Thermodynamics of Indium Dissolution in Molten CaO-based Slags

*Kyu Yeol KO and Joo Hyun PARK**

School of Materials Science and Engineering, University of Ulsan, Ulsan 680-749, Korea

Abstract: The solubility of indium in the $CaO\text{-}SiO_2\text{-}Al_2O_3$ slag was measured by a thermochemical equilibration technique. The dissolution mechanism of indium into the $CaO\text{-}SiO_2\text{-}Al_2O_3$ slag at 1773 K under reducing atmosphere was elucidated. The indium solubility increases in calcium silicate based flux and decreases in calcium aluminate based flux with increasing oxygen partial pressure. Also, it decreases by increasing the basicity of slag, followed by an increase with increasing basicity of slag, indicating that indium dissolution mechanism changes according to the basicity of slag. Therefore, a dissolution mechanism of indium can be constructed as following equation;

$$\mathrm{In(s)} + \frac{1}{4}\mathrm{O_2(g)} = (\mathrm{In^+}) + \frac{1}{2}(\mathrm{O^{2-}}) \quad \text{(in high silica region)}$$

$$\mathrm{In(s)} + \frac{1}{2}(\mathrm{O^{2-}}) = (\mathrm{In^-}) + \frac{1}{4}\mathrm{O_2(g)} \quad \text{(in low silica region)}$$

The enthalpy change of indium dissolution reaction is negative, indicating that the dissolution is an exothermic reaction. The solubility of indium is strongly dependent on the content of silica. The activity coefficient, and thus the excess free energy of In_2O linearly decreases with increasing silica content, indicating that the In_2O is believed to behave as a weak basic oxide in high silica region. Therefore, it is recommended to use suitable flux which corresponds to the $CaO\text{-}Al_2O_3\text{-}20wt\%\ SiO_2$ in order to minimize the indium loss during pyrometallurgical processing of In-containing materials.

Key words: Indium, Solubility, Basicity, Dissolution mechanism, $CaO\text{-}SiO_2\text{-}Al_2O_3$ slag

1. Introduction

Indium is usually produced as a minor by-product of lead and zinc smelting and refining processes, and is used in flat panel display (Indium-Tin-Oxide, ITO) and thin film solar cell ($CuInSe_2$, $CuInGaSe_2$), etc. Recently, the pyrometallurgical recycling of indium-containing electric parts and dental materials has been issued in terms of "Urban Mining" due to very high cost and scarceness of indium.[1,2] However, the dissolution mechanism of indium into the slag phase has not been fully understood yet.

The literature contains only two experimental studies on the distribution of indium between lead and slags. One of them was carried out on the distribution of indium between molten lead and the $SiO_2\text{-}CaO\text{-}MgO\text{-}FeO\text{-}PbO\text{-}Al_2O_3$ slags by Johnson et al.[3] The experiments were conducted at 1473 K and oxygen partial pressure of $p(O_2)=10^{-12}$ atm using a $CO\text{-}CO_2$ gas mixture. They found that the indium distribution ratio between metal and slag, i.e. $[\text{wt\% In}]_{\text{metal}} / (\text{wt\% In})_{\text{slag}}$, was about 50, and it increased as the basicity, expressed as $(CaO+MgO)/SiO_2$, increased for the FeO/SiO_2 values from 1.3 to 1.8. In addition, it was independent of the FeO/SiO_2 ratio in the basicity ranges from 0.4 to 0.8. Nevertheless, this was not certain because the scatter in the data was substantial.[3] The other was performed by Hoang and Swinbourne between molten lead and the FeO-CaO-SiO_2-8wt% Al_2O_3 slag system under $p(O_2)=10^{-12}\sim10^{-10}$ atm.[4] It was found that the indium distribution ratio between metal and slag was a function of the FeO/SiO_2 ratio and was independent of the CaO/SiO_2 ratio, and the highest values of the indium distribution ratio were for the most FeO rich slag. Besides, indium has been shown to exist in the FeO-CaO-SiO_2-Al_2O_3 slag as "InO", i.e. indium was divalent.[4] Dissolution mechanism of indium, however, was not established in their experiments.

In the present work, therefore, the solubility of indium in the CaO-SiO_2-Al_2O_3 slag was measured at 1773 K and under highly reducing atmosphere over a wide range of composition within the liquid area in the slag system in order to elucidate the dissolution mechanism of indium in the metallurgical slags under reducing conditions.

