

論文の内容の要旨

論文題目 Thermodynamics of Rhodium and Platinum in Molten Slag

(溶融スラグ中におけるロジウム及び白金の熱力学)

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In recent decades, platinum group metals (ruthenium, rhodium, palladium, osmium, iridium, and platinum) have been the key materials in a variety of specific applications including catalysts, conductive layers in electronic devices, and high corrosion resistant equipments. The scarcity, high demands and high prices of platinum group metals resources have made recycling of platinum group metals a worldwide significant issue.

Most of platinum group metals have high stability as a metal at high temperature. Therefore, the recovery of platinum group metals by a pyrometallurgical method is an outstanding option. In this study, the recovery of platinum group metals by using liquid copper or liquid iron as a collector metal has been targeted. The process of interest consists of two main steps: (1) the melting of scraps containing platinum group metals with fluxes and the collector metal in a reducing atmosphere where platinum group metals from scraps are collected in liquid metal phase; and (2) the removal of the collector metal by oxidation to enrich platinum group metals in the metal phase.

Theoretically, platinum group metals are more stable as metals at a high temperature; therefore, the high recovery in a reducing atmosphere is expected. However, for the enrichment process, the loss of platinum group metals to slag due to oxidation in the highly oxidizing atmosphere can be critical. In order to improve the recovery of platinum group metals in an oxidizing atmosphere by minimization of the loss of platinum group metals into slag, the behavior of platinum group metals in molten slag and in the collector metal has been studied.

In fact, there is only a little information on properties of platinum group metals in molten slag and liquid collector metals. Thus, more investigations for most of metals in the platinum group, especially rhodium, ruthenium, iridium and osmium, are needed. Due to the critical situations from the scarcity, high demands, high prices, difficulties of separation due to chemical inertness, and availability in the same type of scrap of rhodium and platinum, a great concern has been put on investigations for rhodium and platinum with extended discussions in comparison to ruthenium.

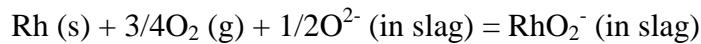
With the objective to obtain knowledge for the improvement of the recovery process of platinum group metals, three topics were examined as follow.

Firstly, in order to understand the behavior of platinum group metals in molten slag, the dissolution behavior of platinum group metals at various conditions was studied. The dissolution mechanism of platinum and ruthenium was previously reported. In the present study, the

dissolution mechanism of rhodium in Na₂O-SiO₂ slag at 1423 K to 1623 K and in CaO-SiO₂ slag at 1773 K to 1873 K in an oxidizing atmosphere were investigated.

The solubility of rhodium in the slags was measured by equilibrating the pure metallic Rh with the Na₂O-SiO₂ slag at 1423–1623 K and oxygen partial pressure between 0.0042 and 1 atm, and with the CaO-SiO₂ slag at 1773–1873 K and oxygen partial pressure between 0.100 and 1 atm.

The solubility of rhodium in both slag systems increased with increasing oxygen partial pressure, temperature, and basic oxide content in slags. The correlation between the solubility of rhodium and oxygen partial pressure suggested that rhodium dissolved in the slag as RhO_{1.5}. The dissolution of rhodium was slightly endothermic: the enthalpy change of the dissolution of solid rhodium was determined to be +50 ± 10 kJ/mol for the 50(mass pct)Na₂O-50SiO₂ and +188 ± 94 kJ/mol for the 56(mass pct)CaO-44SiO₂ slag systems. In the 50(mass pct)Na₂O-50SiO₂ melt, the enthalpy change of dissolution of rhodium was less positive than that of platinum (i.e. +37 kJ/mol) while that of ruthenium was reported to be a large negative value of -130 ± 20 kJ/mol. The increase in the solubility of rhodium with basic oxide content indicated that rhodium exhibits acidic behavior in slag. The correlation between the solubility of rhodium and sulfide capacity of the slag, a representative of slag basicity, suggested that the ionic species of rhodium in slag is rhodate ion, RhO₂⁻. Consequently, the following dissolution reaction of rhodium into slag was proposed.



From the dissolution reaction, rhodate capacity, the capacity of the slag to absorb rhodium as the rhodate ion, was defined. Rhodate capacity showed a linear correlation with theoretical optical basicity of the binary slags which was calculated from slag composition. The temperature dependence of rhodate capacity at a particular optical basicity was found to be very small. Since optical basicity of slags is considered as a generic measure of slag basicity, the use of the correlation between rhodate capacity and optical basicity to estimate the possible rhodium content in various slag systems was proposed.

