Research Article

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Determination of chromium valence state in the CaO–SiO₂–FeO–MgO–CrOₓ system by X-ray photoelectron spectroscopy

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Abstract: The chromium valence states in the CaO–SiO₂–FeO–MgO–CrOₓ system were investigated by X-ray photoelectron spectroscopy (XPS). The results indicated that the XPS peaks of Cr 2p₃/₂ and Cr 2p₁/₂ locate at the binding energy of ~577 and ~586 eV, respectively. There are three kinds of chromium ions such as bivalent Cr(II), trivalent Cr(III), and hexavalent Cr(VI) in the CaO–SiO₂–FeO–MgO–CrOₓ slag. Cr(II) is the dominant valence state, and more than 77.99% Cr is trivalent Cr(III). The fraction of Cr(III)/Cr is in the range of 11.24–17.22%. The fraction of Cr(VI)/Cr is below 4.80%. The fraction of Cr(III)/Cr decreases with increasing slag basicity, Cr₂O₃ content, temperature, or oxygen pressure log(PO₂), while the fraction of Cr(II)/Cr increases with increasing basicity, Cr₂O₃ content, temperature, or oxygen pressure. The trend of change is opposite. Low log(PO₂), high Cr₂O₃ content, and high temperature are beneficial to reduce the toxic hexavalent Cr(VI). The slab basicity has little influence on the fraction of Cr(VI)/Cr.

Keywords: chromium-containing steel slag, XPS, Cr, valence state

1 Introduction

Steel slag is a by-product of steelmaking industry. In the steelmaking process, the amount of steel slag is about 10%–15% of the crude steel output [1,2]. Since the domestic steel slag comprehensive utilization level is lower than the developed countries [3,4], although the yield of Chinese crude steel is huge, still a large amount of steel slag is untreated and only stockpiled for disposal [5]. Some steel slags such as stainless steel slag, electric arc furnace steel slag, and chromium-containing hot metal steelmaking slag contain a certain amount of chromium oxides. It is possible that part of the chromium may exist in the form of toxic hexavalent chromium Cr(VI) in steel slag. Steel slag stockpiled in the open-air slag yard would pollute air, soil, and groundwater. The chromium element may exist in the form of bivalent Cr(II), trivalent Cr(III), and hexavalent Cr(VI) in silicate melts or metallurgical slag [6,7]. Thus, the chromium oxides can be expressed as CrOₓ. Therefore, study on the valence state of chromium in the metallurgical slag and its influencing factors has a very important significance for the clarification of the existing forms of chromium-containing phases and prevention of the pollution of toxic hexavalent chromium.

Considering the testing cost and the accuracy of testing results, a simple method for rapid detection of chromium valence states in slag is still sparse. Some studies also investigated the chromium valence states through thermodynamic calculation. Xiao and Mirzayousef-Jadid et al. [8,9] calculated the chromium valence states in the CaO–SiO₂–CrOₓ system. It was found that both bivalent and trivalent chromium coexist in these slags. Low slag basicity and low oxygen potential lead to the increase in divalent chromium oxide, instead of trivalent chromium oxide. Pretorius et al. [10] calculated the chromium valence states in CrOₓ–SiO₂–CrOₓ systems and found that the valence states of chromium were mostly affected by the oxygen partial pressure. In recent years, X-ray photoelectron spectroscopy (XPS) was applied to valence state detection in metallurgical slag [11–13]. XPS can carry out not only qualitative analysis of the valence states of elements in metallurgical slag but also quantitative analysis.

In this article, the research object is the CaO–SiO₂–FeO–MgO–CrOₓ system, which is the main component of...
chromium-containing steel slag. The slag samples were prepared under different experimental conditions and XPS was used to determine the chromium valence states [14,15] in the slag through qualitative analysis and semi-quantitative analysis. Through the investigation of influence factors affecting chromium valence states, we expect to provide a theoretical reference for reducing the toxic hexavalent chromium.

2 Experimental

2.1 Materials

The chemical compositions of chromium-containing steel slag used in the present study are given in Table 1. Analytical reagents CaO (≥98.0%), MgO (≥98.0%), and SiO₂ (≥99.0%) were provided by Chengdu Kelong Chemical Reagent Factory. FeO was synthesized using analytical reagent Fe₂O₃ and reduced iron powder (Fe). Fe₂O₃ (≥70.0% Fe) and Fe were obtained from Tianjin HengXing Chemical Reagent Co., Ltd and Macklin Reagent, respectively. Highly purified Cr₂O₃ (≥99.0%) from Wenzhou Dongsheng Chemical Reagent Factory was used as the starting chromium oxide.

