Thermodynamic Study of the Equilibrium Distribution of Platinum Group Metals Between Slag and Molten Metals and Slag and Copper Matte

Katsunori Yamaguchi

Abstract Secondary materials, that contain relatively high concentrations of platinum group metals, (PGMs) are treated in copper smelting process. The PGMs lost in the slag is increasing with increasing quantities of scrap treated amount. To determine the portion of the PGMs chemically dissolved and that associated with the mechanically trapped matte in the slag will be a key factor to improve the recovery of those metals. An experimental study was carried out to determine the distribution of palladium between the FeO_x–SiO_2 slag and the liquid Cu_2S–FeS matte at 1573 K and a fixed partial pressure of SO_2 of 0.1 atm. It was found that the distribution ratios are around 10^{-3} for platinum and palladium. The distribution ratios show a tendency to increase when the grade of matte is increased above 60 mass% Cu. In addition, the solubility of platinum in FeO_x–SiO_2 slag equilibrated with a pure palladium and the Pd-Cu alloy was determined at 1573 K and the range of oxygen partial pressure from 10^{-9} to 10^{-7} atm. The solubility of palladium in the slag tends to increase with increasing oxygen partial pressure and activity of $CuO_{0.5}$ in the slag.

Keywords Iron-silicate slag · Distribution ratio · Solubility
Platinum · Palladium

Introduction

There is an increasing trend in copper smelters to process secondary materials, which contain relatively high concentrations of precious metals such as gold, silver, platinum, palladium and rhodium. As a consequence of the increasing of amount of secondary materials treated, the precious metals lost in the slag phase is also

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increasing. The ratio of the precious metals chemically dissolved and that associated with the mechanically trapped matte in the slag will be a key factor in improving the recovery of those precious metals. The distribution ratio of silver metals between iron silicate slag and Cu_2S–FeS matte at 1573 K has been reported by Roghani et al. [1]. The distributions of Ag, Au, Pd, Pt, and Rh between copper matte and silica-saturated iron silicate slag were determined at 1250–1350 °C by Avarmaa et al. [2].

The present study was carried out at the oxygen smelting conditions with $p_{SO2} = 0.1$ atm and controlled partial pressures of O_2 and S_2. The distribution ratios of platinum group metals (PGMs) of platinum and palladium between iron silicate slag and Cu_2S–FeS matte were measured at 1573 K. The results are intended to indicate the lowest content of PGMs that would be expected in the industry and also a give clear indication of the range of matte grade where recovery of precious metals can be optimized.

The distribution of PGMs has been found to increase with increasing concentration of copper in the slag and increasing oxygen partial pressure. The solubility of palladium in the FeO_x–SiO_2 slag equilibrated with a pure palladium and the Pd–Cu alloy has been is investigated at 1573 K and the range of oxygen partial pressure from 10^{-9} to 10^{-7} atm controlled with CO–CO_2 gas mixture. Nakamura and Sano reported the solubility of platinum in molten BaO–CuO_x, BaO–MnO_x, CaO_{satd}–SiO_2–FeO_x, $KO_{0.5}$–SiO_2, $NaO_{0.5}$–SiO_2, and $NaO_{0.5}$–$PO_{2.5}$ slag [3, 4]. Shuto et al. measured the ruthenium solubility in the CaO–SiO_2, Na_2O–SiO_2, and Na_2O–SiO_2–Al_2O_3 slag [5]. There are no reports of the palladium solubility in the FeO_x–SiO_2 slags.

Experimental

The experimental apparatus used in this study is shown in Fig. 1. The furnace consists of a silicon carbide heating element and an alumina reaction tube. CO–CO_2–SO_2 gas mixtures with a flow rate at 120 mL/s were used to control the partial pressures of S_2, O_2 and SO_2. CO_2 gas passed through a P_2O_5 column to trap moisture. The gas mixture was introduced into an alumina reaction tube with an inner diameter of 6×10^{-4} m and a height of 0.6 m. The partial pressures of S_2, O_2 and SO_2 were calculated by using FactSage software [6]. The experiments were made under the partial pressure of SO_2 at 0.1 atm under conditions typical of oxidation of the matte with air.