2. Experimental

2.1 Sample preparation

The slag samples were prepared using reagent-grade Al_2O_3, SiO_2, and CaO calcined from $CaCO_3$ at 1273 K for 10 hours. The slag (3.0g) and indium (1.0±0.2g) were held in graphite crucibles under a CO atmosphere for equilibration. For measuring the effect of oxygen partial pressure on the indium solubility, CO was diluted by Ar, which was purified using not only silica gel but also Mg turnings at 723 K. The oxygen partial pressure can be calculated according to the following reaction;[5]

$$\mathrm{C(s)}+\frac{1}{2}\mathrm{O_2(g)}=\mathrm{CO(g)},\quad \Delta G^{\mathrm{o}}=-114{,}445-85.8T\ \mathrm{(J/mol)} \qquad [1]$$

where $a_{\mathrm{C}} = 1$ because a graphite crucible was used in this study. As the CO/(CO+Ar) ratio varied from 1.0 to 0.3, the oxygen partial pressure changed from $p(O_2)=1.96\times10^{-16}$ to 1.76×10^{-17} atm at 1773 K. CO gas was passed through the Drierite®, $Mg(ClO_4)_2$, silica gel, and soda lime for eliminating moisture and impurities. The time for equilibration was preliminarily determined.

2.2 Measurement

A super-kanthal electric furnace was used for an equilibration of the CaO-SiO_2-Al_2O_3 slag and pure (99.99% purity) indium metal. The temperature was controlled within ±2 K using a B-type (Pt-30wt% Rh/Pt-6wt% Rh) thermocouple and a PID controller. The schematic diagram of experimental apparatus is shown in Figure 1.

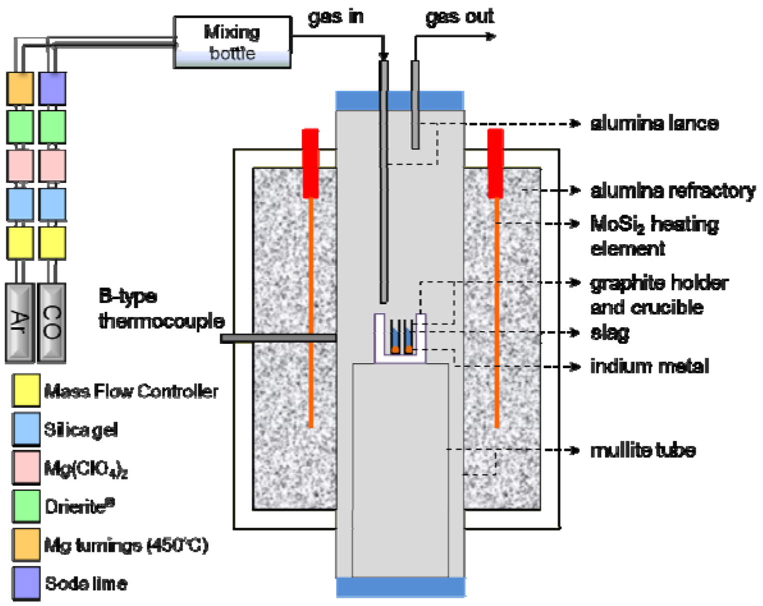

Fig.1 Schematic diagram of the experimental apparatus.

After equilibrating for 12 hours, the samples were quenched by dipping the crucible into brine and crushed for chemical analysis. The indium content in the slag samples was determined using ICP-AES (iCAP6500, Thermo Scientific, Waltham, MA) and the equilibrium composition of slag was determined using XRF spectroscopy (S4 Explorer, Bruker AXS Inc., Madison, WI).

3. Results and Discussion

3.1 Dependence of the solubility of Indium on the oxygen partial pressure

The general formula of the indium dissolution reaction into the slag can be described by the following equation:

$$\mathrm{In(s)} + m\mathrm{O_2(g)} + n(\mathrm{O^{2-}}) = (\mathrm{InO}^{2n-}_{(2m+n)}) \qquad [2]$$

$$K_{[2]} = \frac{a_{\mathrm{InO}^{2n-}_{(2m+n)}}}{a_{\mathrm{In}} \cdot p^m_{\mathrm{O_2}} \cdot a^n_{\mathrm{O^{2-}}}} = \frac{f_{\mathrm{InO}^{2n-}_{(2m+n)}} \cdot (\mathrm{wt\,\%\,InO}^{2n-}_{(2m+n)})}{p^m_{\mathrm{O_2}} \cdot a^n_{\mathrm{O^{2-}}}} \qquad [3]$$

where $K_{[2]}$, a_i, f_i and $p_{\mathrm{O_2}}$ are the equilibrium constant of Eq. [2], the activity and the activity coefficient of component *i*, and the oxygen partial pressure, respectively. As the standard state of indium is taken as the pure solid indium, the activity of indium is unity. Thus,

$$\log(\text{wt\% InO}_{(2m+n)}^{2n-}) = m\log p_{O_2} + n\log a_{O^{2-}} - \log f_{\text{InO}_{(2m+n)}^{2n-}} + C' \qquad [4]$$

From Eq. [4], the solubility of indium is expected to have a linear relationship with the oxygen partial pressure at a fixed temperature and slag composition in logarithmic form.

