Influence of B$_2$O$_3$ on Crystallization Behavior of Cr-bearing Phase in Stainless Steel Slag

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Abstract. This paper discussed the effects of B$_2$O$_3$ addition on the crystallization of Cr-bearing phase in synthetic stainless steel slag after different duration of molten slag at 1500 °C. The crystallized slag with or without B$_2$O$_3$ were then characterized by using X-ray diffraction (XRD), scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectrometer (EDS) and electron probe microanalysis (EPMA). The results show that B$_2$O$_3$ does not change the phase components of slag. However, the growth of Cr-bearing phase, magnesiochromite spinel, is enhanced and the content of Cr$_2$O$_3$ in the phase attains 52.66 wt.% higher than that in the slag without B$_2$O$_3$.

Introduction

As reported by Specific Steel Enterprises Association of China, the crude stainless steel production was over 27 million tonnes in 2017 [1]. Meanwhile, significant amounts of waste slags were generated and accumulated in landfill areas. Because the byproducts contain a certain amount of chromium oxide, the experimental studies [2,3] indicated that, chromium, even if existing as Cr$^{3+}$ in slag, could oxidize to the hexavalent state (Cr$^{6+}$) in presence of CaO at ambient temperatures. The soluble Cr$^{6+}$ could leach out and cause environmental pollution. So, if chromium in slag is not adequately stabilized/imobilized, utilization of stainless steel slag is thus restricted.

In slags, chromium can be present in different mineralogical phases depending on the chemical composition, cooling process and oxygen partial pressure [4,5]. Numerous studies [6-8] have revealed that when Cr is precipitated and bound to the stable spinel structure like MgCr$_2$O$_4$ or FeCr$_2$O$_4$, Cr-leaching is greatly reduced. As a matter of fact, Cr-bearing spinels contain Cr$_2$O$_3$, Al$_2$O$_3$, FeO, MgO and Fe$_2$O$_3$ [9], which precipitate under suitable thermodynamic and kinetic conditions. Moreover, since the components in stainless steel slag are complex, the treatment conditions must be strictly controlled in order to stabilize the spinel phase in slags. Kühn et al. [10] has suggested an empirical correlation of “factor sp” to describe the factor of spinel forming in EMF stainless steel slag.

\[
\text{Factor sp} = 0.2\text{MgO} + 1.0\text{Al}_2\text{O}_3 + n\text{FeO}_x - 0.5\text{Cr}_2\text{O}_3 \ [\text{wt.\%}].
\] (1)

Where \( n \) is a number between 1 and 4, depending on the oxidation state of the slag. Obviously, the component of Al$_2$O$_3$, MgO and FeO$_x$ would be beneficial for spinel forming and then for chromium immobilizing.

Recently, W. Li and X. Xue [11] found that the stable spinel phase has a great increase in size and chromium distribution with the increasing addition of B$_2$O$_3$ content. Unfortunately, the effect of B$_2$O$_3$ on crystal growth of Cr-bearing spinel phase is not discussed in detail. It needs to be explored deeply.

The present study aims to discuss the influence of B$_2$O$_3$ on the crystallization of synthetic stainless steel slag. We focus on the precipitation of Cr$_2$O$_3$ into spinel phase and the growth of Cr-bearing phase based on XRD analysis and SEM investigation. This study will provide an alternative
technology to handle stainless steel slag both from stabilization and recovery of Cr-riched spinel in the further.

**Experimental**

**Materials Preparation**

A typical EAF stainless steel slag from factories has the following chemical composition: CaO 47.7%; SiO$_2$ 31.8%; MgO 5.0%; Al$_2$O$_3$ 4.5%; Fe$_2$O$_3$ 6.5% and Cr$_2$O$_3$ 4.0% [12]. In order to prepare the synthetic slag, analytical grade CaCO$_3$, SiO$_2$, MgO, Fe$_2$O$_3$, Cr$_2$O$_3$, Al$_2$O$_3$ and H$_3$BO$_3$ were used as raw materials. The reagents were weighed, mixed in an agate mortar with pestle to prepare batches. Isopropyl alcohol was used as the mixing medium. The total weight of each batch was 100 grams. The mixture was put into a magnesia crucible and then loaded in a bottom-loading furnace. The samples were heated in air to 1650 °C and held at this temperature for 30 min. Then, the crucible with its content was taken immediately out of the furnace and quenched in water. The quenched slags were then dried and crushed. The final compositions of the two slags by X-ray fluorescence (XRF) are shown in Table 1. It can be seen that MgO content in the two slags is small higher due to some dissolved MgO from the corrosion of magnesia crucible.