Secondly, since it was known that the dissolution of platinum group metals is apparently influenced by slag composition, the loss minimization of platinum group metals in an oxidizing atmosphere by controlling slag composition can be an option. Since there are a number of materials coexisting in scraps, the proximate identification of the real slag system is difficult. In this study, effect of oxides addition to slag on the dissolution behavior of rhodium and platinum was determined.

Automobile catalysts have been the major scraps for the recycling of rhodium and platinum. Therefore, MgO, Al₂O₃, and SiO₂, which are from a honeycomb structure (Cordierite, MgO-Al₂O₃-SiO₂) in the catalysts, have been candidates of slag components. Moreover, by the removal of liquid copper or liquid iron by oxidation during the enrichment process, the content of either CuO_x or Fe₂O₃ in slag can be relatively high. Thus, CuO_x and Fe₂O₃ are considered as the major components of the recycling slag.

The solubility of rhodium and platinum was measured by equilibrating $\text{Na}_2\text{O-SiO}_2\text{-MgO}$, $\text{Na}_2\text{O-SiO}_2\text{-Al}_2\text{O}_3$, $\text{Na}_2\text{O-SiO}_2\text{-Fe}_2\text{O}_3$, and $\text{Na}_2\text{O-SiO}_2\text{-CuO}_x$ slags (at a constant $\text{Na}_2\text{O/SiO}_2$ ratio of 0.97) with pure solid rhodium or pure solid platinum in air (oxygen partial pressure at 0.21 atm) at 1473 K. The dissolution of copper or iron from slag into solid rhodium or solid platinum was observed. Hence, instead of the solubility, the activity coefficients of $\text{RhO}_{1.5}$ and PtO (the species of platinum in slag which was reported by previous research) in slags were used to compare the effects of oxides addition.

From experiments, Al_2O_3 and Fe_2O_3 behaved acidic in the slag. Al_2O_3 was found to drastically suppress the dissolution of rhodium and platinum into slag, whereas the activity coefficients of $\text{RhO}_{1.5}$ and PtO in slag were only slightly increased with increasing content of Fe_2O_3 . Since MgO is less basic than Na_2O , it behaved as a diluent for the solubility of rhodium and platinum in slag. Activity coefficients of $\text{RhO}_{1.5}$ and PtO in slag were found to decrease with increasing content of CuO_x in slag.

In the industrial view points, when the highly basic flux is used, Al_2O_3 and MgO can be the candidates of the recycling slag components which help suppressing the dissolution of rhodium and platinum into slag. Furthermore, when comparing the effect of Fe_2O_3 and CuO_x addition on the dissolution behavior of rhodium and platinum in slag, it is deduced that the use of liquid iron as a collector metal for recovery of rhodium and platinum in an oxidizing atmosphere is more preferable than copper.

Referred to the dissolution reaction of platinum which was reported previously, platinate capacity of slag was derived in this study. From experimental results, the relations between rhodate capacity and platinate capacity of the ternary slags and the calculated theoretical optical basicity were obtained. Combined to the results for the binary slags, the linear regressions between rhodate capacity or platinate capacity and theoretical optical basicity were found to be the best fit relationship. With assumptions of slag composition, activities of rhodium or platinum in the collector metal, and oxygen partial pressure, the contents of rhodate ion and platinate ion in multi-component slags were estimated.

Thirdly, since thermodynamic properties of a platinum metal in the collector metal are the important factors which affect the effectiveness of the recovery process, with the focus on the use of copper as the collector metal, thermodynamic properties of the Cu-Rh system was examined.

The activity coefficients of copper in Cu-Rh solid alloys were determined by equilibrating the Cu-Rh alloys with pure solid Cu_2O at 1473 K at different activities of copper in the alloys 1473 K. The calculation of the activity of copper was made by referring pure solid copper and pure solid Cu_2O , which was assigned to unity, as standard states. The activity of rhodium in copper at 1473 K was then estimated by Gibbs-Duhem relation. The collectability of copper for rhodium was discussed in comparison to that of iron.

From experimental results, the activity of copper in Cu-Rh solid alloys showed the large positive deviation from ideality, in which the content of copper in the solid alloys varied from 0.05 to 0.48 for $0.27 < a_{\text{Cu}} < 0.86$. Previous study suggested that, at 1473 K, the activity of iron in Fe-Rh (Rh rich, $X_{\text{Fe}} < 0.3$) solid alloys at exhibited the negative deviation from ideality.

Accordingly, it was considered that iron is a more preferable collector metal for rhodium than copper. In case of platinum, the activity of platinum in both the Cu-Pt system (1373 K, 1473 K, and 1542–1673 K) and the Fe-Pt system (1473–1673 K and 1823 K) exhibited a large negative deviation from ideality. Therefore, it was deduced that both copper and iron can be the collector metal candidates for platinum.