In Figure 2, the solubility of indium in the 31wt% CaO-56wt% SiO_2-13wt% Al_2O_3 system and that in the 48wt% CaO-11wt% SiO_2-41wt% Al_2O_3 system at 1773 K are shown as a function of oxygen partial pressure. In high silica region, indium solubility, log (wt% In), linearly increases with increasing oxygen potential, $\log p_{O_2}$, with the slope of 0.27, which is close to 0.25, indicating that the stoichiometric coefficient of "*m*" in Eqs. [2] and [4] would be 1/4. In low silica region, the solubility of indium follows different mechanism. The solubility of indium at low silica region decreases with increasing oxygen potential. The slope of -0.28, which is close to -0.25, indicating that the stoichiometric coefficient of "*m*" in Eqs. [2] and [4] would be -1/4. The dependence of indium solubility on the oxygen partial pressure is very similar to that of silver in the 55mol% CaO-45mol% B_2O_3 flux at 1773 K and that of copper (Cu^+) in the CaO-Al_2O_3-MgO slag at 1873 K.[5,6]

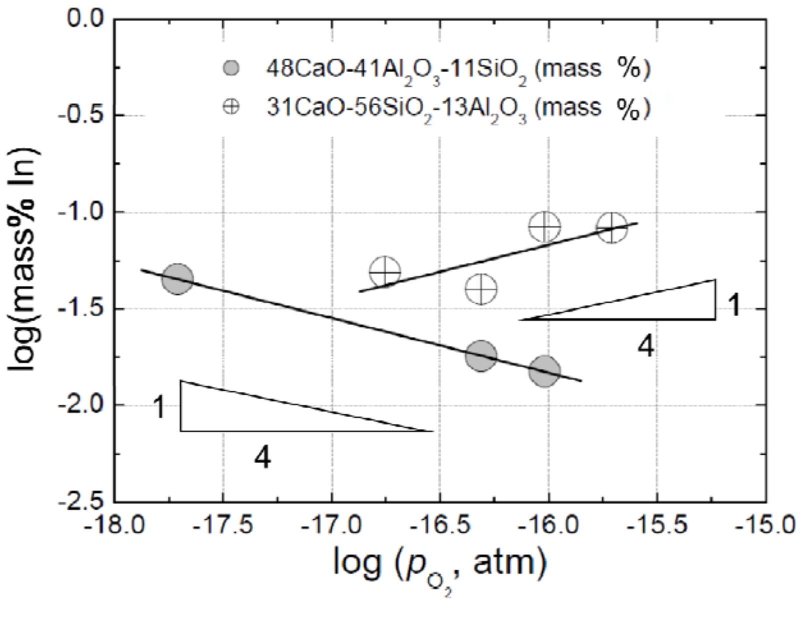

Fig. 2 Dependence of indium solubility in the CaO-SiO_2-Al_2O_3 system on the oxygen partial pressure at 1773K

3.2 Relationship between the solubility of Indium and the activity of basic oxide

The effect of basicity on the dissolution behavior of indium can be estimated by considering the relationship between log (wt% In) and log a_{CaO} from Eq. [4], assuming that the activity of CaO is in proportion with that of O^{2-} ions at a given oxygen partial pressure.[7-11] In Figure 3, the solubility of indium is plotted against the activity of CaO in the entire slag at 1773 K. The indium solubility, log (wt% In), linearly decreases by increasing the activity of CaO at high silica region. The slope closes to -1/2, although some experimental scatters are observed. From this experimental finding, it is suggested that the stoichiometric coefficient "*n*" in Eqs. [2] and [4] is -1/2. In low silica region, the indium solubility linearly increases by increasing the activity of CaO. The slope closes to 1/2, indicating that the stoichiometric coefficient "*n*" in Eqs. [2] and [4] is 1/2. Here, the activity of CaO in the CaO-SiO_2-Al_2O_3 slag at 1773 K was calculated by FactSage^{TM}6.2 (ESM Software, Hamilton, OH), which is a commercial thermochemical computing program.[12,13] This software has been successfully applied in metallurgical slag systems.[14-18]