<table>
<thead>
<tr>
<th>Slag No.</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CaO</td>
</tr>
<tr>
<td>Slag-1</td>
<td>47.23</td>
</tr>
<tr>
<td>Slag-2</td>
<td>47.15</td>
</tr>
</tbody>
</table>

In order to study the effect of holding time B$_2$O$_3$ on the crystallization of stainless steel slag. 5×10 g of the above two slags in magnesia crucibles were all loaded into the even temperature zone (height: 50 mm) of a vertical furnace equipped with a MoSi$_2$ heating element. The slags were heated to 1650 °C at 5 °C/min in air and soaked for 10 min, cooled to 1500 °C at the rate of 3 °C/min. The slag samples were then held at 1500 °C for 10 min, 40 min, 90 min, 230 min and 350 min, respectively. At each end of holding time, one crucible with slag was taken out of the furnace, quenched in water and then dried for characterization.

**Methods for Characterization**

The mineralogy of the slag samples was determined using X-ray diffraction (XRD). Spectra were collected in 20 range from 10° to 80° with a step size of 0.02° using an X-ray diffractometer (D8 Advance, Bruker AXS).

In order to investigate the micro-morphology, samples were embedded, grinded, polished, and carbon coated. Backscattered electron (BSE) images were collected using an accelerating voltage of 15 kV by a scanning electron microscope (SEM, Philips XL 30). Energy dispersive X-ray spectroscopy (EDS) analysis was performed to determine the composition of microzone in the samples. Element scanning was performed at JEOL JXA-8100 (JEOL LTD).

The Photoshop software was used for backscattered electron images treatment. The boundaries of Cr-bearing phase were manually marked by the pen tool and filled with the foreground color, and then all the Cr-bearing phase grains in an image were selected together using the magic wand tool with tolerance of zero. After operations of inverse selection and deletion, only Cr-bearing phase existed in the image. And then we calculated the area of the particles with the help of NIH image J software. Area of particles were measured when the Cr-bearing phase was distinguished exactly from the backscattered electron image. A one-dimensional length L from the area was calculated using Eq.(2) [13]:

\[
L = \sqrt{\frac{4A}{\pi}}.
\]
A refers to the area of the cross-section of particles, L is the diameter of a circle with equivalent area as the crystal. So, the true diameter (D) can be calculated according to Eq.(3) [14]:

\[
L = \frac{4L}{\pi}.
\]  

(3)

**Results and Discussions**

**Influence of B\textsubscript{2}O\textsubscript{3} on Crystallization of Stainless Steel Slag**

Figure 1 shows the XRD patterns of the two slag samples crystallized at 1500 °C for 10 min. The two patterns are almost identical. Well-defined peaks are observed and the main crystalline phases are merwinite (Ca\textsubscript{3}Mg(SiO\textsubscript{4})\textsubscript{2}), magnesiochromite (MgCr\textsubscript{2}O\textsubscript{4}) and dicalcium silicate (Ca\textsubscript{2}SiO\textsubscript{4}).

Results of EDS analysis given in Table 2 show that the chemical elements in magnesiochromite phase is Mg, Fe, Al, Cr. The atomic ratio of Mg to the sum of Fe, Al and Cr is roughly equal 1/2. So we assume that Cr\textsuperscript{3+} is precipitated into spinel phase which is termed as Cr-bearing phase -Mg(Al, Cr, Fe)\textsubscript{2}O\textsubscript{4}. As presented in Table 2, the content of Cr\textsubscript{2}O\textsubscript{3} in Cr-bearing phase in Slag-2 attains 52.66 wt.%, much higher than 35.65 wt.% in slag-1. It is suggested that B\textsubscript{2}O\textsubscript{3} promotes the precipitation of chromium into spinel phase. Also, other phases analyzed by EDS microanalysis are in good consistent with the phases Ca\textsubscript{3}Mg(SiO\textsubscript{4})\textsubscript{2} and Ca\textsubscript{2}SiO\textsubscript{4} identified by XRD.

