J. Min. Metall. Sect. B-Metall. 49 (2) B (2013) 131 - 138

Journal of Mining and Metallurgy,
Section B: Metallurgy

EFFECT OF Al_2O_3, MgO AND CuO_X ON THE DISSOLUTION BEHAVIOR OF RHODIUM IN THE Na_2O-SiO_2 SLAGS

C. Wiraseranee[a,*], T. Yoshikawa[b], T.H. Okabe[b], K. Morita[b]

[a] *Central Research Institute, Mitsubishi Materials Corporation, Japan*
[b] *The University of Tokyo, Institute of Industrial Science, Tokyo, Japan*

(Received 21 December 2012; accepted 17 June 2013)

Abstract

Aiming to optimize rhodium recovery in the high temperature recycling process by minimizing rhodium loss into slags in an oxidizing atmosphere by controlling slag composition, the effects of representative slag components, such as Al_2O_3, MgO, and CuO_x, on the dissolution behavior of rhodium into the Na_2O-SiO_2 slags was investigated. The solubility of rhodium was measured by equilibrating the sodium silicate based slags with pure solid rhodium at 1473 K in air. Considering that rhodium dissolved into slags as $RhO_{1.5}$, the effect of the oxide addition on the activity coefficient of $RhO_{1.5}$ in slags was determined. The dissolution of rhodium in slags was suppressed by the addition of Al_2O_3 and MgO, where Al_2O_3 behaved as an acidic oxide and MgO behaved as a diluent of slag basicity at a fixed Na_2O/SiO_2 ratio of 0.97. The content of copper in solid rhodium equilibrated with the CuO_x bearing slags slightly increased with increasing content of CuO_x, and CuO_x was found to slightly enhance the dissolution of rhodium. Rhodate capacity of all slag systems increased with increasing optical basicity, suggesting that the correlation between rhodate capacity and the optical basicity enables the estimation of the content of rhodium in slags of which thermodynamic properties of rhodium are not clarified.

Key words: *Rhodium; Platinum group metals; Solubility; Molten slag; Thermodynamics; Recycling.*

Introduction

Rhodium is extensively used as a key material in various specialized applications, such as catalysts in automobiles, high corrosion resistance containers for molten glass, and high electrical conductive layers in electronic devices. In recent decades, the worldwide scarcity and high price of rhodium make the recycling of rhodium essential [1].

Because rhodium is chemically inert, the recovery of rhodium from scrap using liquid copper or liquid iron as a collector metal has been one of the major recovery methods [2-4]. In the process, rhodium in scrap is collected into the collector metal after melting the scrap with fluxes and the collector metal in a reducing atmosphere. Then, a rhodium-rich alloy is obtained as a product when the collector metal is partly removed into slags by oxidation. Theoretically, rhodium is rather stable as a metal at high temperature. However, loss of rhodium into slags during oxidation in a highly oxidizing atmosphere can be critical. Thus, the process conditions must be carefully controlled in order to minimize the loss of rhodium into slags.

Previously, it was found that the dissolution of rhodium into slags was apparently influenced by slag composition [5]. This suggests the minimization of rhodium loss into slags by controlling slag composition can be viable. In order to effectively control slag composition, the effects of oxide components in slags on the dissolution behavior of rhodium in an oxidizing atmosphere is needed to be clearly understood.

In the recycling process, the composition of "recycling slag" varies with the composition of scrap materials, fluxes, and oxides of the collector metal. Spent automobile catalysts have been the major source for rhodium; hence, MgO, Al_2O_3, and SiO_2 from the honeycomb structure (cordierite, MgO-Al_2O_3-SiO_2) can be the major components of the recycling slag. Moreover, by the oxidation of liquid copper (i.e. the collector metal), both Cu_2O and CuO are likely to coexist, and the content of a mixture of copper oxides (CuO_x) in slags can be relatively high.

The effects of Al_2O_3 and CuO_x addition to slags on the dissolution behavior of other platinum group metals were investigated in previous studies. The solubility of platinum in the CaO-Al_2O_3-SiO_2 slag (at a fixed CaO/SiO_2 mole ratio of 1.07) was found to increase with increasing content of Al_2O_3 at 1873 K [6]. The solubility of ruthenium in the $50Na_2O$-$40SiO_2$-$10Al_2O_3$ slag was higher than that in the

---

* *Corresponding author: cwira@mmc.co.jp*

DOI:10.2298/JMMB121221018W

MOLTEN12 - Conference Special Issue
Ninth International Conference on Molten Slags, Fluxes and Salts

$50Na_2O$-$50SiO_2$ slag at the same oxygen partial pressure at 1473 K [7]. Furthermore, when the Cu-Rh or Cu-Pt binary alloys were equilibrated with the CaO-SiO_2-Fe_2O_3-CuO_x slag at 1573 K in air, it was found that the content of either rhodium or platinum increased significantly with increasing content of copper in slags [8].

