Research Article

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Determination of chromium valence state in the $\text{CaO-SiO}_2\text{-FeO-MgO-CrO}_x$ system by X-ray photoelectron spectroscopy

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Abstract: The chromium valence states in the $\text{CaO-SiO}_2\text{-FeO-MgO-CrO}_x$ system were investigated by X-ray photoelectron spectroscopy (XPS). The results indicated that the XPS peaks of Cr $2p_{3/2}$ and Cr $2p_{1/2}$ 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 $\text{CaO-SiO}_2\text{-FeO-MgO-CrO}_x$ slag. Cr(III) is the dominant valence state, and 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%. The fraction of Cr(II)/Cr decreases with increasing slag basicity, Cr_2O_3 content, temperature, or oxygen pressure $\log(\text{PO}_2)$, while the fraction of Cr(III)/Cr increases with increasing basicity, Cr_2O_3 content, temperature, or oxygen pressure. The trend of change is opposite. Low $\log(\text{PO}_2)$, high Cr_2O_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(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 CrO_x . 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 $\text{CaO-SiO}_2\text{-CrO}_x$ system. It was found that both divalent 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 $\text{CrO}_x\text{-SiO}_2$, $\text{CaO-CrO}_x\text{-SiO}_2$, and $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-CrO}_x$ 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 $\text{CaO-SiO}_2\text{-FeO-MgO-CrO}_x$ system, which is the main component of

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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 ($\geq 98.0\%$), MgO ($\geq 98.0\%$), and SiO₂ ($\geq 99.0\%$) were provided by Chengdu Kelong Chemical Reagent Factory. FeO was synthesized using analytical reagent Fe₂O₃ and reduced iron powder (Fe). Fe₂O₃ ($\geq 70.0\%$ Fe) and Fe were obtained from Tianjin HengXing Chemical Reagent Co., Ltd and Macklin Reagent, respectively. Highly purified Cr₂O₃ ($\geq 99.0\%$) from Wenzhou Dongsheng Chemical Reagent Factory was used as the starting chromium oxide.

2.2 Methods

A horizontal tube MoSi₂ furnace (SGL-1700; Shanghai Jvjing Precision Instrument Manufacturing Co., Ltd) with a proportional–integral–differential controller was used to prepare the slag samples. Fine powders of the raw

Table 2: Volume ratios of CO/CO₂

$\log(\text{PO}_2)$	T/K	$\log K$	$V_{\text{CO}}/V_{\text{CO}_2}$
–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

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 $\log(\text{PO}_2)$ values are around –5.6 to –3.0. Therefore, the designed $\log(\text{PO}_2)$ 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 at equilibrium states were gained by equation (1) [16]. The calculated volume ratios of CO/CO₂ are listed in Table 2.

$$2\text{CO} + \text{O}_2 = 2\text{CO}_2 \quad \Delta G^\theta = -565390 + 175.17T. \quad (1)$$

In view of the sensitivity of chromium to oxygen, the experiments were started by evacuating and filling the furnace chamber with purified argon before the CO–CO₂ gas mixture was introduced. Figure 1 shows the temperature control curves in experiments. When the target temperature of each experiment was reached, the samples were held for 60 min in the furnace chamber. After experiments, the MgO

Table 1: Slag compositions and experiment parameters

No.	Slag composition/mass%					R	$\log(\text{PO}_2)$	T/K
	CaO	SiO ₂	Cr ₂ O ₃	FeO	MgO			
R1	41	16	6	25	12	2.56	–4	1,873
R2	42	15	6	25	12	2.80	–4	1873
R3	43	14	6	25	12	3.07	–4	1,873
R4	44	13	6	25	12	3.38	–4	1,873
Cr5	46.8	15.2	2	25	12	3.07	–4	1,873
Cr6	44.9	14.6	3.5	25	12	3.07	–4	1,873
Cr7	41.1	13.4	8.5	25	12	3.07	–4	1,873
O8	43	14	6	25	12	3.07	–3.5	1,873
O9	43	14	6	25	12	3.07	–4.5	1,873
O10	43	14	6	25	12	3.07	–5	1,873
T11	43	14	6	25	12	3.07	–4	1,823
T12	43	14	6	25	12	3.07	–4	1,773

Figure 1: Temperature control curves in experiments.