A total 6 g of pre-melted slag of approximate composition of 65 mass%FeO-35 mass%SiO_2 was equilibrated with a same amount of Cu_2S–FeS in a magnesia crucible with an inner diameter of 0.011 m and a height of 0.05 m. The master slag was synthesized in an iron crucible. The Cu_2S and FeS were prepared by vacuum sealing the required metals and sulfur in a quartz ampoule. The temperature of the sample was measured by another Pt/Pt-Rh thermocouple attached to the magnesia crucible. Preliminary experiments have clarified that the equilibrium could be made

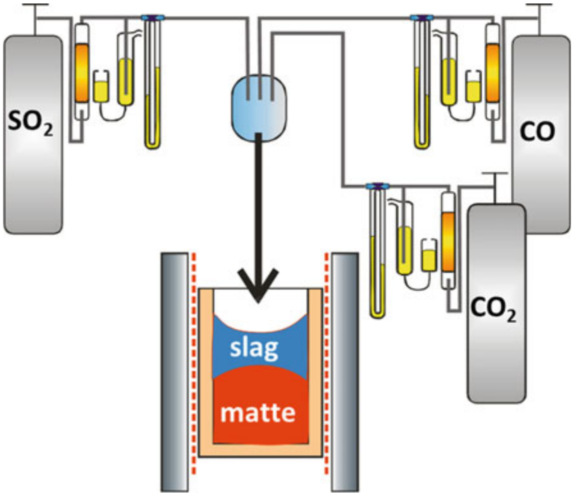


Fig. 1 Schematic diagram of experimental apparatus

in a restricted time of less than 24 h by adjusting the Cu_2S–FeS content of the starting alloy phase so that it is near in composition to that of the estimated equilibrium value reported by Roghani et al. [1]. The sample was cooled rapidly by flushing a large amount of argon gas onto a surface of the slag layer to prevent the segregation of the slag components during the solidification. The chemical analysis was made for the solidified matte and slag specimens after physical separation of the phases using an ICP analysis.

The experimental apparatus and procedure of the palladium solubility in the iron silicate slag are same as in the previous study of the distribution of the precious metals between the slag and matte. A mixture of CO–CO_2 was used to control p_{O2}. The starting slag had 65 mass%FeO_x-35 mass%SiO_2 were synthesized in an iron crucible. 10 g of the slag and 0.2 g of pure solid palladium or 1 g of Pd–Cu alloy were put in a magnesia crucible with an inner diameter of 0.018 m and a height of 0.04 m. The sample was heated at 1573 K for 24 h, which was long enough to reach the equilibrium, as confirmed in previous study [1]. After that, it was cooled rapidly by flushing a large amount of argon gas onto a surface of the slag layer during the solidification. The palladium and copper in the slag sample were analyzed by an ICP analysis.

Results and Discussion

Distribution of Platinum and Palladium Between Slag and Matte

The 65 mass%FeO_x-35 mass%SiO_2 slag and Cu_2S–FeS equilibrium was carried out at the oxygen-smelting conditions with $p_{SO2} = 0.1$ atm and controlled partial pressures of S_2 and O_2 at 1573 K. The slag separated completely from the Cu_2S–FeS matte with copper concentration from 50 to 75 mass%. The MgO concentration in the present slag at 1573 K was less than 8 mass%. The affect of MgO in the distribution of minor elements can be assumed small. Experimental data obtained on the copper content in the slag as a function of copper content in the matte are shown in Fig. 2. The copper concentration in the slag increases with increasing matte grade and increase remarkably in the range of higher matte grade. The copper concentration in the slag at 1573 K and p_{SO2} of 0.1 atm determined by Roghani et al. shows an agreement with the present results [1].

The distribution ratio of platinum and palladium between the 8 mass%MgO-35 mass%SiO_2-FeOx slag and Cu_2S–FeS matte phases is defined by following equation:

$$L_X^{s/M} = (\text{mass\% X in slag}) / [\text{mass\% X in slag}] \tag{1}$$

and distribution ratio was determined from the chemical analysis of the slag and matte phases.

