In order to understand the formation mechanism of Cr(VI) in chromium-containing steel slag, X-ray diffractionmetry (XRD), X-ray absorption spectroscopy (XAS) in the region of X-ray absorption near edge structure (XANES), and X-ray photoelectron spectroscopy (XPS) measurements were performed for analyzing the chromium contained in the model slag of CaO–SiO₂ base. The model slag was annealed under different temperatures and atmospheres to change the chemical state of chromium. XRD results showed that a diffraction peak that can be assigned to CaCrO₄ comprising of Cr(VI) was detected in the model–slag sample annealed under a high partial pressure of oxygen (air). XANES results showed that the Cr(VI) concentration in the slag increased by annealing under a high partial pressure of oxygen, while it was very low in the slag sample annealed under a low partial pressure of oxygen. The XANES results were consistent with the XRD results. The formation conditions of Cr(VI) were discussed on the basis of the thermodynamic characteristics of a Ca–Cr–O system. The XPS results for the slag surface were dependent on the leaching tests performed on the slag, while the XANES results were insensitive to the leaching tests. This indicates that Cr(VI) dissolved from only a surface layer of the model slag. The chromium that dissolved from the slag in an aqueous solution by the leaching test was also analyzed and was found to be in the form of Cr(VI); further, its concentration depended on the annealing conditions of the slag.

KEY WORDS: X-ray absorption near edge structure; X-ray photoelectron spectroscopy; X-ray diffraction; chemical state; chromium; slag.

1. Introduction

As a large amount of blast furnace slag and steel slag is produced and used as construction material, it is necessary to immobilize of the heavy elements contained in the slag. Steel slag is composed of several elements such as calcium, silicon, aluminum, magnesium, iron, and oxygen. In addition to these elements, a few percentages of chromium are contained in stainless steel and ferrochromium slag. The chromium that is bound in a slag matrix in the form of silicate or spinel phases can be regarded as immobilized; therefore, such slag can be utilized as construction material. However, a number of experimental results on leaching tests indicated that when slag was exposed to atmospheric oxygen, the trivalent chromium Cr(III) contained in it was very gradually oxidized to hexavalent chromium Cr(VI) that is toxic and environmentally unfavorable. Therefore, the rates of the oxidation reaction of Cr(III) were investigated in a number of long-term experiments using both original slag samples and mixtures of chromium and calcium oxides. These experiments revealed that the oxidation rate of the chromium contained in the slag was an exponentially decreasing function of time, and the oxidation reaction almost ceased in the long term. Further, in the mixtures of calcium and chromium oxides, the oxidation reaction appeared to occur at the interfaces between the chromium oxide and calcium oxide phases under atmospheric oxygen, which results in the formation of calcium chromate. However, it was earlier considered that in the slag consisting of a solid solution of calcium and chromium oxides, the oxidation reaction was likely to occur at the slag surface. Further, while the enhanced formation of Cr(VI) by calcium oxides was discussed on the basis of leaching tests, the dissolution of Cr(VI) was also investigated in practical ferrochromium slag. In order to change the chemical state of Cr(VI), the reduction of Cr(VI) contained in slag and that dissolved in water was studied by using additives such as copper smelter slag, silicates, bacteria and also by using heat treatments. In most of these studies, the concentration of Cr(VI) dissolved in water has been analyzed. Further, while the enhanced formation of Cr(VI) by calcium oxides was discussed on the basis of leaching tests, the dissolution of Cr(VI) was also investigated in practical ferrochromium slag.
sample was deduced through these procedures. On the other hand, in order to consider the storage or reuse of slag, the concentration of Cr(VI) was analyzed using X-ray absorption near-edge structure (XANES) measurements, which were carried out using synchrotron radiation. In spite of these efforts, few aspects are still unclear, for example, the concentration of Cr(VI) in slag, the dissolution processes of Cr(VI) from slag, and the influence of annealing conditions on the chemical state of the chromium contained in slag, and so on.