In the present study, in order to design slag composition for the recovery of rhodium using copper as the collector metal in an oxidizing atmosphere, the effects of Al_2O_3, MgO, and CuO_x addition on the dissolution behavior of rhodium in slags was examined.

2. Experimental

Slag samples were prepared by melting the mixtures of reagent grade Na_2CO_3, SiO_2, Al_2O_3, MgO, and Cu_2O in a pure platinum crucible in air at 1573 K.

Experiments were carried out by equilibrating 4 g of molten slags, such as the Na_2O-SiO_2-Al_2O_3, the Na_2O-SiO_2-MgO, and the Na_2O-SiO_2-CuO_x systems, in a pure rhodium crucible (18 mm I.D., 20 mm O.D., 20 mm in depth) in an electrical resistance (SiC) furnace. The schematic diagram of the experimental setup is shown in Figure 1. When the Na_2O-SiO_2-CuO_x slags was melted, the slight dissolution of copper into solid rhodium was observed. In order to determine the content of copper in solid rhodium in equilibrium with the Na_2O-SiO_2-CuO_x slags, a piece of rhodium sheet (thickness 125 µm, purity ≥ 99.9 %) was added into the slags.

The oxygen partial pressure in the system was controlled by flowing dried air. The gas flow rate was controlled at 100 mL/min. Moisture and CO_2 in the dried air was removed by passing the gas through silica gel, soda lime, and magnesium perchlorate, respectively. The temperature was controlled within an accuracy of ±1 K using a proportional-integral-derivative (PID) controller with a Pt/6%Rh-Pt/30%Rh thermocouple. After equilibration, samples were removed from the furnace and quenched at room temperature by flushing Ar gas.

The slag composition in quenched samples and the content of copper in solid rhodium equilibrated with the Na_2O-SiO_2-CuO_x slag were determined by wet chemical analysis. The content of rhodium, sodium, aluminum, magnesium, and copper were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES). The content of silicon in slags was determined by the gravimetric method.

3. Results and Discussion

Experimental results of the dissolution of rhodium in slags were summarized in Table 1, and the content of copper in solid rhodium equilibrated with the Na_2O-SiO_2-CuO_x slag was summarized in Table 2.

3.1 Equilibrium attainment

Equilibration time for the dissolution of rhodium

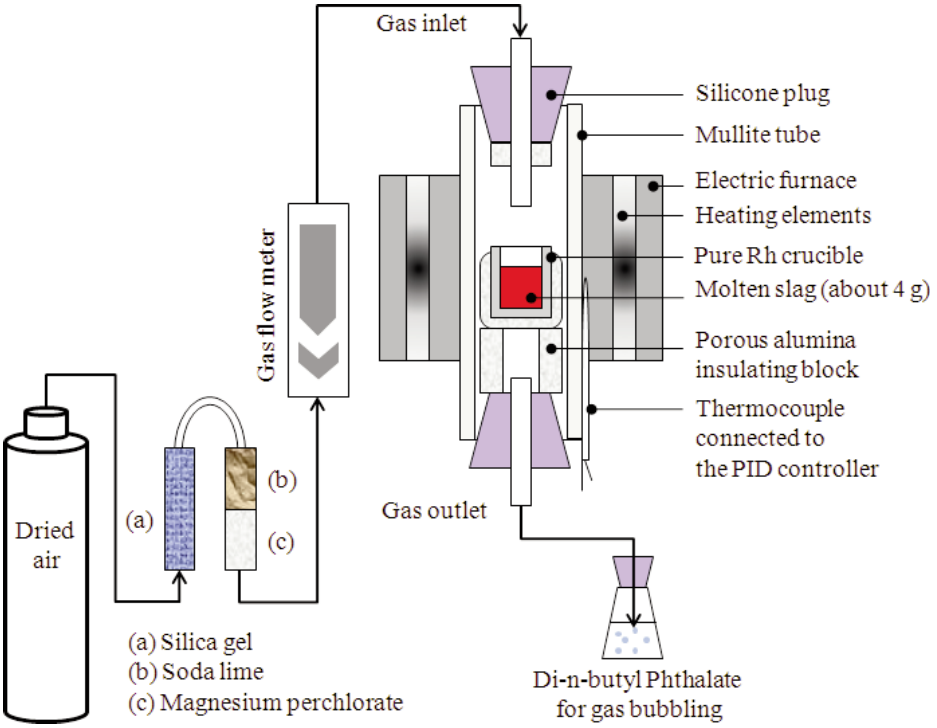

Figure 1. *Schematic diagram of the experimental apparatus.*

Table 1. *Experimental results of the dissolution of rhodium in slags (Na_2O/SiO_2 = 0.97) at 1473 K and p_{O_2}= 0.21 atm*

