Note

Selective Chlorination Reaction of Cu_2O and FeO Mixture by CaCl_2

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1. Introduction

With the development of metallurgical industry, the waste steel scrap has been recycled as a valuable iron source. However, due to some deleterious elements, mainly copper, cannot be removed by oxidizing- or reducing-refining during the present steelmaking process, the accumulation of tramp elements has become a widely concerned problem. Additionally, a large amounts of the secondary resources such as the copper slag contained high iron content (about 40 mass% or higher) need to be utilized. However, the residual copper content of copper slag is approximately 2 mass% (Jinchuan, China), which affected the utilization of copper slag as a valuable iron source. Therefore, the separation and removal of copper from iron had become so important to the recycling of Cu-contained scrap and the utilizing of secondary resource of copper slag.

Under the current ironmaking and steelmaking process, the copper in scrap or in copper slag will be almost entirely transferred to the molten iron or steel. However, due to the thermodynamic reason, it is difficult to separate copper and iron by oxidation and reduction reactions during the steelmaking process. Some investigations have been made on the removal of copper in melt using sodium sulfide or sodium sulfate fluxes,^{1,2)} or from solid scrap by $\text{O}_2\text{--Cl}_2$ gas mixtures reaction,³⁾ or from carbon saturated molten iron by FeCl_2 ⁴⁾ or oxidative removal *via* Ag phase.⁵⁾ Recently, the selective chlorination^{6–18)} has been used to separate Zn and Pb from the steelmaking dust. In our previous works,^{16,17)} CaCl_2 was employed as the chlorinating agent to selectively chlorinate Zn from $\text{ZnO--Fe}_2\text{O}_3$ or ZnFe_2O_4 system. In present study, the selective chlorination of copper from $\text{Cu}_2\text{O--FeO}$ mixture by CaCl_2 will be investigated. The thermodynamics of chlorination reaction and the chlorination

behavior of copper in the Fe--Cu--O--CaCl_2 system were discussed.

2. Thermodynamic Analysis of the Cu--Fe--O--CaCl_2 System

Figure 1 shows the chemical potential diagram of the Cu--Fe--Ca--O--Cl system at 1 273 K calculated by FactSage 6.1, where mole ratios of both Cu and Ca to Fe--Cu--Ca are 0.2, and the activities of CuCl(l) and $\text{CaCl}_2\text{(l)}$ are unity. Copper could be selectively chlorinated while iron oxide is stable in the most of the region in the figure. Figure 2 shows the vapor pressures of the chloride of Cu, Fe and Ca. It is seen that FeCl_3 has a higher vapor pressure than Cu_3Cl_3 , CuCl , FeCl_2 and CaCl_2 . Therefore, it is necessary to control the chemical potential in a certain region in Cu--Fe--O system for the removal and separation of Cu from iron. And the chlorination process of $\text{Cu}_2\text{O--FeO}$ with CaCl_2 will be expected as reaction (1) not reaction (2).

The calculated standard Gibbs energy change of the reac-

Fig. 1. Chemical potential diagram of the Cu--Fe--Ca--O--Cl system at 1 273 K.

Fig. 2. The vapor pressures of the chloride of Cu, Fe and Ca.

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tion (3) from (1) and (2) shows that FeO is stable than Cu₂O above 1675 K. But if the vapor pressures of FeCl₂ and CuCl, expressed by Eqs. (4) and (5), were considered, the Gibbs energy change of the reaction (3) changed to Eq. (6), FeO will be stable than Cu₂O at any temperature. The reaction (1) will occur if the partial pressure of gaseous product of CuCl or Cu₃Cl₃ was decreased to enough low pressure. Because of the high vapor pressure of copper chlorides, it is considered that copper could be removed from the Cu–Fe–O system by chlorination and evaporation with certain conditions.

$$\lg(p_{\text{CuCl}}/p^\theta) = 5.18 - \frac{10\,074}{T} \quad (1\,000\text{--}1\,700\text{ K}) \dots (4)$$

$$\lg(p_{\text{FeCl}_2}/p^\theta) = 5.14 - \frac{6\,794}{T} \quad (1\,000\text{--}1\,700\text{ K}) \dots (5)$$

$$\Delta G^\circ = -31\,124 - 34T \dots (6)$$

3. Experimental

The chlorination reaction of Cu₂O–FeO–CaCl₂ was measured by gravimetry in the temperature between 1123 and 1273 K in N₂ gas atmosphere. **Figure 3** shows the schematic diagram of experimental apparatus. The samples were prepared by mixing reagent Cu₂O, FeO and CaCl₂ powders dehydrated at 473 K for 2 hours with the weight ratio of 1.0 g /9.0 g /0.8 g. 1.5 g of sample was put into an Al₂O₃ crucible and the crucible was inserted into a hot zone of an electric furnace (FeCrAl coil) flowed by N₂ as carrier gas. The weight changes of the samples before and after the experiments were measured at 1123, 1223 and 1273 K with 1, 2, 3 and 4 hours. In order to avoid the effect of water absorption of chloride on weight of sample, after each experiment, all residues in the crucible were dissolved with acid, and their chemical compositions were analyzed by atomic absorption spectrophotometer. So the amount of Cu, Fe and Ca in sample can be determined, respectively.