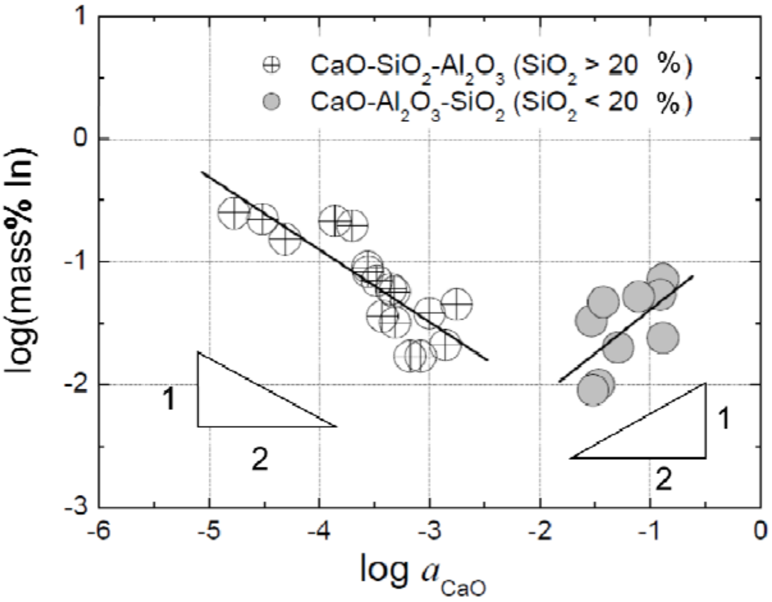

Fig. 3 Dependence of indium solubility on the activity of CaO in the CaO-SiO_2-Al_2O_3 slag at 1773K

Consequently, Eq. [2] can be rewritten as follows;

$$\mathrm{In(s)} + \frac{1}{4}\mathrm{O_2(g)} = (\mathrm{In^+}) + \frac{1}{2}(\mathrm{O^{2-}}) \qquad \text{(in high silica region)} \qquad [5]$$

$$\mathrm{In(s)} + \frac{1}{2}(\mathrm{O^{2-}}) = (\mathrm{In^-}) + \frac{1}{4}\mathrm{O_2(g)} \qquad \text{(in low silica region)} \qquad [6]$$

3.3 Correlation between the Indium capacity and the sulfide capacity

From a dissolution reaction of indium which is given in Eqs. [5] and [6], the indium capacity can be defined using an equilibrium constant of Eqs. [5] and [6] as follows.

$$C_{\mathrm{In}^+} = \frac{K_{[5]}}{f_{\mathrm{In}^+} \cdot a_{\mathrm{O}^{2-}}^{0.5}} = (\mathrm{wt\%\ In}^+) \cdot \frac{1}{p_{\mathrm{O}_2}^{0.25}} \qquad [7]$$

$$C_{\mathrm{In}^-} = \frac{K_{[6]} \cdot a_{\mathrm{O}^{2-}}^{0.5}}{f_{\mathrm{In}^-}} = (\mathrm{wt\%\ In}^-) \cdot (p_{O_2})^{0.25} \qquad [8]$$

Alternatively, the dissolution of sulfur into molten slag is expressed by Eq. [9] and thus the sulfide capacity is defined as Eq. [10];[19,20]

$$\frac{1}{2}\mathrm{S}_2(\mathrm{g}) + (\mathrm{O}^{2-}) = (\mathrm{S}^{2-}) + \frac{1}{2}\mathrm{O}_2(\mathrm{g}) \qquad [9]$$

$$C_{\mathrm{S}^{2-}} = \frac{K_{[9]} \cdot a_{\mathrm{O}^{2-}}}{f_{\mathrm{S}^{2-}}} = (\mathrm{wt\%\ S}^{2-}) \cdot \left[\frac{p_{\mathrm{O}_2}}{p_{\mathrm{S}_2}}\right]^{\frac{1}{2}} \qquad [10]$$

Eliminating the $a_{\mathrm{O}^{2-}}$ term in Eqs. [7] and [8] and [10], the relationship between indium and sulfide capacities in the high and low silica region is derived, respectively, as follows:

$$\log C_{\mathrm{In}^+} = -\frac{1}{2}\log C_{\mathrm{S}^{2-}} - \log(f_{\mathrm{In}^+} \cdot f_{S^{2-}}^{0.5}) + \log(K_{[5]} \cdot K_{[9]}^{0.5}) \qquad [11]$$

$$\log C_{\mathrm{In}^-} = \frac{1}{2}\log C_{\mathrm{S}^{2-}} + \log\frac{f_{\mathrm{S}^{2-}}^{0.5}}{f_{\mathrm{In}^-}} + \log\frac{K_{[6]}}{K_{[9]}^{0.5}} \qquad [12]$$

Thus, the indium capacity is expected to have a linear relationship with the sulfide capacity at a fixed temperature in logarithmic form assuming that the composition dependence of the second term in the right-hand side would not be significant.