Sample No.	Slag composition/ mass pct			$X_{Al_2O_3}$	Time / h	Solubility of Rh / mass ppm	$\gamma^o_{RhO_{1.5}}$	$C_{RhO_2^-}$ $\times 10^3$
	Na_2O	SiO_2	Al_2O_3					
0	50.1	49.9	-	0	18	375	630	158
1	41.2	41.1	17.7	0.13	18	53	4190	22
2	41.2	41.1	17.7	0.13	42	50	4420	21
3	45.8	46.1	8.1	0.06	18	138	1670	58
4	39.6	39.6	20.8	0.14	18	25	8720	9
Sample No.	Slag composition/ mass pct			X_{MgO}	Time/ h	Solubility of Rh/ mass ppm	$\gamma^o_{RhO_{1.5}}$	$C_{RhO_2^-}$ $\times 10^3$
	Na_2O	SiO_2	MgO					
5	44.3	47.8	7.9	0.12	18	200	1240	84
6	43.7	48.4	7.9	0.12	18	195	1270	82
7	44.3	47.8	7.9	0.12	36	207	1200	87
8	45.7	48.1	6.2	0.09	18	276	890	117
9	44.2	46.6	9.2	0.13	18	206	1210	87
Sample No.	Slag composition/ mass pct			X_{Cu}	Time/ h	Solubility of Rh/ mass ppm	$\gamma^o_{RhO_{1.5}}$	$C_{RhO_2^-}$ $\times 10^3$
	Na_2O	SiO_2	CuO_x					
10	37.6	38.6	23.8	0.18	18	335	610	109
11	37.5	38.9	23.6	0.17	18	377	550	122
12	37.5	38.9	23.6	0.17	36	338	n.d.	n.d.
13	37.5	38.9	23.6	0.17	48	362	570	117
14	37.5	38.9	23.6	0.17	92	364	n.d.	n.d.
15	47	47.1	5.9	0.05	18	347	n.d.	n.d.
16	44.1	44.1	11.8	0.09	18	343	650	111
17	44.3	44.1	11.6	0.09	18	373	600	120
18	32.5	32.6	34.9	0.26	18	358	540	116
n.d.: not determined								

Table 2. *The content of copper in solid rhodium in equilibrium with the Na_2O-SiO_2-CuO_x slag at 1473 K and p_{O_2}= 0.21 atm*

Sample No.	Slag composition/ mass pct			X_{Cu} in slag	Time / h	X_{Cu} in alloy	X_{Rh} in alloy
	Na_2O	SiO_2	CuO_x				
0	50.1	49.9	-	-	18	-	1
11	37.6	38.6	23.8	0.18	18	0.0021	0.9979
13	37.5	38.9	23.6	0.17	48	0.0023	0.9977
16	44.1	44.1	11.8	0.09	18	0.0004	0.9996
17	44.3	44.1	11.6	0.09	18	0.0005	0.9995
18	32.5	32.6	34.9	0.26	18	0.0045	0.9955

into slags was firstly determined. According to the time-dependence plot (Figure 2), the solubility of rhodium in each slag system increased with time and became steady after 18 h. In case of the Na_2O-SiO_2-CuO_x slag, the dissolution of copper from the slags into solid rhodium was observed. From the measurement, the content of copper in solid rhodium after 18 h was steady (Figure 3). Therefore, the equilibration time for the Na_2O-SiO_2-Al_2O_3, the Na_2O-SiO_2-MgO, and the Na_2O-SiO_2-CuO_x slag systems was assigned to be 18 h.

3.2 The solubility of rhodium in Al_2O_3, MgO and CuO_x bearing slags

The solubility of rhodium in the Na_2O-SiO_2-Al_2O_3, the Na_2O-SiO_2-MgO, and the Na_2O-SiO_2-CuO_x slags was measured at 1473 K and p_{O_2}= 0.21 atm by varying the contents of Al_2O_3, MgO and CuO_x in slags at a fixed Na_2O/SiO_2 mol ratio of 0.97. It was found that

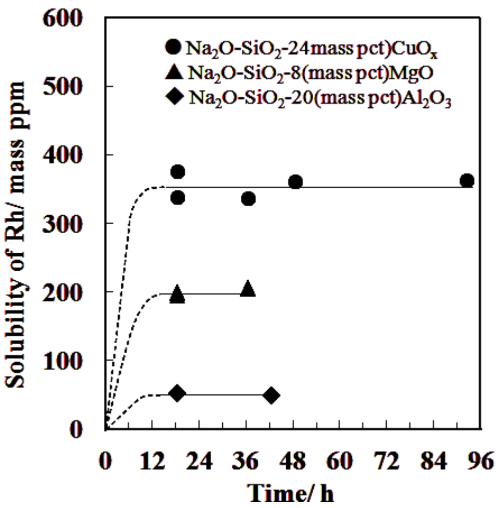

Figure 2. *Dependence of the solubility of rhodium in the* Na_2O*-*SiO_2*-*Al_2O_3*, the* Na_2O*-*SiO_2*-MgO, and the* Na_2O*-*SiO_2*-*CuO_x *slags (*Na_2O/SiO_2 *= 0.97) on experimental times at 1473 K in air (* p_{O_2} *= 0.21 atm).*

