Utilization of steelmaking slag is indispensable for sustainable growth of steelmaking industry. Steelmaking slag contains nutrition such as phosphorus, silicon and iron and may be utilized as a fertilizer if elution of environmentally regulated elements is negligible. Chromium is contained in stainless steel slag as an oxide and stabilization of this chromium oxide in the slag is very important in the view of environmental protection.

Elution behavior of elements from chromium containing phases into seawater was investigated to observe the stability of phases that may exist in steelmaking slag. It was found that the existence of 2CaO·SiO2 enhanced the dissolution of chromium into seawater. Elution behavior of chromium from especially synthesized stainless steel slag into seawater was investigated. Finally, fixation of chromium was conducted by control of mineralogical phase with SiO2 addition to stainless steel slag. Addition of SiO2 to the slag was very effective for prevention of chromium elution into seawater.

**KEY WORDS:** stainless steel slag; chromium; elution; thermodynamics; phase diagram.

1. Introduction

More than 11 million tons of steelmaking slags are produced and about 0.28 million tons of steelmaking slags are landfilled per year in Japan.1) Utilization of steelmaking slag is indispensable for sustainable growth of steelmaking industry. Large amount of carbon dioxide is discharged from steelmaking industries and it is threatening the global environment at any minute. Therefore, immediate action for CO2 suppression is required. Previously, the authors2–5) have reported the dissolution behavior of constituents in steelmaking slag into seawater. The amount of nutrition dissolution such as phosphorus, silicon and iron was found to be sufficient for propagation of phytoplankton, which can fixate carbon dioxide at unit earth surface area more than any other creatures on the earth. Hence, large amount of carbon dioxide can be fixated by adding steelmaking slag into seawater. Addition of steelmaking slag into seawater as a nutrition for propagation of phytoplankton is one of the effective utilization methods of steelmaking slag.2)

Various elements are added to steel to satisfy the required material properties. For instance, chromium is added to produce stainless steel. Slag will be discharged during steel production and some amount of chromium will be distributed into stainless steel slag as an oxide. As hexavalent chromium is toxic, its elution from slag into seawater must be avoided. Stabilization by mineralogical control in slag will be effective to prevent leaching of chromium into seawater.

Elution behavior of elements from chromium containing phases that may exist in stainless steelmaking slag into seawater was investigated in the present work. Also, elution behavior of chromium from especially synthesized stainless steel slag into seawater was investigated. Finally, fixation of chromium was conducted by changing mineralogical phase in the stainless steel slag by controlling the slag composition.

2. Experimental

Crystal phases such as FeO·Cr2O3 and MgO·Cr2O3 exist in stainless steel slag.6) It is known that MgO·Cr2O3 dissolves slightly into 2CaO·SiO2 and forms solid solution and also 2CaO·SiO2 dissolves slightly into MgO·Cr2O3 according to MgO·Cr2O3–2CaO·SiO2 pseudo-binary phase diagram.7) These phases were synthesized and prepared in the laboratory for elution experiments into seawater. Also, reagent grade Cr2O3 and chromium ore provided from steelmaking company were submitted for elution experiment. Phase FeO·Cr2O3 was synthesized by placing pressed tablet of FeO and Cr2O3 mixture into a Fe crucible and heating at 1573 K under Ar atmosphere for 6 hours. Phase MgO·Cr2O3 was synthesized by placing pressed tablet of MgO and Cr2O3 mixture into MgO crucible and heating at 1673 K under Ar atmosphere for 48 hours. Solid solution of (MgO·Cr2O3–1 mass% 2CaO·SiO2)s.s. and (2CaO·SiO2–1 mass%MgO·Cr2O3)s.s. were synthesized by placing pressed tablet of oxide mixture into MgO crucible and heating at 1573 K under Ar atmosphere for 6 hours. Phase MgO·Cr2O3 was synthesized by placing pressed tablet of MgO and Cr2O3 mixture into MgO crucible and heating at 1673 K under Ar atmosphere for 48 hours. Solid solution of (MgO·Cr2O3–1 mass% 2CaO·SiO2)s.s. and (2CaO·SiO2–1 mass%MgO·Cr2O3)s.s. were synthesized by placing pressed tablet of oxide mixture into MgO crucible and heating at 1673 K under Ar atmosphere for 48 hours. Composition of chromium ore was 15 mass%FeO–13 mass%MgO–54 mass%Cr2O3–18 mass%Al2O3.
Specially prepared steel slag that contain high amount of Cr$_2$O$_3$ was provided from steel making company. The concentration of CaO, SiO$_2$, Cr$_2$O$_3$, MgO and Fe in mass% was 43.1, 35.7, 10.6, 5.1 and 0.9, respectively. Contents of other oxide were less than 3 mass%. This slag was mixed with SiO$_2$ reagent with mass ratio of 100:0, 98:2, 95:5 and 90:10 and placed in a MgO crucible, re-melted at 1823 K under Ar atmosphere and resulted in being synthesized to observe the effect of slag composition to Cr elution behavior. The sample was kept at 1823 K for 30 min and then cooled in the electric furnace with the cooling rate of 1 K/min. Also, slag sample that was not mixed with SiO$_2$ was re-melted and quenched to observe the effect of cooling rate on Cr elution behavior into seawater. The sample was quenched by withdrawing out from the furnace and immediately impinging He gas.