Figure 4 shows the relationship between the indium capacity and the sulfide capacity, which was measured by Kalyanram et al.,[21] in logarithmic form in the CaO-SiO_2-Al_2O_3 slag at 1773 K. The indium capacity at high silica region decreases linearly with increasing sulfide capacity at a fixed temperature in logarithmic form. The slope of the line obtained from least square regression is about -0.64, which is close to -1/2. In the low silica region, indium capacity increases linearly with increasing sulfide capacity. The slope is 0.45, which is close to 0.5. Therefore, Eqs. [5] and [6] are comparatively reasonable from the viewpoint of slag basicity.

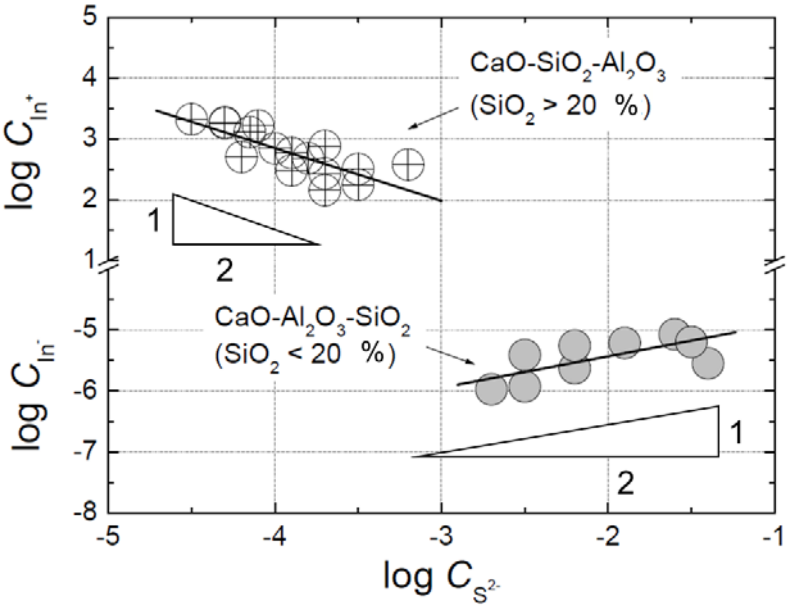

Fig.4 Relationship between the sulfide capacity and the indium capacity of the CaO-SiO_2-Al_2O_3 slag at 1773K

3.4 Dependence of the solubility of Indium on temperature

Dependence of the solubility of indium in the CaO-SiO_2-Al_2O_3 system on temperature is shown in Figure 5. The solubility of indium, log (wt% In) linearly decreases with increasing temperature. The enthalpy changes for dissolution of solid indium in the 70wt% SiO_2 and 33wt% SiO_2 melts (CaO/Al_2O_3=1.0) are calculated from the slopes of the lines based on the van’t Hoff equation which is given in Eq. [13].[22]

$$\left[\frac{\partial \log K}{\partial\left(\frac{1}{T}\right)}\right]_P = -\frac{\Delta H_r^{\circ}}{2.303R} \qquad [13]$$

The enthalpy changes calculated from Figure 5 and Eq. [13] for each system are -139.0 and -90.0 kJ/mol, respectively, indicating that the dissolution is an exothermic reaction.