In this study, in order to understand the mechanism of the formation of chemical compounds containing Cr(VI) in chromium-containing steel slag, we employed CaO–SiO$_2$ base as the model slag and characterized the crystal structure and the chemical state of the chromium by using several analytical methods such as X-ray absorption spectroscopy (XAS) in the region of XANES, X-ray diffractometry (XRD), and X-ray photoelectron spectroscopy (XPS). The model slag was annealed under different conditions, in order to vary the concentrations of Cr(VI) left in the slag and that dissolved in water. In addition, the chromium concentration in the leach solution of slag particles was also determined for discussing the dissolution process of Cr(VI) from the slag samples annealed under different conditions.

2. Experimental Procedure

2.1. Sample Preparation

Referring to the content of elements in industrially produced stainless steel slag, model slag was prepared from a mixture of oxides of 51 mass% CaO, 34 mass% SiO$_2$, 5 mass% MgO, 5 mass% Al$_2$O$_3$, and 5 mass% Cr$_2$O$_3$, of which the basicity of slag (Ca/Si) was about 1.5. For simplicity, iron was not added to the model slag. After 1 mass% CaF$_2$ was added to the model slag to decrease the melting point, the model slag was melted at 1 800 K in air. The melted slag was cooled to room temperature; then, it was crashed and sieved to particles of 150 to 355 μm in diameter. These slag particles were annealed under different conditions: high partial pressure of oxygen (air) and low partial pressure of oxygen (Ar–10%H$_2$ gas with residual oxygen). In order to investigate the influence of the chemical state of Cr(VI) contained in the slag, the slag particles were annealed under a low partial pressure of oxygen, after annealing them at 1 073 K under high partial pressure of oxygen. The partial pressure of oxygen in the atmosphere of Ar–10%H$_2$ gas was estimated from the measurements of the dew point of the gas.

2.2. Measurements

The crystalline oxide components of the model slag were identified using the XRD method. The apparatus used in this study was a Rigaku RINT2000 diffractometer, in which the Cu Kα radiation was used as the incident X-rays.

In order to analyze the chemical state of chromium, the XANES spectra of the slag at Cr K absorption edge were recorded using an in-house X-ray absorption spectrophotometer, namely, Rigaku R-XAS Looper. In the XAS experiments, the Ge(311) Johannson-type bent single crystal was used as the monochromator crystal in order to obtain a high energy resolution enough to detect separately. The energy resolution ΔE calculated by using Georgopoulos and Knapp’s equation is 1.3 eV at E=6 keV (ΔE/E=2.2×10$^{-4}$) in case of the present crystal. All XANES spectra were measured by the fluorescence yield mode using a scintillation counter. In the XANES spectra, backgrounds mainly due to the elastic scattering were subtracted; then, the spectra were normalized by using absorbance calculated under assumption as isolated atom of chromium. For the model slag, the molar-concentration ratio of Cr(VI) to the total chromium (Cr(III) + Cr(VI)), denoted as R(XANES) (%), was estimated from the intensities of the pre-edge peaks arising from Cr(VI) in the normalized Cr K XANES spectra.

Cr 2p XPS spectra were recorded using an XPS apparatus, namely, a Perkin-Elmer PHI 5600 spectrometer, in which the Mg Kα radiation was used as the incident X-rays, and the photoelectron take-off angle was 45°. The ratio of the Cr(VI) concentration to the total concentration in XPS, R(XPS) (%), was estimated from the XPS spectra using the peak separation parameters of Cr(III) and Cr(VI) obtained from reference samples.

An aqueous slag solution was prepared using crashed slag particles for determining the total chromium and Cr(VI) contained in the slag by using leaching tests; the aqueous solution was vibrated in order to enhance the dissolution of chromium from the slag particles. The absorption spectrometric method using diphenylcarbazide and the inductively coupled plasma-atomic emission spectrometry (ICP-AES) measurements were employed to determine the concentrations of Cr(VI) and total Cr in the solution, respectively. These procedures are mostly described in JIS K0400-65-20.