Weighted 1 g of steelmaking slag (270 mesh under) was put in the teflon vessel together with 0.5 l of artificial seawater (Senjyu Seiyaku, Tokyo, Japan) and kept for the aimed period under the constant oscillation mode (oscillation width 40 mm, 80 cycles per minute). Concentration of Ca and Mg in artificial seawater was 337 mg/l and 990 mg/l, respectively. Concentration of Fe, Si, Ca, Mg in artificial seawater was negligible. Temperature of the seawater was kept constant at 293 K with the aid of isothermal circulator. By adding adequate amount of reagent grade of HCl, pH of the solution was periodically adjusted to 8, which is the pH of natural seawater. At the aimed period, seawater was separated from solid substances by filtration and supplied for chemical analysis. The concentration of Fe, Si, Ca, Mg, total Cr in solutions was determined by the Induction Coupled Plasma Spectroscopy (ICP). The concentration of Cr$^{6+}$ in solutions was determined by colorimetric analysis.

3. Results and Discussion

The results of dissolution experiments from chromium containing phase into seawater are shown in Figs. 1 to 3. Dissolution of Fe from FeO·Cr$_2$O$_3$ and Cr ore was limited. Dissolution of Si from (MgO·Cr$_2$O$_3$ –1 mass% 2CaO·SiO$_2$)s.s. and (2CaO·SiO$_2$–1 mass%MgO·Cr$_2$O$_3$)s.s. was observed. Elution of Ca from the samples was not observed except for (2CaO·SiO$_2$–1 mass%MgO·Cr$_2$O$_3$)s.s. Low Mg content in seawater was observed from (2CaO·SiO$_2$–1 mass%MgO·Cr$_2$O$_3$)s.s.. Dissolution of Cr from FeO·Cr$_2$O$_3$, Cr$_2$O$_3$ and Cr ore was not observed, and Cr content in seawater in the MgO·Cr$_2$O$_3$ elution experiment was below 0.2 mg/l. However, elution of Cr from (MgO·Cr$_2$O$_3$ –1 mass% 2CaO·SiO$_2$)s.s. and (2CaO·SiO$_2$–1 mass%MgO·Cr$_2$O$_3$)s.s. into seawater was observed. Dissolution behavior of Cr$^{6+}$ was similar as that of total Cr and it was found that Cr in seawater exist mostly as hexavalent Cr. Due to some analytical error, Cr$^{6+}$ concentration was larger than total Cr concentration for some occasion. Relative error for total Cr content by measured by ICP was assumed to be approximately 0.5% and that for Cr$^{6+}$ concentration measured by colorimetric analysis was estimated to be approximately 2% by repeat measurement of identical samples. Magnesium content in seawater decreased by Mg(OH)$_2$-
Cipitation with calcium dissolution from samples as follows.

\[
\text{CaO} + \text{H}_2\text{O} + \text{Mg}^2+ = \text{Mg(OH)}_2 + \text{Ca}^{2+}
\]

Relation between \(\text{Cr}_2\text{O}_3\) contents in samples and concentration of total Cr in seawater after 30 days was shown in Fig. 4. Phases \(\text{FeO}\cdot\text{Cr}_2\text{O}_3\) and \(\text{MgO}\cdot\text{Cr}_2\text{O}_3\) are reported to exist in stainless steel slag and Cr elution from these phases was limited in spite of high \(\text{Cr}_2\text{O}_3\) contents in the sample. However, Cr elution from \((\text{MgO}\cdot\text{Cr}_2\text{O}_3 - 1\text{ mass}\% \ 2\text{CaO} \cdot \text{SiO}_2)\) s.s. and \((2\text{CaO} \cdot \text{SiO}_2 - 1\text{ mass}\% \ \text{MgO} \cdot \text{Cr}_2\text{O}_3)\) s.s. was observed. Especially, \(\text{Cr}_2\text{O}_3\) content in \((2\text{CaO} \cdot \text{SiO}_2 - 1\text{ mass}\% \ \text{MgO} \cdot \text{Cr}_2\text{O}_3)\) s.s. is little, while Cr elution was 4.5 mg/l after 30 days experiment. It was found that not the content of \(\text{Cr}_2\text{O}_3\) but the kind of crystal phase controlled the behavior of Cr elution into seawater.