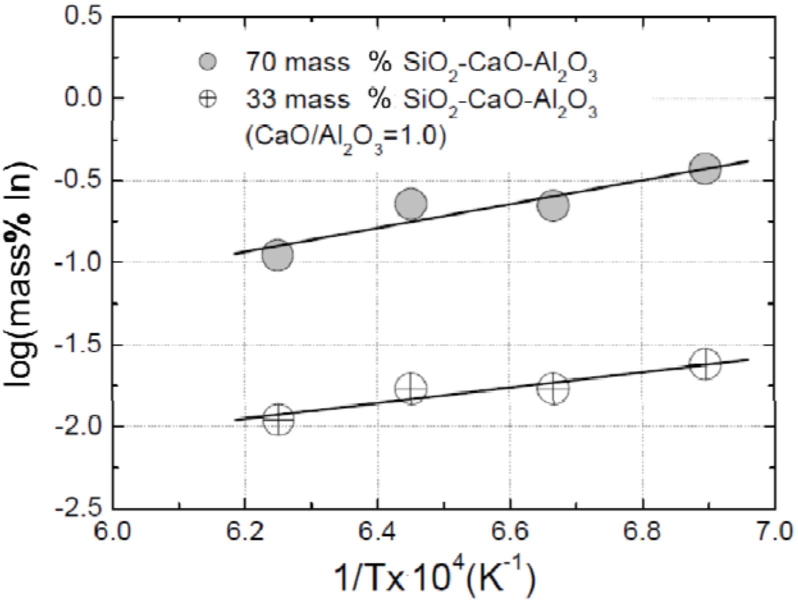

Fig. 5 Effect of temperature on the solubility of indium in the CaO-SiO_2-Al_2O_3 melts.

Hoang and Swinbourne reported that indium exists as 'InO' in the FeO-SiO_2-CaO-8wt% Al_2O_3 slag under relatively oxidizing atmosphere, $p(O_2)=10^{-12}\sim10^{-10}$ atm.[4] However, indium oxide in the present work is expected to exist as 'In_2O' in the CaO-SiO_2-Al_2O_3 (SiO_2 > 20wt%) slag under highly reducing atmosphere. Based on this finding, the indium dissolution reaction in a molecular form may be written as follows;[5,23]

$$2\text{In(s)} + \frac{1}{2}\text{O}_2\text{(g)} = \text{In}_2\text{O(g)}, \quad \Delta H_f^o = -33.2 \text{ kJ/mol} \qquad [14]$$

$$\text{In}_2\text{O(g)} = \text{In}_2\text{O(in slag)}, \qquad \Delta H_d^o \qquad [15]$$

The value of ΔH_d^o is estimated to be about -105.8 and -56.8 kJ/mol, respectively, for the very high (70wt%) silica and the moderate (33wt%) silica concentration. Thus, it is believed that metallic indium potentially oxidizes into the gaseous In_2O, followed by dissolution into the slag as In^+ ionic form in high silica region as likely as silver, Ag^+.[6] From the present experimental results of the temperature dependency of the indium solubility, indium oxide as a reaction product is more stable in the highly polymerized melts than in the depolymerized melts. The more quantitative thermodynamic consideration will be given in Section 3.5.

3.5 Effect of slag composition on the solubility of Indium

In Figure 6, the solubility of indium in the CaO-SiO_2-Al_2O_3 slag at 1773 K under condition of $p(O_2)=10^{-16}$ atm is plotted against the content of silica. As can be seen in Figure 6, the indium solubility decreases by increasing the content of silica and shows a minimum solubility, followed by an increase with increasing contents of silica. The system has a minimum point, suggesting that the indium ion in the melts has a different form on either side of the minimum point, i.e., In^+ in the high silica region and In^- in the low silica region.

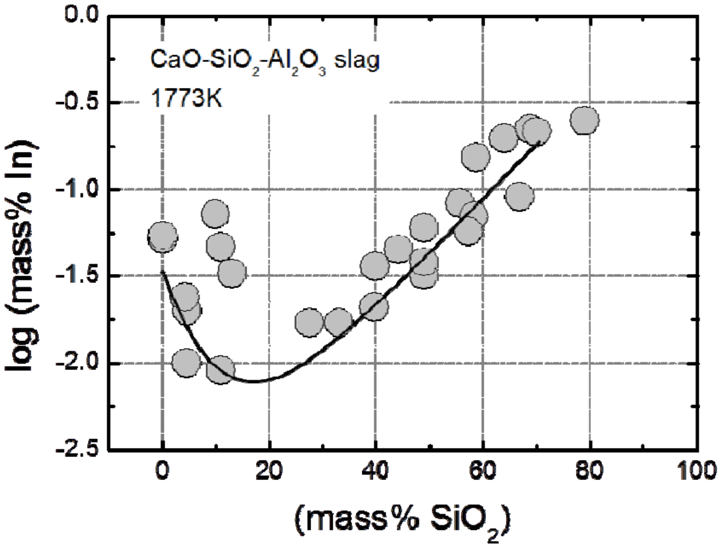

Fig. 6 Dependence of In solubility on content of SiO_2 in the CaO-SiO_2-Al_2O_3 system at 1773K

Figure 7 shows the iso-indium solubility contours in the CaO-SiO_2-Al_2O_3 ternary system at 1773 K under a reducing atmosphere. The solubility of indium predominantly increases by increasing the content of silica at high silica region, i.e. SiO_2 > 20wt%, whereas it increases with increasing lime content at low silica region, i.e. SiO_2 < 20wt%, respectively. Therefore, it is recommended to use suitable flux which corresponds to the CaO-Al_2O_3-20wt% SiO_2 system in order to minimize the indium loss during pyrometallurgical processing of In-containing materials.