3. Results and Discussion

3.1. XRD Analyses

Figure 1 shows an XRD pattern of as-cooled untreated slag that was obtained from the melt state. The pattern shows that the slag was composed primarily of Ca–Si–O oxide systems such as Ca$_5$SiO$_4$, Ca$_{14}$Mg$_2$(SiO$_4$)$_8$, and Ca$_5$(Mg$_5$(SiO$_4$)$_4$)$_3$; the diffraction peak positions for these oxides are also indicated in Fig. 1. In this study, these diffraction peaks were fundamentally observed for slag particles annealed under different conditions as well. However, it is noted that a significant peak assigned to CaCrO$_4$ appeared in the XRD pattern of the slag annealed at 1 073 K under a high partial pressure of oxygen, as shown in Fig. 2.

The formation condition of CaCrO$_4$ (calcium chromate) should be discussed here. The standard Gibbs free energy of the formation of CaCrO$_4$ was determined in a few studies. In the following formation reaction of CaCrO$_4$,

$$\text{CaO(s) + 1/2Cr}_2\text{O}_3(s) + 3/4\text{O}_2(g) = \text{CaCrO}_4(s)$$

the standard free-energy change for CaCrO$_4$ is expressed as

$$\Delta G^\circ = -219 250 + 121.767 T (\text{J/mol}) \ldots$$

Figure 3 shows the free-energy diagram for the formation of CaCrO$_4$, CaO, and Cr$_2$O$_3$ based on these results, in which the annealing conditions of high and low partial pressures of oxygen employed in the present study are also plotted. As the amount of chromium in the present model slag is
low, the formation condition of pure CaCrO$_4$ shown in Fig. 3 may not be necessarily applied to general cases. Nevertheless, the plots shown in Fig. 3 indicate that CaCrO$_4$ can be formed by annealing under a high partial pressure of oxygen and that CaCrO$_4$ is more easily formed at lower temperatures. Although the slag may be composed of a number of phases, this is consistent with the XRD result, indicating that the appearance of different phases sensitively depends on heat treatments.

The crystallographic structure of CaCr(VI)O$_4$ belongs to space group I 4$_1$/amdZ, which is described by calcium and Cr(VI)O$_4$ tetrahedral units. As the CaCrO$_4$ phase is formed by annealing under a high partial pressure of oxygen, the CrO$_4$ tetrahedral units are relatively as stable as the crystal of CaCrO$_4$ at low temperatures. In this study, the crystallographic phases are mainly studied by the XRD method, and the formation of the CrO$_4$ units in the slag is detected using XANES.

### 3.2. XANES Analyses

Figure 4(a) shows the XANES spectra of the untreated slag, Cr$_2$O$_3$ consisting of Cr(III), and Na$_2$CrO$_4$·4H$_2$O comprising of Cr(VI). A sharp pre-edge peak is observed at about 5.993 eV, which is assigned mainly to Cr(VI). The concentration ratio of Cr(VI) to total chromium is estimated from the pre-edge peak intensities using a relationship between the peak intensity and the Cr(VI) concentration. These spectra reveal that Cr(VI) exists in the untreated slag.
Figures 4(b) and 4(c) show the XANES spectra of the slag annealed under high and low partial pressures of oxygen, respectively; the reference spectra shown in Fig. 4(a) are also included in these figures. The results show that Cr(VI) was not detected in the slag annealed under a low partial pressure of oxygen (Ar–10%H₂ gas), and the Cr(VI) concentration in a sample annealed at 1073 K is higher than that in a sample annealed at 1273 K under a high partial pressure of oxygen. This is in agreement with the thermodynamic characteristics of Cr(VI) and Cr(III) compounds, as shown in Fig. 3, and appears to be consistent with the structural results obtained by XRD. The R(XANES) value was obtained from the above XANES spectra. Figure 5 shows the R(XANES) value as a function of the annealing time under the high partial pressure of oxygen (air). These results indicate that Cr(VI) in the untreated slag is slightly reduced by annealing at 1273 K, while it is oxidized by annealing at 1073 K.