2.2 Methods

A horizontal tube MoSi₂ furnace (SGL-1700; Shanghai Jyjing Precision Instrument Manufacturing Co., Ltd) with a proportional–integral–differential controller was used to prepare the slag samples. Fine powders of the raw materials were carefully weighed and well-mixed together in an agate mortar. A 40 g mixture was charged into a MgO crucible. The MgO crucibles containing the slag samples were positioned inside a square alumina holder. The alumina holder was pushed into the even-temperature zone of the tube MoSi₂ furnace.

According to the equilibrium of C–O reaction and the process conditions of steelmaking end point, the calculated oxygen potential log(PO₂) values are around −5.6 to −3.0. Therefore, the designed log(PO₂) values in the present work are −5.0 to −3.5 and are listed in Table 1. Gas mixtures of CO–CO₂ were employed to obtain the targeted oxygen potential. The gas compositions of CO–CO₂ were gained by equation (1) [16]. The calculated volume ratios of CO/CO₂ are listed in Table 2.

\[ \Delta G^0 = -565390 + 175.17T \] (1)

Table 1: Slag compositions and experiment parameters

| No.  | Slag composition/mass% | CaO | SiO₂ | Cr₂O₃ | FeO | MgO | R | log(PO₂) | T/K |
|------|------------------------|-----|------|-------|-----|-----|---|---------|----|
| R1   | R2                     | R3  | R4   | Cr5   | Cr6  | Cr7  | O8 | O9      | O10| T11  | T12 |
|      |                        |     |      |       |      |      |    |         |     |      |     |
| 41   | 16                     | 6   | 25   | 12    | 2.56 | −4   | 1,873 |
| 42   | 15                     | 6   | 25   | 12    | 2.80 | −4   | 1,873 |
| 43   | 14                     | 6   | 25   | 12    | 3.07 | −4   | 1,873 |
| 44   | 13                     | 6   | 25   | 12    | 3.38 | −4   | 1,873 |
| 46.8 | 15.2                   | 2   | 25   | 12    | 3.07 | −4   | 1,873 |
| 44.9 | 14.6                   | 3.5 | 25   | 12    | 3.07 | −4   | 1,873 |
| 41.1 | 13.4                   | 8.5 | 25   | 12    | 3.07 | −4   | 1,873 |
| 43   | 14                     | 6   | 25   | 12    | 3.07 | −3.5| 1,873 |
| 43   | 14                     | 6   | 25   | 12    | 3.07 | −4   | 1,873 |
| 43   | 14                     | 6   | 25   | 12    | 3.07 | −5   | 1,873 |
| 43   | 14                     | 6   | 25   | 12    | 3.07 | −4   | 1,823 |
| 43   | 14                     | 6   | 25   | 12    | 3.07 | −4   | 1,773 |

Table 2: Volume ratios of CO/CO₂

| log(PO₂) | T/K   | log K | V_co/V_co₂ |
|----------|-------|-------|------------|
| −3.5     | 1,873 | 6.62  | 36:1       |
| −4       | 1,873 | 6.62  | 20:1       |
| −4       | 1,823 | 7.05  | 33:1       |
| −4       | 1,773 | 7.51  | 57:1       |
| −4.5     | 1,873 | 6.62  | 11:1       |
| −5       | 1,873 | 6.62  | 6:1        |
Crucibles were quickly pulled out of the reaction tube and quenched in liquid nitrogen. The slag samples were separated from the crucibles and milled to below 0.074 µm, then subjected to XPS analyses.

The XPS measurements on the slag sample prepared under various conditions were carried out by means of a spectrometer (Thermo Scientific Escalab 250Xi). In the testing, Al K Alpha was used as the source gun type, and the energy type size was 0.1 eV. The measurements were conducted with a spot size of 500 µm. In order to ensure the experimental results, the vacuum degree was controlled below $5 \times 10^{-9}$ mbar.

### 3 Results and discussion

#### 3.1 Chromium spectra

Figure 2 illustrates the typical XPS wide scan spectrum of the CaO–SiO$_2$–FeO–MgO–CrO$_x$ slag. The auger peaks of the constituent elements in the slag were marked on the spectrum. Two minor peaks around the binding energies of 573–593 eV represent Cr 2p. A major peak at a binding energy of ∼284.6 eV [17] represents C 1s, which appeared due to the contamination of hydrocarbon.