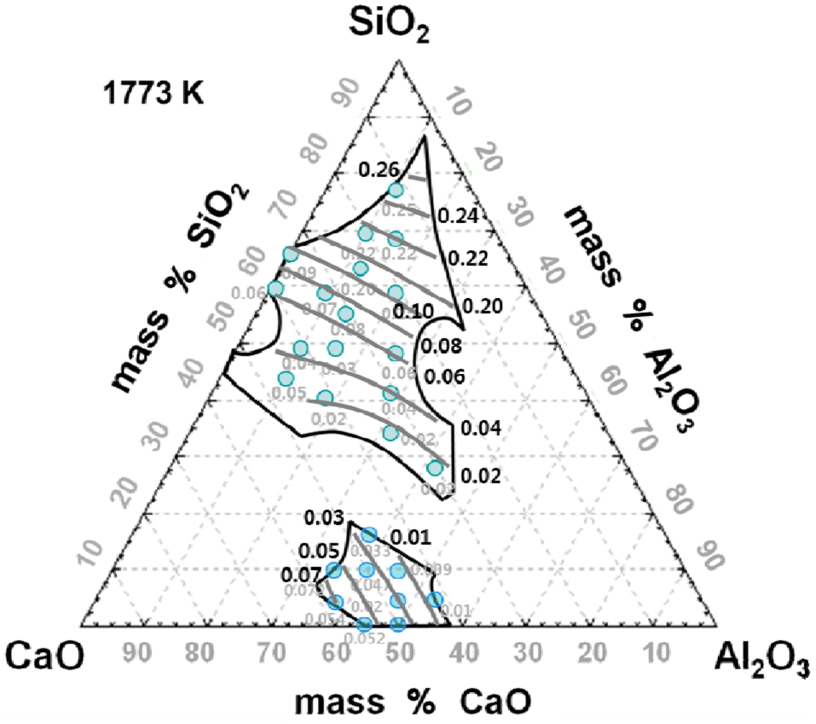

Fig. 7 Iso-indium solubility contours in the CaO-SiO_2-Al_2O_3 system at 1773K

4. Conclusions

The solubility of indium in molten CaO-SiO_2-Al_2O_3 system was measured at 1773 K in order to establish the dissolution mechanism of indium under highly reducing atmosphere. The results of this study can be summarized as follows.

1) The solubility of indium in a molten CaO-SiO_2-Al_2O_3 system was measured at 1773 K. The indium solubility increases in calcium silicate based flux and decreases in calcium aluminate based flux with increasing oxygen partial pressure. Also, it decreases by increasing the basicity of slag, followed by an increase with increasing basicity of slag. Therefore, a dissolution mechanism of indium was established as follows:

$$\mathrm{In(s)} + \frac{1}{4}\mathrm{O_2(g)} = (\mathrm{In^+}) + \frac{1}{2}(\mathrm{O^{2-}}) \qquad \text{(in high silica region)}$$

$$\mathrm{In(s)} + \frac{1}{2}(\mathrm{O^{2-}}) = (\mathrm{In^-}) + \frac{1}{4}\mathrm{O_2(g)} \qquad \text{(in low silica region)}$$

2) The relationship between indium and sulfide capacity in the CaO-SiO_2-Al_2O_3 slag at 1773 K showed a good correlation consistent with the theoretical expectation.

3) The enthalpy change of the indium dissolution reaction is negative, which indicates that the dissolution is an exothermic reaction.

4) The careful design of flux system is required to enhance indium recovery during pyrometallurgical flux treatment.

References

[1] E. Yamasue, R. Minamino, T. Numata, K. Nakajima, S. Murakami, I. Daigo, S. Hashimoto, H. Okumura, and K. Ishihara. Novel Evaluation Method of Elemental Recyclability from Urban Mine –Concept of Urban Ore TMR-. *Mater. Trans.*, 2009, vol. 50, p1536-1540.

[2] O. Terakado, T. Saeki, R. Irizato, and M. Hirasawa. Pyrometallurgical Recovery of Indium from Dental Metal Recycling Sludge by Chlorination Treatment with Ammonium Chloride. *Mater. Trans.*, 2010, vol. 51, p1136-1140.