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 5×10^{-9} mbar.

3 Results and discussion

3.1 Chromium spectra

Figure 2 illustrates the typical XPS wide scan spectrum of the CaO–SiO₂–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

Figure 2: XPS wide scan spectrum of slag sample R3.

Figure 3: The fitted Cr 2p spectrum of slag example R3.

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(PO₂) 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:

According to the stoichiometry of chromium,

$$n_{\text{Cr}} = n_{\text{Cr}^{2+}} + n_{\text{Cr}^{3+}} + n_{\text{Cr}^{6+}}, \quad (4)$$

$$n_{\text{O}} = n_{\text{Cr}^{2+}} + 1.5n_{\text{Cr}^{3+}} + 3n_{\text{Cr}^{6+}}. \quad (5)$$

Therefore, x can be calculated by the following equation:

$$\begin{aligned} x = \frac{n_{\text{O}}}{n_{\text{Cr}}} &= \frac{1.0 + 1.5 \frac{\text{Cr}^{3+}}{\text{Cr}^{2+}} + 3.0 \frac{\text{Cr}^{6+}}{\text{Cr}^{2+}}}{1.0 + \frac{\text{Cr}^{3+}}{\text{Cr}^{2+}} + \frac{\text{Cr}^{6+}}{\text{Cr}^{2+}}} \\ &= \frac{1.0 + 1.5k_1 p_{\text{O}_2}^{1/4} + 3.0k_1 k_2 p_{\text{O}_2}}{1.0 + k_1 p_{\text{O}_2}^{1/4} + k_1 k_2 p_{\text{O}_2}}. \end{aligned} \quad (6)$$

The value of x can be obtained by relating $\text{Cr}(\text{III})/\text{Cr}(\text{II})$ and $\text{Cr}(\text{VI})/\text{Cr}(\text{II})$ to the oxygen pressure using the law of mass action. As it is very difficult to detect the fractions of $\text{Cr}(\text{II})/\text{Cr}$, $\text{Cr}(\text{III})/\text{Cr}$, and $\text{Cr}(\text{VI})/\text{Cr}$, 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 x and experimental x in the present study. It can be found that the x in CrO_x increases with increasing oxygen pressure $\log(\text{PO}_2)$. The result is consistent with Jadid's finding in the $\text{CaO-SiO}_2\text{-CrO}_x$ slag and the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-CrO}_x$ slag [16]. Statistics of the various valence states of chromium in the $\text{CaO-SiO}_2\text{-FeO-MgO-CrO}_x$ slag are shown in Figure 5. The fraction of $\text{Cr}(\text{II})/\text{Cr}$ decreases with increasing oxygen pressure $\log(\text{PO}_2)$, while $\text{Cr}(\text{III})/\text{Cr}$ and $\text{Cr}(\text{VI})/\text{Cr}$ increase. However, the increase tendency

Figure 5: Fractions of $\text{Cr}(\text{II})/\text{Cr}$, $\text{Cr}(\text{III})/\text{Cr}$, and $\text{Cr}(\text{VI})/\text{Cr}$ as a function of oxygen pressure in the $\text{CaO-SiO}_2\text{-FeO-MgO-CrO}_x$ slag.

of $\text{Cr}(\text{VI})/\text{Cr}$ is not obvious, and the fraction of $\text{Cr}(\text{VI})/\text{Cr}$ 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 $\text{Cr}(\text{II})/\text{Cr}$, $\text{Cr}(\text{III})/\text{Cr}$, and $\text{Cr}(\text{VI})/\text{Cr}$ as a function of slag basicity in the $\text{CaO-SiO}_2\text{-FeO-MgO-CrO}_x$ slag. It is obvious that $\text{Cr}(\text{III})/\text{Cr}$ increases with increasing slag basicity, while $\text{Cr}(\text{II})/\text{Cr}$ decreases. It is in good agreement with the increase tendency of x in CrO_x in Jadid's study [8], and the results of comparison are shown in Figure 7. This can be interpreted as more CaCr_2O_4 and MgCr_2O_4 generated

Figure 4: x in CrO_x under different oxygen pressure.