For qualitative and quantitative analyses, the valence state of chromium element in the slag samples and the broad peak covering several peaks were analyzed. The Cr 2p spectra were divided into Cr 2p$_{1/2}$ and Cr 2p$_{3/2}$ by spin–orbit interaction. As shown in Figure 3, the peaks of Cr 2p$_{3/2}$ and Cr 2p$_{1/2}$ locate at the binding energy of ∼577 and ∼586 eV, respectively. The broad peak was deconvoluted into several separate peaks to determine the individual area of each peak. Generally, it can be deconvoluted into three individual valence states, i.e., Cr(II), Cr(III), and Cr(VI). The proportions of above three kinds of ions in the slag samples were deduced from the area under the computer-resolved peaks. As can be seen in Figure 3, Cr(III) is the main existing form of Cr element, Cr(II) comes second, while only trace amount of Cr(VI) in the slag. The result is consistent with that of Mittal [18]. The reason for the existence of Cr(II) and Cr(VI) is that the trivalent chromium can be reduced by the FeO in the slag and oxidized by the small amount of oxygen in the atmosphere.

#### 3.2 Effect of log($P_{O_2}$) on the valence state of chromium

In view of the absence of Cr(II) and Cr(VI) in the starting materials, the redox reactions of Cr(III) can be described as follows:
\[
\text{Cr}^{2+} + \frac{1}{4} \text{O}_2 = \text{Cr}^{3+} + \frac{1}{2} \text{O}_2^2 - \frac{\text{Cr}^{3+}}{\text{Cr}^{2+}} = k_1 P_{\text{O}_2}^{1/4}, \tag{2}
\]

\[
\text{Cr}^{3+} + \frac{3}{4} \text{O}_2 = \text{Cr}^{6+} + \frac{3}{2} \text{O}_2^2 - \frac{\text{Cr}^{6+}}{\text{Cr}^{3+}} = k_2 P_{\text{O}_2}^{3/4}. \tag{3}
\]

According to the stoichiometry of chromium,

\[
n_{\text{Cr}} = n_{\text{Cr}^{2+}} + n_{\text{Cr}^{3+}} + n_{\text{Cr}^{6+}}, \tag{4}
\]

\[
n_{\text{O}} = n_{\text{Cr}^{2+}} + 1.5 n_{\text{Cr}^{3+}} + 3 n_{\text{Cr}^{6+}}. \tag{5}
\]

Therefore, \( x \) can be calculated by the following equation:

\[
x = \frac{n_{\text{O}}}{n_{\text{Cr}}} = \frac{1.0 + 1.5 \frac{\text{Cr}^{2+}}{\text{Cr}^{3+}} + 3.0 \frac{\text{Cr}^{6+}}{\text{Cr}^{3+}}}{1.0 + \frac{\text{Cr}^{2+}}{\text{Cr}^{3+}} + \frac{\text{Cr}^{6+}}{\text{Cr}^{3+}}}
= \frac{1.0 + 1.5 k_1 P_{\text{O}_2}^{1/4} + 3.0 k_2 P_{\text{O}_2}}{1.0 + k_1 P_{\text{O}_2}^{1/4} + k_2 P_{\text{O}_2}}. \tag{6}
\]

The value of \( x \) can be obtained by relating \( \text{Cr}^{(iii)}/\text{Cr}^{(ii)} \) and \( \text{Cr}^{(vi)}/\text{Cr}^{(ii)} \) to the oxygen pressure using the law of mass action. As it is very difficult to detect the fractions of \( \text{Cr}^{(ii)}/\text{Cr}, \text{Cr}^{(iii)}/\text{Cr}, \text{and} \text{Cr}^{(vi)}/\text{Cr} \), we applied the ion and molecule coexistence theory \([19–21]\) to obtain these fractions. The calculation process is detailed in one of our previous study \([22]\).