3.3. XPS Analyses

XPS analyses were carried out for the slag particles annealed under different conditions, in order to compare the XANES results with the surface-sensitive information obtained by XPS. Figure 6 shows the Cr2p XPS spectra of the slag sample annealed at 1073 K under high partial pressure of oxygen before and after subjecting it to a leaching test. In these spectra, the Cr(VI) components were clearly observed. The results showed that the Cr(VI) concentration in the surface layer of the slag was decreased by leaching, indicating that in this case, Cr(VI) was dissolved from the surface layer. The R(XPS) values are estimated using the peak separation method. Figure 7 summarizes the R(XANES) and R(XPS) values for different samples. The XPS results were not always consistent with the XANES results; this may be attributed to the fact that during leaching tests, the reduction or oxidation reactions occur in a very thin surface layer.

3.4. Total Chromium and Hexavalent Chromium Concentrations Dissolved in Solution

The total chromium and Cr(VI) concentrations dissolved in the aqueous solution from the model slag were analyzed using the ICP-AES and absorption spectrometry. The total chromium and Cr(VI) concentrations dissolved from the untreated slag were 16 and 22 ppm, respectively. These values are fairly comparable, in spite of a difference in the measured concentrations. The results indicate that the chromium dissolved in the solution was formed as Cr(VI).

The concentrations of the total chromium and Cr(VI) dissolved from the slag annealed at 1073, 1173, and 1273 K under a high partial pressure of oxygen are plotted as a function of the annealing time, as shown in Fig. 8(a). The Cr(VI) concentration in the solution, which is almost equal to the total chromium concentration, increased with the annealing time for the slag annealed at a low temperature, whereas it decreased with the annealing time for the slag annealed at a high temperature. This result is in good agreement with the XANES results shown in Figs. 5 and 7.

The slag annealed at 1073 K, which contained about 40 ppm of Cr(VI), was subsequently annealed at different temperatures under low partial pressure of oxygen. The total chromium and Cr(VI) concentrations dissolved from the slag are shown in Fig. 8(b) as a function of the annealing time. The total chromium and Cr(VI) concentrations dissolved in the aqueous solutions from the slag were lower than those for the samples annealed at a high partial pressure of oxygen. These results are also consistent with the XANES results. Thus, although Cr(VI) in the aqueous solution dissolved from the surface layers of the slag particles, the Cr(VI) dissolved in the aqueous solution is strictly correlated to the concentration of Cr(VI) obtained in the XANES measurements. This also suggests that the particle size or the surface area of the slag must be one of the important factors, which influences the Cr(VI) concentration in an aqueous solution, as suggested in a previous study.3)
of Cr(VI) in the slag increased by annealing under a high partial pressure of oxygen, while the concentration of Cr(VI) is very low in the slag annealed under a low partial pressure of oxygen. These results were consistent with the structural results obtained by XRD. The formation of chromate compounds can be interpreted on the basis of the thermodynamic characteristics of a Ca–Cr–O system.

(3) The XPS results showed that the concentration of Cr(VI) on the slag surface was dependent on the leaching tests performed of the slag, while the bulk concentration of Cr(VI) determined by XANES were insensitive to the leaching tests. This can be attributed to the fact that XPS mainly provided the information of the surface layer, and not from a subsurface region, of a sample.

(4) The solution analyses showed that the concentration of Cr(VI) dissolved from the slag annealed under a high partial pressure of oxygen was fundamentally higher than that from the slag annealed under a low partial pressure of oxygen, and it also depended on the annealing temperature.

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