Calculation of stability diagram was carried out as the same manner as the previous work\(^4,5\)) to consider the Cr elution behavior from Cr containing phases into seawater. The standard potential, activity coefficient at 298 K was referred from the previous work. The standard potential of \(\text{FeO}\cdot\text{Cr}_2\text{O}_3\) and \(\text{MgO}\cdot\text{Cr}_2\text{O}_3\) at 298 K were estimated as \(-1500\) kJ and \(-1816\) kJ, respectively.\(^8\)) Stability diagram of trivalent and hexavalent chromium ions in seawater are shown in Figs. 5 and 6. Filled circles in these figures indicate the pH and Cr content in natural seawater. The trivalent chromium content in seawater equilibrating with \(\text{FeO}\cdot\text{Cr}_2\text{O}_3\) and \(\text{MgO}\cdot\text{Cr}_2\text{O}_3\) are very low according to Fig. 5. Hence, trivalent chromium ion will not elute into seawater from these substances. Also, hexavalent chromium ion will not elute from \(\text{FeO}\cdot\text{Cr}_2\text{O}_3\), however it may elute from \(\text{MgO}\cdot\text{Cr}_2\text{O}_3\) to some extent. These estimation agree with the present result shown in Fig. 3.

It has been made clear previously\(^5\)) that \(2\text{CaO} \cdot \text{SiO}_2\) is unstable and elute into seawater. Dissolution of Si from \((\text{MgO}\cdot\text{Cr}_2\text{O}_3 - 1\text{ mass}\% \ 2\text{CaO} \cdot \text{SiO}_2)\) s.s. and \((2\text{CaO} \cdot \text{SiO}_2 - 1\text{ mass}\% \ \text{MgO} \cdot \text{Cr}_2\text{O}_3)\) s.s. into seawater and that of Ca from \((2\text{CaO} \cdot \text{SiO}_2 - 1\text{ mass}\% \ \text{MgO} \cdot \text{Cr}_2\text{O}_3)\) s.s. were observed. Dissolution of Cr from \((\text{MgO}\cdot\text{Cr}_2\text{O}_3 - 1\text{ mass}\% \ 2\text{CaO} \cdot \text{SiO}_2)\) s.s.
and (2CaO-SiO₂–1 mass%MgO·Cr₂O₃)s.s. was observed. It has been found in the present work that Cr that exists in unstable 2CaO·SiO₂ is forced to elute into seawater. Hence, prevention of 2CaO·SiO₂ formation during slag cooling would be effective to stabilize Cr in stainless steel slag.

The 2CaO·SiO₂ formation region in CaO–MgO–Al₂O₃–SiO₂ system during slow cooling are shown in Figs. 7 and 8. Controlling slag composition where 2CaO·SiO₂ is not formed by oxide addition will be essential for preventing Cr elution into seawater. Addition of MgO is not clearly effective according to Figs. 7 and 8. Addition of relatively large amount of CaO or Al₂O₃ could be effective for Cr stabilization. However, SiO₂ addition will be the best option to control the slag composition out of 2CaO·SiO₂ formation region.

The results of chromium dissolution experiments from specially prepared steel slag and re-melted slags are shown in Fig. 9. Again Cr⁶⁺ concentration was larger than total Cr concentration for some samples due to analytical error. Addition of SiO₂ to slag and remelting was effective except for 2 mass% SiO₂ addition. It was confirmed that control of slag composition by SiO₂ addition to stainless steel slag is effective for preventing Cr elution. The prevention of 2CaO·SiO₂ formation during cooling will be the key to stabilize Cr in stainless steel slag.

Controlling slag composition by SiO₂ addition to stainless steel slag is effective for preventing Cr elution. The formation of unstable 2CaO·SiO₂–MgO·Cr₂O₃ solid solution was prevented due to the lack of time for efficient Cr diffusion into 2CaO·SiO₂.

4. Conclusions

Constituents dissolution experiments from chromium containing phase into seawater were conducted. Dissolution of Cr from FeO·Cr₂O₃, Cr₂O₃ and Cr ore was not observed, and Cr content in seawater for the MgO·Cr₂O₃ elution experiment was below 0.2 mg/l. Elution of Cr from (MgO·Cr₂O₃–1 mass% 2CaO·SiO₂)s.s. and (2CaO·SiO₂–1 mass%MgO·Cr₂O₃)s.s. was observed. Dissolution behavior of total Cr were similar to that of Cr⁶⁺ and it is found that Cr in seawater exist mostly as hexavalent Cr ion. It was found that not the content of Cr₂O₃ but the kind of crystal phase controls the behavior of Cr elution into seawater.

Fig. 7. Region of 2CaO·SiO₂ formation in CaO–MgO–Al₂O₃–SiO₂ system during cooling.

Fig. 8. Region of 2CaO·SiO₂ formation in CaO–MgO–Al₂O₃–SiO₂ system during cooling.

Fig. 9. Dissolution behavior of total Cr and Cr⁶⁺ from remelted Cr-containing slags into artificial seawater.
steel slag was effective for preventing 2CaO·SiO2 formation and Cr elution into seawater. Also, quenching the slag sample was found to be very effective to stabilize Cr in the slag.

REFERENCES