[3] E. Johnson, L. Oden and J. Koch. Laboratory investigations on the behavior of accessory elements in lead blast furnace smelting, Report no.8753, Albany Res. Cent., US Bur. Mines. 1988.

[4] G.B. Hoang and D.R. Swinbourne. Indium distribution between FeO-CaO-SiO_2 slags and lead bullion at 1200°C. *Min. Process. Extract. Metall. (Trans. Inst. Min. Metall. C)*, 2007, vol. 116, p133-138.

[5] E.T. Turkdogan. Physical Chemistry of High Temperature Technology, Academic Press, New York, NY, 1980, p1-24.

[6] J.H. Park and D.J. Min. Quantitative Analysis of the Relative Basicity of CaO and BaO by Silver Solubility in Slags. *Metall. Mater. Trans. B*, 1999, vol. 30B, p689-694.

[7] S.H. Lee, S.M. Moon, J.H. Park and D.J. Min. Thermodynamic behavior of nickel in CaO-SiO_2-Fe_tO slag. *Metall. Mater. Trans. B*, 2002, vol. 33B, p55-59.

[8] J.H. Park and D.J. Min. Carbide Capacity of CaO-SiO_2-CaF_2(-Na_2O) Slags. *ISIJ Int.*, 2004, vol. 44, p223-228.

[9] J.H. Park and D.J. Min. Effect of ZrO_2 Addition to the CaO-SiO_2-MgO-CaF_2 Slags on the Sulfur Removal from the 16Cr-14Ni Stainless Steel Melts. *Mater. Trans.*, 2006, vol. 47, p2038-2043.

[10] J.H. Park, G.H. Park and Y. E. Lee. Carbide Capacity of CaO-SiO_2-MnO Slag for the Production of Manganese Alloys. *ISIJ Int.*, 2010, vol. 50, p1078-83.

[11] G.H. Park, Y.B. Kang and J.H. Park. Sulfide Capacity of the CaO-SiO_2-MnO Slag at 1873K. *ISIJ Int.*, 2011, vol. 51, p1375-1382.

[12] www.factsage.com (accessed April 2011).

[13] C.W. Bale, E. Belisle, P. Chartrand, S.A. Degterov, G. Eriksson, K. Hack, I.-H. Jung, Y.-B. Kang, J. Melancon, A.D. Pelton, C. Robelin and S. Petersen. FactSage thermochemical software and databases –recent developments. *Calphad*, 2009, vol. 33, p295-311.

[14] M.O. Suk and J.H. Park. Corrosion Behaviors of Zirconia Refractory by CaO-SiO_2-Mgo-CaF_2 Slag. *J. Am. Ceram. Soc.*, 2009, vol. 92, p717-723.

[15] J.H. Park, I.H. Jung and S.B. Lee. Phase diagram study for the CaO-SiO_2-Cr_2O_3-5 mass% MgO-10 mass% MnO system. *Met. Mater. Int.*, 2009, vol. 15, p677-681.

[16] J.H. Park. The effect of boron oxide on the crystallization behavior of $MgAl_2O_4$ spinel phase during the cooling of the CaO-SiO_2-10 mass% MgO-30 mass% Al_2O_3 system. *Met. Mater. Int.*, 2010, vol. 16, p987-092.

[17] J.H. Park, J.G. Park, D.J. Min, Y.E. Lee and Y.B. Kang. In situ observation of the dissolution phenomena of SiC particle in CaO-SiO_2-MnO slag. *J. Eur. Ceram. Soc.*, 2010, vol. 30, p3181-3186.

[18] J.H. Park, M.O. Suk, I.H. Jung, M. Guo and B. Blanpain. Interfacial Reaction between Refractory Materials and Metallurgical Slags containing Fluoride. *Steel Res. Int.*, 2010, vol. 81, p860-868.

[19] C.J.B. Finchan and F.D. Richardson. *J. Iron Steel Inst.*, 1954, vol. 178, p4-15.

[20] C.J.B. Finchan and F.D. Richardson. The Behaviour of Sulphur in Silicate and Aluminate Melts. *Proc. Roy. Soc. London A.*, 1954, vol. 223A, p40-62.

[21] M.R. Kalyanram, T.G. MacFarlane and H.B. Bell. *J. Iron Steel Inst.*, 1960, vol. 195, p58-64.

[22] C.H.P. Lupis. Chemical Thermodynamics of Materials, Prentice Hall, New York, NY, 1993, p114-120.

[23] J. Valderraman and K.T. Jacob. Vapor pressure and dissociation energy of (In_2O). *Thermochim. Acta*, 1977, vol. 21, p215-224.