4. Results and Discussion

From the change of the amount of Cu, Fe and Ca in the initial sample and residues, the evaporation ratios of Cu, Fe and Ca were calculated by Eq. (7).

$$R_i^{\text{eva}} = \frac{w_{0,i} - w_i}{w_{0,i}} \dots (7)$$

where, R_i^{eva} (mass%) is the evaporation ratio of element i ; $w_{0,i}$ and w_i (g) are the amounts of element i in the initial sample and residues; and i represents Cu, Fe and Ca, respectively.

Figure 4 shows the change of evaporation ratio of Cu, Fe and Ca with time at 1123, 1223 and 1273 K. The evaporation ratios of Cu increased with the reaction time and temperature. At 1273 K and 4 hours, the evaporation ratios of Cu reached 55.5%, but the evaporation ratios of Fe and Ca were simultaneously 4.0% and 2.1%, respectively. These results have demonstrated that copper in the Fe–Cu–O system could be selectively chlorinated by CaCl₂ and removed from the reaction system.

In our previous works,^{16,17)} the selective chlorination

Fig. 3. Schematic diagram of experimental apparatus.

Fig. 4. Change of evaporation ratio of Cu, Fe and Ca with time at different temperature.

reaction between ZnO–Fe₂O₃ or ZnFe₂O₄ and CaCl₂ was considered as a liquid-solid reaction, and the rate-determining step is chemical reaction, such as the chlorination reaction of zinc oxide, or the interfacial evaporation of ZnCl₂ from reaction system. The similar mechanism should be proposed for FeO–Cu₂O–CaCl₂ system. So the increases of the reaction rate of FeO–Cu₂O and CaCl₂, and vapor pressures of Cu₃Cl₃ or CuCl, will enhance the effect of the separation of copper and iron, and the removal rate of copper from FeO–Cu₂O–CaCl₂ system.

Additionally, according to the reaction (1), if the acidic oxide composition is added into the reaction system, thermodynamically, the reaction (1) would be occurred more easily. So, in our future work, the composition of reaction system will be investigated to obtain an optimal separation of copper and iron.

5. Conclusions

Copper can be separated from Fe–Cu–O system by using the selective chlorination and evaporation process thermodynamically and experimentally. For FeO–Cu₂O–CaCl₂ system, the evaporation ratio of Cu increased with the reaction time and temperature, and reached 55.5% at 1273

K and 4 hours. Simultaneously, the evaporation ratios of Fe and Ca were 4.0% and 2.1%, respectively.

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REFERENCES

- 1) T. Imai and N. Sano: *Tetsu-to-Hagané*, **74** (1988), 640.
- 2) C. Wang, T. Nagasaka, M. Hino and S. Ban-ya: *ISIJ Int.*, **31** (1991), 1300.
- 3) K. Matsumaru, M. Susa and K. Nagata: *Tetsu-to-Hagané*, **82** (1996), 799.
- 4) M. Sasabe, E. Harada and S. Yamashita: *Tetsu-to-Hagané*, **82** (1996), 129.
- 5) K. Yamaguchi and H. Ono: *ISIJ Int.*, **52** (2012), 18.
- 6) B. Zhang, X. Yan, K. Shibata, T. Uda, M. Tada and M. Hirasawa: *Mater. Trans.*, **41** (2000), 1342.
- 7) Y. Zhang and E. Kasai: *ISIJ Int.*, **44** (2004), 1457.
- 8) J.-M. Yoo, B.-S. Kim, J.-C. Lee, M.-S. Kim and C.-W. Nam: *Mater. Trans.*, **46** (2005), 323.
- 9) H. Matsuura and F. Tsukihashi: *ISIJ Int.*, **45** (2005), 1804.
- 10) W.-G. Seo, H. Matsuura and F. Tsukihashi: *Metall. Mater. Trans. B*, **37B** (2006), 239.
- 11) H. Matsuura and F. Tsukihashi: *Metall. Mater. Trans. B*, **37B** (2006), 413.
- 12) H. Matsuura, T. Hamano and F. Tsukihashi: *ISIJ Int.*, **46** (2006), 1113.
- 13) H. Matsuura, T. Hamano and F. Tsukihashi: *Mater. Trans.*, **47** (2006), 2524.
- 14) G. De Micco, G. G. Fougá and A. E. Bohe: *Metall. Mater. Trans. B*, **38B** (2007), 853.
- 15) K. Yajima, H. Matsuura and F. Tsukihashi: *ISIJ Int.*, **49** (2009), 10.
- 16) T. Guo, X. J. Hu, H. Matsuura, F. Tsukihashi and G. Z. Zhou: *ISIJ Int.*, **50** (2010), 1084.
- 17) T. Guo, X. J. Hu, X. M. Hou, H. Matsuura, F. Tsukihashi and G. Z. Zhou: *J. Univ. Sci. Technol. B.*, **33** (2011), 474.
- 18) D. Zhu, D. Chen, J. Pan and G. L. Zheng: *ISIJ Int.*, **51** (2011), 1773.
- 19) E. T. Turkdogan: *Physical Chemistry of High Temperature Technology*, Academic Press, New York, (1980), 7, 10, 11.