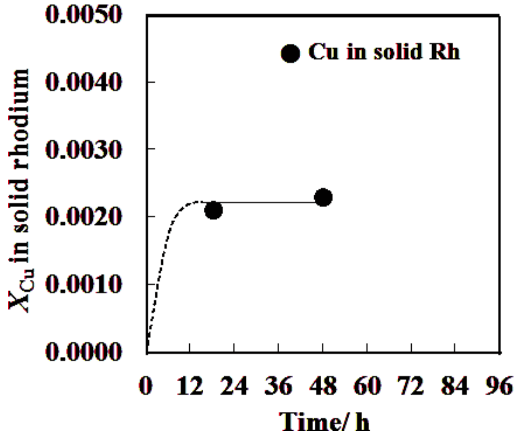

Figure 3. *Dependence of the content of copper in solid rhodium equilibrated with the 38*Na_2O*-38*SiO_2*-24*CuO_x *slag (20 mass pct Cu) on experimental times at 1473 K in air (* p_{O_2}*= 0.21 atm).*

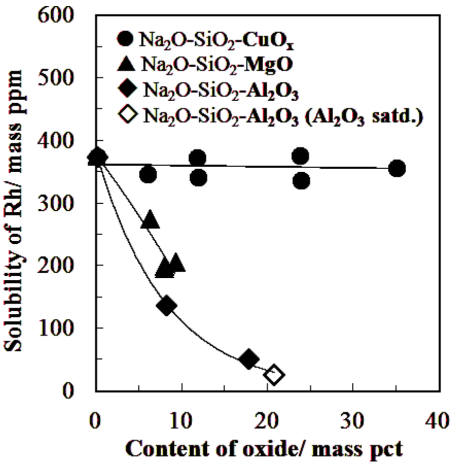

Figure 4. *Dependence of the solubility of rhodium on the contents of* Al_2O_3*, MgO and* CuO_x *in slags at a fixed* Na_2O/SiO_2 *mol ratio of 0.97 at 1473 K in air (* p_{O_2}*= 0.21 atm).*

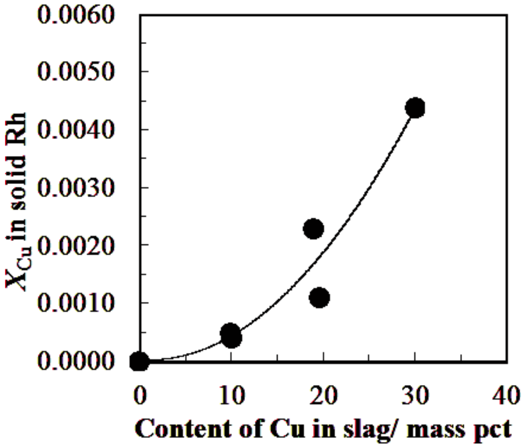

Figure 5. *Dependence of the content of copper in the Cu-Rh alloys on the content of copper in the* Na_2O*-*SiO_2*-*CuO_x *slags in air (* p_{O_2}*= 0.21 atm) at 1473 K.*

the solubility of rhodium drastically decreased when the contents of Al_2O_3 and MgO in slags increased, but was fairly constant when the content of copper in slags increased (Figure 4).

In the CuO_x bearing slags, the dissolution of copper into solid rhodium was observed. The content of copper in solid rhodium increased with increasing content of copper in the slags (Figure 5).

The dissolution of copper into solid rhodium causes the decrease in the activity of solid rhodium from unity. Thus, the effect of CuO_x addition on the dissolution of rhodium into slags cannot be determined solely by the dependence of the solubility of rhodium on the content of CuO_x in slags. Consequently, the comparison of the effect of oxide addition on the dissolution of rhodium into slags was made by using the activity coefficient of rhodium and rhodate capacity in slags as discussed in the following sections.

3.3 The activity coefficient of $RhO_{1.5}$ *in* Al_2O_3*, MgO and* CuO_x *bearing slags*

The activity coefficient of rhodium in slags were determined by considering that rhodium dissolved into slags as $RhO_{1.5}$ (Eq. (1)) as proposed in the previous study [5]. The activity coefficient of $RhO_{1.5}$ in slags was calculated by the following equations, referring to pure solid $RhO_{1.5}$ as a standard state.