Figure 6: Fractions of $\text{Cr}(\text{II})/\text{Cr}$, $\text{Cr}(\text{III})/\text{Cr}$, and $\text{Cr}(\text{VI})/\text{Cr}$ as a function of slag basicity in the $\text{CaO-SiO}_2\text{-FeO-MgO-CrO}_x$ slag.

Figure 7: x in CrO_x under different basicity.

with increasing CaO content [23,24]. Meanwhile, it is also found that the fraction of $\text{Cr(VI)}/\text{Cr}$ is almost constant with the increase in slag basicity.

3.4 Effect of Cr_2O_3 on the valence state of chromium

Compared with ordinary steel slag, the chromium-containing steel slag contains a higher Cr_2O_3 content. Therefore, it is necessary to make clear whether the increase in Cr_2O_3 content has an effect on the valence distribution of chromium. The influence of Cr_2O_3 content on the fractions of $\text{Cr(II)}/\text{Cr}$, $\text{Cr(III)}/\text{Cr}$, and $\text{Cr(VI)}/\text{Cr}$ in the slag can be seen in Figure 8. With the increase in Cr_2O_3 content, the fraction of $\text{Cr(III)}/\text{Cr}$ increases obviously, and

Figure 8: Fractions of $\text{Cr(II)}/\text{Cr}$, $\text{Cr(III)}/\text{Cr}$, and $\text{Cr(VI)}/\text{Cr}$ as a function of Cr_2O_3 content in the CaO–SiO₂–FeO–MgO–CrO_x slag.

Figure 9: Fractions of $\text{Cr(II)}/\text{Cr}$, $\text{Cr(III)}/\text{Cr}$, and $\text{Cr(VI)}/\text{Cr}$ as a function of temperature in the CaO–SiO₂–FeO–MgO–CrO_x slag.

$\text{Cr(II)}/\text{Cr}$ shows an opposite trend. Furthermore, the fraction of $\text{Cr(VI)}/\text{Cr}$ shows a slight downward trend. It can be concluded that increasing the amount of Cr_2O_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 $\text{Cr(II)}/\text{Cr}$, $\text{Cr(III)}/\text{Cr}$, and $\text{Cr(VI)}/\text{Cr}$ in the CaO–SiO₂–FeO–MgO–CrO_x slag. With the increase in temperature, the fractions of $\text{Cr(II)}/\text{Cr}$ and $\text{Cr(VI)}/\text{Cr}$ decrease slightly, while the fraction of $\text{Cr(III)}/\text{Cr}$ increases 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–SiO₂–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 $\text{Cr(II)}/\text{Cr}$ is in the range of 11.24–17.22%. The fraction of $\text{Cr(VI)}/\text{Cr}$ is below 4.80%.
- (2) The fraction of $\text{Cr(II)}/\text{Cr}$ decreases with increasing slag basicity, Cr_2O_3 content, temperature, or oxygen pressure $\log(\text{PO}_2)$, while the fraction of $\text{Cr(III)}/\text{Cr}$ increases with increasing basicity, Cr_2O_3 content,

temperature, or oxygen pressure. The trend of change is just the opposite.

- (3) Low $\log(\text{PO}_2)$, high Cr_2O_3 content, and high temperature are beneficial to reduce the toxic hexavalent $\text{Cr}(\text{VI})$. The slag basicity has little influence on the fraction of $\text{Cr}(\text{VI})/\text{Cr}$.

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