Interestingly, we find that the addition of B\textsubscript{2}O\textsubscript{3} does not change the phase compositions of synthetic slag by comparing the spectra in Figure 1. In the XRD pattern of Slag-2, no B-containing phase is observed, as is shown in Figure 2, boron is found mainly in the phase of merwinite, dicalcium silicate and matrix. We previously found that most of boron is distributed in matrix phase when the slag with 0.5 % B\textsubscript{2}O\textsubscript{3} was annealed at 1500 °C for 30 min [15]. Therefore, in the early crystallization of slag, B\textsubscript{2}O\textsubscript{3} acts as a flux. As increasing of holding time, B\textsubscript{2}O\textsubscript{3} will precipitated into merwinite and dicalcium silicate to form solid solution in the later stages of solidification.

![Figure 1. X-ray patterns of the slag held at 1500 °C for 10 min. (a) Slag-1 (b) Slag-2.](image)

**Influence of B\textsubscript{2}O\textsubscript{3} on Growth of the Cr-bearing Phase**

Figure 3 shows SEM-BSE images of the two slag samples held at 1500 °C for different times. From the images, it is intuitively seen that the size of Cr-bearing phase (marked by A) in Slag-2 is growing larger with the increase of holding time. In order to achieve more Cr-bearing phases, more than five SEM-BSE images of each specimen were chosen. According to calculation based on above 100 grains, the average diameter of Cr-bearing phase in Slag-2 grew from 6.28 to 27.21 μm as the holding time increasing from 10 to 350 min at 1500 °C. In comparison, the grains of Cr-bearing phases in Slag-1 only attain 9.27 μm after holding for 350min at 1500 °C.

It is found that the relationship between the average diameter of Cr-bearing phase (D) and the holding time (t) at 1500°C can be best fitted by Eq.(4):

\[
D = C \times t^n.
\]  

(4)
\[ D = k t^m. \]  

(4)

where \(k\) and \(m\) are constants, which are mainly decided by the holding temperature. The best fitted curves are presented in Figure 4 based on Eq.(4) and the fitted results are listed in Table 3. It is indicated that \(m\) of Slag-2 is 0.40 and much bigger than \(m=0.13\) of Slag-1. This means that the addition of \(B_2O_3\) also has a function on enhancing the growth of Cr-bearing phase obviously. It is consistent with the investigations by W. Li and X. Xue [11].

Figure 2. Element mapping of Slag-2 crystallized at 1500 °C for 230 min by EPMA.

Figure 3. SEM-BSE images of slag samples after different duration at 1500 °C. (a) 10 min(Slag-2); (b) 40 min(Slag-2); (c) 90 min(Slag-2); (d) 230 min(Slag-2); (e) 350 min(Slag-2); (f) 350 min(Slag-1).
Table 2. EDS analysis on microzones for sample corresponding to Figure 3(e) and 3(f), wt %.

<table>
<thead>
<tr>
<th>Compositions</th>
<th>A-phase</th>
<th>B-phase</th>
<th>C-phase</th>
<th>D-Matrix phase</th>
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<tr>
<td></td>
<td>Slag-1</td>
<td>Slag-2</td>
<td>Slag-1</td>
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Figure 4. Nonlinear fitted curves of the relationship between average diameter of Cr-bearing phase and holding time.

Table 3. Parameters of nonlinear fitting of the relationship between average diameter and holding time.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Slag-1</th>
<th>Slag-2</th>
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<tr>
<td>k</td>
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<tr>
<td>m</td>
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<td>R²</td>
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<td>0.99</td>
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</table>

Summary

The influence of B₂O₃ on the crystallization of Cr-bearing phase in synthetic stainless steel slag was investigated and conclusions can be drawn as follows:

1. Cr-bearing phase, Ca₃Mg(SiO₄)₂ and Ca₂SiO₄ phases precipitated as the main crystals are observed both in slag with/without B₂O₃.

2. The size of the Cr-bearing phase in slag with B₂O₃ could grow much bigger as an increase of holding time. During the crystallization, the content of Cr₂O₃ in Cr-bearing phase would reach 52.66 wt.%, higher than that in slag without B₂O₃ (35.65 wt.%).

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