$$\mathrm{Rh}(s) + 3/4\mathrm{O}_2(g) = \mathrm{RhO}_{1.5}(s) \qquad \ldots(1)$$

$$\Delta G^{o}_{f,\mathrm{RhO}_{1.5}} = -174.900 + 125T \ (J/mol) \qquad \ldots(2)$$

$$\Delta G^{o}_{f,\mathrm{RhO}_{1.5}} = -RT\ln\frac{\gamma^{o}_{\mathrm{RhO}_{1.5}} X_{\mathrm{RhO}_{1.5}}}{\gamma^{o}_{\mathrm{Rh}} X_{\mathrm{Rh}} p_{O_2}^{3/4}} \qquad \ldots(3)$$

The activity of solid rhodium in equilibrium with the Na_2O-SiO_2-Al_2O_3 and the Na_2O-SiO_2-MgO slags was assigned to unity. Meanwhile, because copper in the Na_2O-SiO_2-CuO_x slag slightly dissolved into solid rhodium, it was assumed that rhodium in the Rh-Cu solid alloys obeys Raoult's law. Hence, the activity of solid rhodium in equilibrium with the Na_2O-SiO_2-CuO_x slag was assigned to the content of rhodium in the solid alloys. Dependence of the activity coefficient of $RhO_{1.5}$ on the contents of Al_2O_3, MgO, and CuO_x in slags was determined in Figure 6.

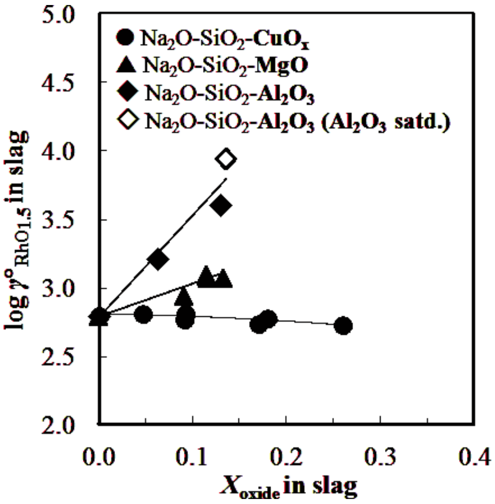

Figure 6. Dependence of the activity coefficient of $RhO_{1.5}$ on the contents of (◆) Al_2O_3, (▲) MgO, and (●) CuO_x at a fixed Na_2O/SiO_2 mol ratio of 0.97 at 1473 K and p_{O_2} = 0.21 atm.

The activity coefficient of $RhO_{1.5}$ slightly decreased with increasing content of CuO_x. Considering that $RhO_{1.5}$ behaves as an acidic oxide in the melts [5], it is deduced that CuO_x behaved as a basic oxide and enhanced the dissolution of rhodium into the slags.

It is generally known that Al_2O_3 is amphoteric. In this study, the drastic increment of the activity coefficient of $RhO_{1.5}$ with increasing content of Al_2O_3 indicated that Al_2O_3 behaved as an acidic oxide in the Na_2O-SiO_2-Al_2O_3 slags and suppressed the dissolution of rhodium. Furthermore, it was reported that, at a fixed Na_2O/SiO_2 ratio of 1, the activity of Na_2O in the Na_2O-SiO_2-Al_2O_3 slags at 1400 K drastically decreased with increasing content of Al_2O_3 [10]. The activity of Na_2O in the Na_2O-SiO_2-Al_2O_3 slags at 1400 K reported in the previous study was determined by referring to the 40(mol pct)Na_2O-60SiO_2 melt. The activity of Na_2O in the Na_2O-SiO_2-Al_2O_3 slags which is used for the discussion in this study was recalculated by changing the standard state to pure liquid Na_2O. From Figure 7, the dissolution of rhodium into slags as an acidic oxide was supported by the increasing trend of the solubility of rhodium when the activity of Na_2O in the Na_2O-SiO_2-Al_2O_3 slags increased.

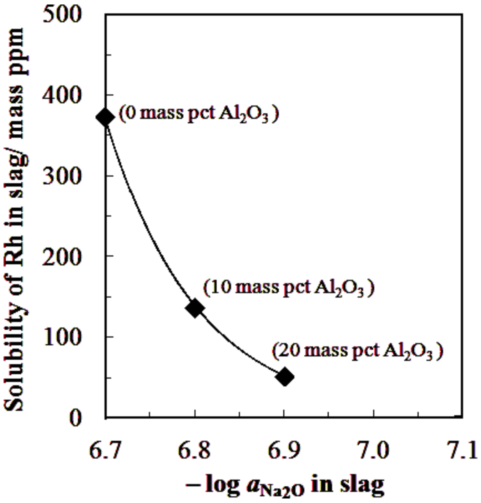

Figure 7. Dependence of the solubility of rhodium in the Na_2O-SiO_2-Al_2O_3 slags at 1473 K on the activity of Na_2O.

In case of the effect of MgO addition, the activity coefficient of $RhO_{1.5}$ gradually increased with increasing content of MgO. Since MgO is commonly considered as a weak basic oxide, especially when compared to Na_2O, it was suggested that at a fixed Na_2O/SiO_2 ratio of 1, MgO in the Na_2O-SiO_2-MgO slags behaved as a diluent of the slag basicity and suppressed the dissolution of rhodium in the slags.