The distribution ratios of palladium and platinum are shown in Fig. 3. It was found that the distribution ratios are approximately 0.001 for platinum and palladium. It is noted that in the range of matte grade between 40 and 65 mass% of copper there is no appreciable variation in the distribution ratios. However, above 60 to 65 mass% of copper in the matte the distribution ratios increase with increasing copper content in the matte. This behavior resembles a tendency of dissolution of copper in the slag. The distribution ratio of the precious metals may depend on the solubility of copper in the slag.

Fig. 2 Copper concentration in the FeO_x-SiO_2 slag against matte grade under p_{SO2} of 0.1 atm at 1573 K

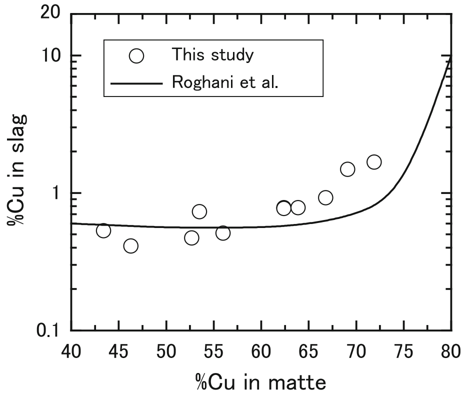
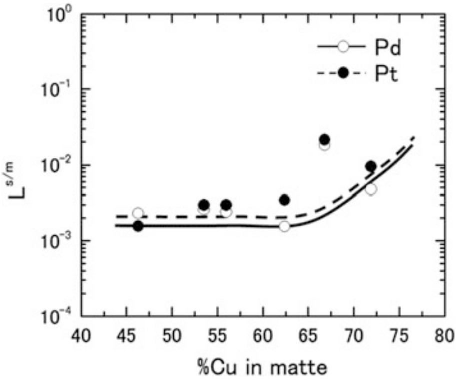


Fig. 3 Distribution ratios of platinum and palladium between the slag and matte phases against copper concentration in the matte under p_{SO2} of 0.1 atm at 1573 K

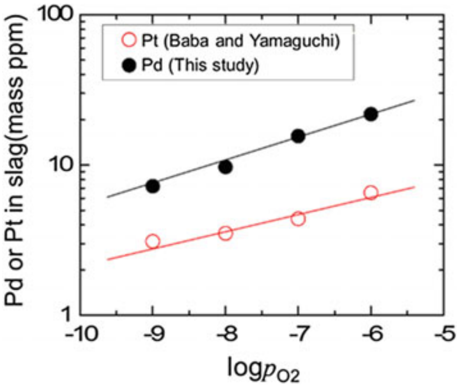


Solubility of Palladium in the FeO_x–SiO_2 Slag

The platinum solubility in the iron silicate slag was measured under controlled p_{O2} using a mixture of CO–CO_2 gases. The palladium concentration in the slag as a function of partial pressure of oxygen at 1573 K are shown in Fig. 4 as compare with the platinum solubility determined by us [7]. As shown in figure, the palladium solubility in the slag is in this range from 7 to 20 mass ppm for the range of conditions investigated and increase with increasing oxygen partial pressure.

The platinum solubility in the iron silicate slag equilibrated with the Pd–Cu alloy was determined at 1573 K. The activity of Cu and Pd in the liquid Cu–Pd alloy at 1573 K were calculated with the thermodynamic data base of FactSage software 6.3 [6]. The copper concentration in the slag, as shown in Fig. 5, increases with increasing activity of copper in the Pd–Cu alloy and decreases with decreasing partial pressure of oxygen. When activity of copper is unity, extrapolated copper solubility as the fixed oxygen partial pressure agree with the reported values by Takeda [8].

Fig. 4 The relationship between the solubility of palladium in the slag and partial pressure of oxygen (atm)



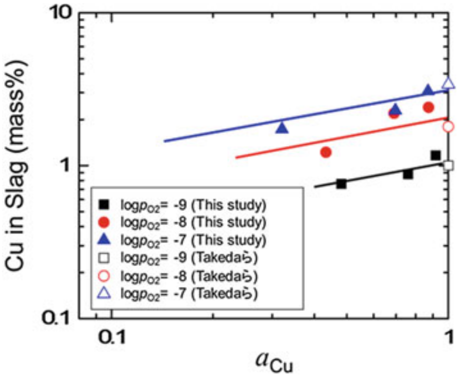


Fig. 5 The solubility of Cu in the slag against activity of Cu in the Pd–Cu alloy

Solubility of palladium in the slag equilibrated the Pd–Cu alloy as function of the activity of palladium shown in Fig. 6. The activities of palladium were estimated with FactSage software 6.3 [6]. The solubility of the palladium depends on the activity of the palladium in the alloy, and it will be large value with the increase of the palladium concentration in the alloy. However, palladium solubility decreases with increasing palladium activity.