Figure 4 shows both the calculated and experimental \( x \) in the present study. It can be found that the \( x \) in \( \text{CrO}_x \) increases with increasing oxygen pressure \( \log(\text{P}_{\text{O}_2}) \). The result is consistent with Jadid’s finding in the \( \text{CaO}–\text{SiO}_2–\text{CrO}_x \) slag and the \( \text{CaO}–\text{SiO}_2–\text{Al}_2\text{O}_3–\text{CrO}_x \) slag \([16]\). Statistics of the various valence states of chromium in the \( \text{CaO}–\text{SiO}_2–\text{FeO}–\text{MgO}–\text{CrO}_x \) slag are shown in Figure 5. The fraction of \( \text{Cr}^{(ii)}/\text{Cr} \) decreases with increasing oxygen pressure \( \log(\text{P}_{\text{O}_2}) \), while \( \text{Cr}^{(iii)}/\text{Cr} \) and \( \text{Cr}^{(vi)}/\text{Cr} \) increase. However, the increase tendency of \( \text{Cr}^{(VI)}/\text{Cr} \) is not obvious, and the fraction of \( \text{Cr}^{(VI)}/\text{Cr} \) is always below 4.5% under the present experimental conditions.

### 3.3 Effect of basicity on the valence state of chromium

Figure 6 illustrates the fractions of \( \text{Cr}^{(ii)}/\text{Cr}, \text{Cr}^{(iii)}/\text{Cr}, \text{and} \text{Cr}^{(vi)}/\text{Cr} \) as a function of slag basicity in the \( \text{CaO}–\text{SiO}_2–\text{FeO}–\text{MgO}–\text{CrO}_x \) slag. It is obvious that \( \text{Cr}^{(iii)}/\text{Cr} \) increases with increasing slag basicity, while \( \text{Cr}^{(ii)}/\text{Cr} \) decreases. It is in good agreement with the increase tendency of \( x \) in \( \text{CrO}_x \) in Jadid’s study \([8]\), and the results of comparison are shown in Figure 7. This can be interpreted as more \( \text{CaCr}_2\text{O}_4 \) and \( \text{MgCr}_2\text{O}_4 \) generated...
with increasing CaO content [23,24]. Meanwhile, it is also found that the fraction of Cr(VI)/Cr is almost constant with the increase in slag basicity.

3.4 Effect of Cr$_2$O$_3$ on the valence state of chromium

Compared with ordinary steel slag, the chromium-containing steel slag contains a higher Cr$_2$O$_3$ content. Therefore, it is necessary to make clear whether the increase in Cr$_2$O$_3$ content has an effect on the valence distribution of chromium. The influence of Cr$_2$O$_3$ content on the fractions of Cr(II)/Cr, Cr(III)/Cr, and Cr(VI)/Cr in the slag can be seen in Figure 8. With the increase in Cr$_2$O$_3$ content, the fraction of Cr(III)/Cr increases obviously, and Cr(II)/Cr shows an opposite trend. Furthermore, the fraction of Cr(VI)/Cr shows a slight downward trend. It can be concluded that increasing the amount of Cr$_2$O$_3$ in the chromium-containing steel slag does not increase the risk of generating toxic hexavalent chromium substances.

3.5 Effect of temperature on the valence state of chromium

Figure 9 shows the effect of temperature on the fractions of Cr(II)/Cr, Cr(III)/Cr, and Cr(VI)/Cr in the CaO–SiO$_2$–FeO–MgO–CrO$_x$ slag. With the increase in temperature, the fractions of Cr(II)/Cr and Cr(VI)/Cr decrease slightly, while the fraction of Cr(III)/Cr increase slightly, but on the whole, all the changes are very small.

4 Conclusions

(1) There are three kinds of chromium ions such as bivalent Cr(II), trivalent Cr(III), and hexavalent Cr(VI) in the CaO–SiO$_2$–FeO–MgO–CrO$_x$ slag. Cr(III) is the dominant valence state, Cr(II) comes second, while only trace amount of Cr(VI) in the slag. More than 77.99% Cr is trivalent Cr(III). The fraction of Cr(II)/Cr is in the range of 11.24–17.22%. The fraction of Cr(VI)/Cr is below 4.80%.

(2) The fraction of Cr(II)/Cr decreases with increasing slag basicity, Cr$_2$O$_3$ content, temperature, or oxygen pressure log(P$_{O_2}$), while the fraction of Cr(III)/Cr increases with increasing basicity, Cr$_2$O$_3$ content,
temperature, or oxygen pressure. The trend of change is just the opposite.

3) Low \( \log(PO_2) \), high Cr\(_2\)O\(_3\) content, and high temperature are beneficial to reduce the toxic hexavalent Cr\((vi)\). The slag basicity has little influence on the fraction of Cr\((vii)\)/Cr.

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