The optical basicity, proposed by Duffy and Ingram [11], is defined as the power of an oxide to donate a negative charge. Table 3 shows optical basicity (Λ) of various oxides.

Table 3. Optical basicity of various oxides

Pure oxides	Optical basicity, Λ	Ref.
Na_2O	1.15	[12]
CaO	1.00	[12]
MgO	0.78	[12]
Al_2O_3	0.6	[12]
SiO_2	0.48	[12]
Cu_2O	0.97	[13]
CuO	0.90	[14]

By the use of the calculated optical basicity (Λ_{th}), the effect of the change in slag basicity due to the addition of Al_2O_3, MgO, and CuO_x on the activity coefficient of $RhO_{1.5}$ in slags was determined (Figure 8). It is noted that the correction on the calculated optical basicity of the Na_2O-SiO_2-Al_2O_3 slag was made considering the charge compensation; namely the fact that Na^+ was consumed for the charge balancing in AlO_4^{5-} tetrahedral [15]. Additionally, the optical basicity of the Na_2O-SiO_2-CuO_x slags was calculated by considering the slags as the Na_2O-SiO_2-Cu_2O-CuO quaternary system. The content of Cu_2O and CuO in the slags was calculated by assuming that the mol ratio of Cu^+/Cu^{2+} in the sodium metasilicate was 1.1 [16].

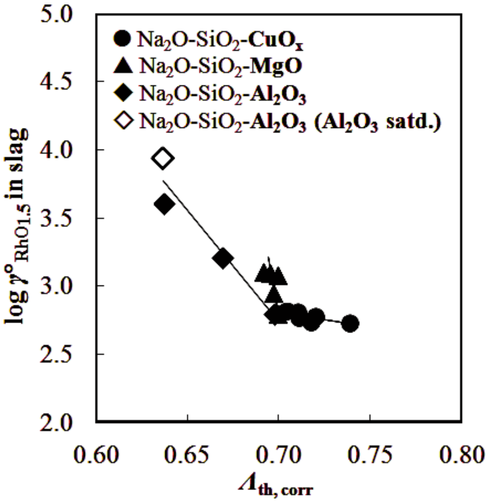

Figure 8. *Dependence of the activity coefficient of $RhO_{1.5}$ on the calculated optical basicity at 1473 K and p_{O_2} = 0.21 atm.*

The activity coefficient of $RhO_{1.5}$ in the Na_2O-SiO_2-Al_2O_3 and the Na_2O-SiO_2-MgO slags sharply increased with decreasing optical basicity after the addition of Al_2O_3 and MgO, indicating that Al_2O_3 and MgO suppressed the dissolution of rhodium in slags. Meanwhile, the optical basicity of the Na_2O-SiO_2-CuO_x slags increased with increasing content of CuO_x in the slags, suggesting that the decrease in the activity coefficient of $RhO_{1.5}$ in the Na_2O-SiO_2-CuO_x slags was resulted from the increase in the slag basicity by the addition of CuO_x.

3.4 The activities of $CuO_{0.5}$ and CuO in the Na_2O-SiO_2-CuO_x slags

The activity of copper in solid rhodium (referred to pure solid copper as a standard state) in equilibrium with the Na_2O-SiO_2-CuO_x slag was derived from the content of copper in solid rhodium and the activities-compositions relation in the Cu-Rh system at 1473 K [17]. Thus, the activities of $CuO_{0.5}$ and CuO (referred to pure solid $CuO_{0.5}$ and pure solid CuO as standard states, respectively) could be determined from the following equations.

$$Cu(s)+1/4O_2(g)=CuO_{0.5}(s) \qquad ...(4)$$

$$\Delta G^{o}_{f,CuO_{0.5}} = -85.000 + 37T \ (J/mol) \qquad [9] \quad ...(5)$$

$$\Delta G^{o}_{f,CuO_{0.5}(s)} = -RT \ln \frac{\alpha_{CuO_{0.5}}}{\gamma^{o}_{Cu} X_{Cu} p_{O_2}^{1/4}} \qquad ...(6)$$

$$Cu(s)+1/2O_2(g)=CuO(s) \qquad ...(7)$$

$$\Delta G^{o}_{f,CuO_{0.5}} = -153.200 + 86T \ (\text{J/mol}) \qquad [9] \quad ....(8)$$

$$\Delta G^{o}_{f,CuO_{0.5}(s)} = -RT \ln \frac{\alpha_{CuO}}{\gamma^{o}_{Cu} X_{Cu} p_{O_2}^{1/2}} \qquad ...(9)$$

The activity of $CuO_{0.5}$ in the Na_2O-SiO_2-CuO_x slags measured in air (p_{O_2} = 0.21 atm) considerably decreased from that in the Na_2O-SiO_2-Cu_2O slags in equilibrium with liquid copper measured at 1573 K in the Ar atmosphere (Figure 9) [18].