The palladium solubility is influenced by oxygen partial pressure and alloy composition. The activity coefficient of PdO for the slag, γ_{PdO}, can be regarded as a normalization of the palladium solubility. The following reaction and equation are available to calculate the activity coefficient:

$$\mathrm{Pd(l)} + 1/2\ \mathrm{O_2(g)} = \mathrm{PdO(s)} \tag{2}$$

$$\gamma_{PdO} = \frac{K a_{Pd} p_{O_2}^{1/2} M_{Pd} n_T}{\text{mass\%Pd}}. \tag{3}$$

where K and a_{Pd} are the equilibrium constant of reaction (2) and activity of palladium in the Pd–Cu alloy calculated with the FactSage software 6.3 [6], respectively. M_{Pd} is atomic weight of palladium, n_T is total mole constituents in 100 g of the slag which are FeO_x, SiO_2 and PdO. Based on the measured palladium solubility and the oxygen partial pressure of experimental conditions, γ_{PdO} was derived

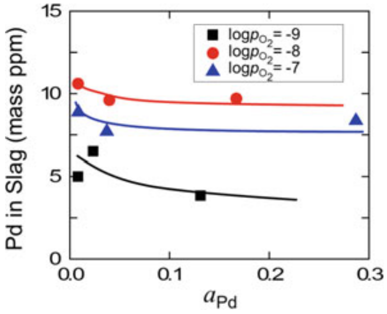


Fig. 6 The palladium solubility in the slag against activity of palladium in the Pd–Cu alloy

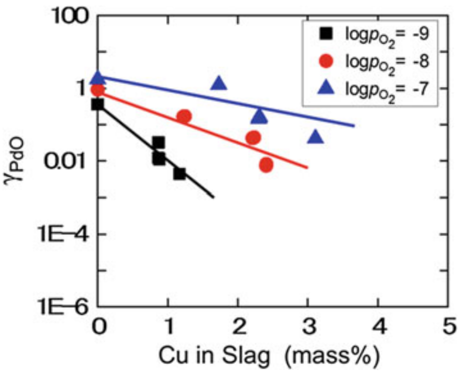


Fig. 7 The relationship between the activity coefficients of PdO and the copper content in the slag

as a function of copper content in the slag. Figure 7 shows the relationship between the activity coefficients of PdO in the slag and the copper solubility in the slag. The activity coefficients of palladium decrease with increasing of the copper content in the slag. It is found that the palladium solubility and the activity coefficient of palladium in the slag depend on the copper content in the slag. Therefore, lower copper content in the slag tend to lower slag loss of the palladium.

Conclusions

As part of the fundamental study related smelting of copper sulfide and the recycling of electronic materials, the phase relation between the FeOx–SiO_2 slag and the Cu_2S–FeS melt and the distribution of platinum and palladium between these phases in a magnesia crucible was investigated at 1573 K under controlled fixed p_{SO2} at 0.1 atm and p_{O2} and p_{S2} in ranges between $6.3 \times 10^{-9} \sim 2.5 \times 10^{-8}$ and $5 \times 10^{-4} \sim 0.01$ atm, respectively.

It is suggested from the distribution ratios that platinum and palladium are preferentially dissolved in the matte phase. The distribution ratio is around 0.001 for Pt and Pd. The distributions increased at matte concentrations greater than 60 mass% Cu, and tended to be clearing dependent on matte grade.

The palladium solubility in the iron silicate slag was measured under controlled p_{O2} using a mixture of CO–CO_2 gases. The palladium solubility in the slag increases with increasing oxygen partial pressure. The activity coefficient of palladium in the slag depends on the copper concentration in the slag. Therefore, lower copper content in the slag tend to lower slag loss of the precious metals.

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