NCFC
Tabular alumina	$8\ mm \le d \le 0.088\ mm$	70	70
Fused alumina	$d \le 0.074\ mm$	10	15
Reactive alumina	$d_{50}=2.125\ \mu m$	5	8
Fused magnesia	$d \le 0.088\ mm$	6	2
Micro-magnesia	$d_{50}=3.37\ \mu m$	–	4
Microsilica		–	1
Calcium aluminate cement		4	–
Chromium oxide		5	–

3. Results

3.1. Depth of infiltration into slots of different widths

Fig. 2 shows the depths of slag infiltration into the two castables (LCKC and NCFC) in slots with different widths over time at 1600 °C. As shown in the figure, in the case of NCFC, the slag-infiltration depths were significantly lower than those in LCKC. This indicated that a greater degree of blockage occurred in the slots of LCKC and that a greater oxygen-burning time would be required to clear these blockages and guarantee blow-off in the case of LCKC. Hence, LCKC was more likely to be damaged than NCFC, owing to the ultrahigh temperature and the high degree of oxidation required during the oxygen-burning process.

Further, it can be seen that the slag-infiltration depth for both castables increased with an increase in the soaking time. In addition, a high slag-infiltration rate was observed during the first three hours of soaking. The slag-infiltration rates during the middle and final three hours of soaking were significantly lower. Further, the slag-infiltration rates for NCFC during the middle and final three hours of soaking were similar; in contrast, for LCKC, the rate during the final three hours was significantly lower than that during the middle three hours.

In addition, the depth of slag infiltration into the slots increased with an increase in the slot width, owing to the resulting decrease in the capillary pressure in the slots.

3.2. Depth of infiltration into slots at different temperatures

The depths of slag infiltration into the two castables (LCKC and NCFC) in the slots with different widths at different temperatures after a soaking time of 9 h are shown in Fig. 3. It should be noted that since the slag had completely infiltrated through the 0.20-mm-wide and 0.25-mm-wide slots of LCKC after soaking at 1670 °C for 9 h (as shown in Fig. 4), it was difficult to measure the infiltration depths with precision. Hence, the infiltration depths for these two samples are not shown in Fig. 3. However, the results for the other samples suggested that the degree of variation was remarkably high. Similarly, NCFC showed significantly smaller slag-infiltration depths at each temperature than did LCKC. Further, for NCFC, too, the slag-infiltration depth increased with an increase in the slot width. In addition, an increase in the soaking temperature also led to an increase in the infiltration depth.

4. Dynamic calculation and analysis

Since the purging plugs were suffering slag corrosion and infiltration simultaneously during the experiment, the dynamic calculation focusing on the dissolution corrosion and slag infiltration was carried out to investigate the slag resistance behavior of the purging plugs. The research objects are the 0.25 mm-wide slots of two purging plugs soaked at 1600 °C for 9 h.

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