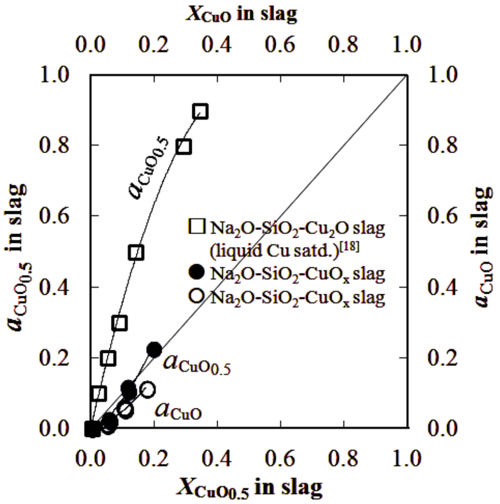

Figure 9. *Dependence of the activities of $CuO_{0.5}$ and CuO in the Na_2O-SiO_2-CuO_x slag at 1473 K (p_{O_2} = 0.21 atm), and the activity $CuO_{0.5}$ of in the Na_2O-SiO_2-Cu_2O slag at 1573 K in equilibrium with liquid copper, on the content of copper in slags at the Na_2O/SiO_2 ratio of 0.97.*

$CuO_{0.5}$ in the Na_2O-SiO_2-Cu_2O slags exhibited the positive deviation from ideality [18], whereas that in the Na_2O-SiO_2-CuO_x slags was likely to exhibit the Raoultian behavior. Meanwhile, CuO in the Na_2O-SiO_2-Cu_2O slags exhibited the slight negative deviation from ideality. It was hypothesized that the existence of CuO in the slags results in the decrease in the activity of $CuO_{0.5}$ in the slags.

3.5 Rhodate capacity of Al_2O_3, MgO and CuO_x bearing slags

Rhodate capacity of slags ($C_{RhO_2^-}$) is defined as the capacity of a rhodate ion (RhO_2^-) in slags [5]. It was proposed by referring that rhodium dissolved into slags in the form of a rhodate ion by the following reaction.

$$\mathrm{Rh(s)} + \frac{3}{4}\mathrm{O_2(g)} + \frac{1}{2}\mathrm{O^{2-}}\ \text{(in slag)} =$$

$$= \mathrm{RhO_2^-}\text{(in slag)} \qquad [5]\ldots(10)$$

Rhodate capacity of a slag system at a particular temperature is determined from the solubility of rhodium in slags, the activity of rhodium, and oxygen partial pressure as follows.

$$C_{\mathrm{RhO_2^-}} = \frac{(\text{mass pct } \mathrm{RhO_2^-} \text{ in slag})}{(a_{\mathrm{Rh}})(p_{\mathrm{O_2}})^{3/4}} = K_{(10)}\frac{(a_{\mathrm{O^{2-}}})^{1/2}}{f_{\mathrm{RhO_2^-}}} \qquad \ldots(11)$$

From Eq. (8), $K_{(10)}$ is the equilibrium constant of Eq. (10), $a_{\mathrm{O^{2-}}}$ is the activity of oxide ion (O^{2-}) in slags, and $f_{\mathrm{RhO_2^-}}$ is the activity coefficient of the rhodate ion in slags. As a basicity index of slags, the optical basicity was employed to investigate the relationship between slag basicity and rhodate capacity of slags. Figure 10 illustrates the relationship between rhodate capacity in the Na_2O-SiO_2-Al_2O_3, the Na_2O-SiO_2-MgO, and the Na_2O-SiO_2-CuO_x slags and the calculated optical basicity.

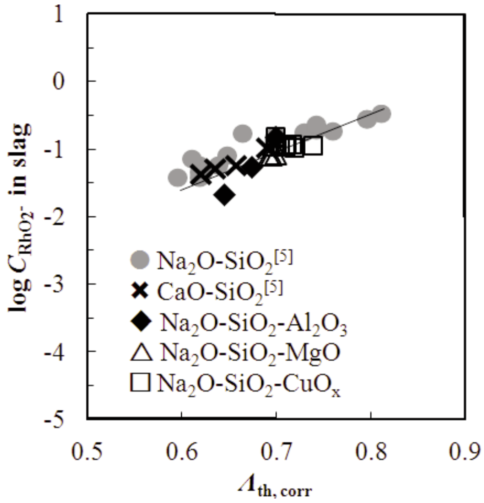

Figure 10. *The correlation between rhodate capacity and the calculated optical basicity.*

Rhodate capacity of slags increased with increasing optical basicity in all slag systems. The "best fit" of the correlation was found to be a linear relationship in Eq. (12). It is noted that the optical basicity of the Na_2O-SiO_2-Al_2O_3 and the Na_2O-SiO_2-CuO_x slags was calculated by the approach which described in the section 3.3.

$$\log C_{\mathrm{RhO_2^-}} = 4.61(\pm 0.41)\Lambda_{th,corr} + 4.14 \qquad \ldots(12)$$

In the recovery of rhodium in an oxidizing atmosphere, it is expected that the recycling slag contains various oxide components where thermodynamic properties of rhodium in those slag systems are not clarified. In order to estimate the possible rhodate capacity of various slag systems, the use of the correlation between the rhodate capacity and the calculated optical basicity was proposed.

4. Conclusions

With the aim to minimize the rhodium loss into slags in the recovery of rhodium in an oxidizing atmosphere, the effects of Al_2O_3, MgO, and CuO_x addition on the dissolution behavior of rhodium in the Na_2O-SiO_2 slags in air (p_{O_2} = 0.21 atm) at 1473 K was investigated. The following findings were revealed.

At a fixed Na_2O/SiO_2 ratio of 0.97, the solubility of rhodium sharply increased with increasing contents of Al_2O_3 and MgO in slags, but rather maintained constant with increasing content of CuO_x.

Copper in the Na_2O-SiO_2-CuO_x slag was found to dissolve into solid rhodium and decreased the activity of solid rhodium in the system.

Al_2O_3 behaved as acidic substance in slags and drastically suppress the dissolution of rhodium.

Since MgO is less basic than Na_2O, it behaved as a diluent of slag basicity, resulted in the increment of the activity coefficient of $RhO_{1.5}$ when the content of MgO increased.

The activity coefficient of $RhO_{1.5}$ in the CuO_x bearing slags decreased with increasing content of CuO_x; therefore, it was deduced that copper oxides behaved as basic substances and enhanced the dissolution of rhodium into slags.

Rhodate capacity was found to increase with increasing optical basicity of slags. The linear relationship was found to be the best-fit correlation between rhodate capacity and the calculated optical basicity. The correlation provides a possibility for the estimation of rhodate capacity in the multi-components recycling slag.

Acknowledgement

This research was supported by the New Energy and Industrial Technology Development Organization (NEDO), Japan. The authors would like to thank Mr. Yuzuru Nakamura, Dowa Metals & Mining Co., Ltd., Japan, for the fruitful advices and discussions.

References

[1] J. Butler, Platinum 2012, Johnson Matthey Plc., Hertfordshire, 2012.

[2] M. Benson, C.R. Bennett, J.E. Harry, M.K. Patel, and M. Cross, Resour., Conserv. Recycl., 31 (2000) 1–7.

[3] C. Hagelüken, World Metall.-Erzmet., 59 (2006) 152–161.

[4] T.H. Okabe, H. Nakada, and K. Morita, J. Surf. Sci. Soc. Jpn., 29 (10) (2008) 592–600 (in Japanese with English abstract).

[5] C. Wiraseranee, T.H. Okabe, and K. Morita, Metall.

Mater. Trans., 44B (2013) 584–592.

[6] S. Nakamura and N. Sano, Metall. Mater. Trans., 28B (1997) 103–108.

[7] H. Shuto, T.H. Okabe, and K. Morita, Mater. Trans., 52 (10) (2011) 1899–1904.

[8] K. Yamaguchi, 42nd Rare Metals Workshop, October 2010, Tokyo, Japan, 2010 (in Japanese).

[9] I. Barin, in Thermochemical Data of Pure Substances, VCH Verlagsgesellschaft, mbH, Weinheim, 1989.

[10] H. Itoh and T. Yokokawa, Trans. Jpn. Inst. Met., 25 (12) (1984) 879–884.

[11] J.A. Duffy and M.D. Ingram, J. Non-Cryst. Solids, 21 (1976) 373–410.

[12] J.A. Duffy, Geochim. Cosmochim. Acta, 57 (1993) 3961–3970.

[13] E. Bordes-Richard and P. Courtine, in Metal Oxides: Chemistry and Applications (J.L.G. Fierro Editor), CRC Press, Boca Raton, FL, 2006, p. 326.

[14] K.C. Mills, in Slag Atlas, 2nd ed. (Verein Deutscher Eisenhüttenleute Editor), Verlag Stahleisen GmbH, Düsseldorf, 1995, p. 11.

[15] K.C. Mills, ISIJ Int., 33 (1) (1993) 148–155.

[16] S. Nakamura and N. Sano, Metall. Mater. Trans., 22B (1991) 823–829.

[17] C. Wiraseranee, Thermodynamics of Rhodium and Platinum in Molten Slag, The University of Tokyo, 2012 (Doctoral thesis).

[18] Y. Takeda, G. Riveros, Y. Park, and A. Yazawa, Trans. Jpn. Inst. Met., 27 (8) (1986) 608–615.