

Purification and Recovery of Rhodium Metal by the Formation of Intermetallic Compounds

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Precious metals have long been used to jewelry and ornaments industry. Platinum group metals (PGMs) are generally referred to the six precious metal elements-platinum, palladium, rhodium, iridium, ruthenium, and osmium. As PGMs have distinguished properties of heat resistance, anti-corrosion and catalytic activity, PGMs are used in many fields, such as electronics, dental alloys and automotive catalysts.¹

The catalysts manufacturing industry is the second largest consumer of PGMs after the jewelry industry. Automotive catalysts comprise refractory oxides support on which two or more precious metals (platinum, palladium, rhodium etc.) are dispersed in very low concentration (0.1-0.3 wt.% of the monolith). The honeycomb type monolith is typically made of a cordierite ($2\text{Al}_2\text{O}_3 \cdot 2\text{MgO} \cdot 5\text{SiO}_2$).² Several researchers have dealt with the recovery of these metals as the recovery of precious metals from spent automotive catalysts is of economical importance.³⁻⁷ Spent autocatalysts are usually smelted in the presence of larger amounts of collector metals (Cu, Fe, Pb, Ni etc.) After leaching the precious metals enriched in the collector metals with acid, the precious metals can be selectively recovered.

Among PGMs, rhodium (Rh) is an exceedingly rare element, comprising only 0.0001 PPM of the earth's crust.⁸ Moreover, rhodium is especially notable for its extreme inertness to acids, even aqua regia. Because of scarcity and high price, the recovery of rhodium from scrap is an important issue. Rhodium has a special catalytic activity to reduce nitrogen oxides (NO_x) to N_2 , and is a main element as an autocatalyst.⁹ Rhodium plated electrodes are used in the soda industry for electrolysis of salt water, and for electrodes for domestic water treatment. Rhodium plating is used widely in the jewelry industry. In the electronics industry, rhodium plating is used for electric contacts, e.g., ferreed switches.¹⁰

The purification and recovery of rhodium from the other precious metals has always been difficult because of its complex aqueous chemistry in chloride solution as well as extreme inertness to acids, even aqua regia.

It should be pointed out that the key factor for success in the separation of rhodium from the other precious metals is the developing an effective dissolution process for rhodium. It is well known that the disulfate melt technique on rhodium metal is utilized for quantitative dissolution of rhodium and

its separation from iridium and platinum.¹¹ Another method has been developed for recovering PGMs from scrap with the propose of improving Rh dissolution in acid. Reactive metal vapours such as magnesium (Mg) and calcium (Ca) were reacted with powdered Rh in a closed stainless steel reaction vessel at a constant temperature ranging from 873 to 1173 K.⁹

Iron(II) oxide with NaCl structure was successfully synthesized in a quartz tube sealed under vacuum. Hematite in an evacuated silica tube progressively loses oxide ions at 1373 K depending on the heating time. Finally, $\alpha\text{-Fe}_2\text{O}_3$ is completely transformed into the well crystallized $\text{Fe}_{0.935}\text{O}$ after heat treatment at 1373 K for 84 h.¹²

Silica tube is very suitable one for the chemical vapour transport reactions in an inert atmosphere because of high-temperature resistance, no-contaminants including foreign metals, and the ease of sealing under vacuum.

In this work, the chemical vapour transport reactions between magnesium and rhodium are attempted using silica ampoules sealed under vacuum. And also, the verifications, such as the formation and dissolution of intermetallic compounds (Mg_xRh_y), purification and recovery of rhodium, are performed.

Experimental Section

Rhodium metal powder (rhodium black) was obtained from GMS21 Co., Ltd. Rhodium black powders (≈ 500 mg) were mixed with magnesium metal powders (≈ 1 g, 50 mesh) and taken into clean dried silica ampoules (24 mm outer diameter, 150 mm in length, and 50 mL inner volume). The silica ampoules were then evacuated at room temperature for 2h and sealed under vacuum ($\approx 3 \times 10^{-3}$ torr). The reaction ampoules were heated in an electric furnace at temperature ranging from 500 to 800 °C for 5h. After thermal treatment, the samples were collected from the opened silica ampoules. X-ray diffraction patterns of powder samples were achieved by Schmadzu 6000 model using $\text{Cu-K}\alpha$ radiation. The samples were dissolved using aqua regia. Rhodium was recovered and purified from the solution by cementation using copper metal powder. The morphologies of recovered rhodium powder were analyzed by scanning electron microscopy (SEM) using S-4200 model of Hitachi under $V_{\text{acc}} \approx 10$ kV.

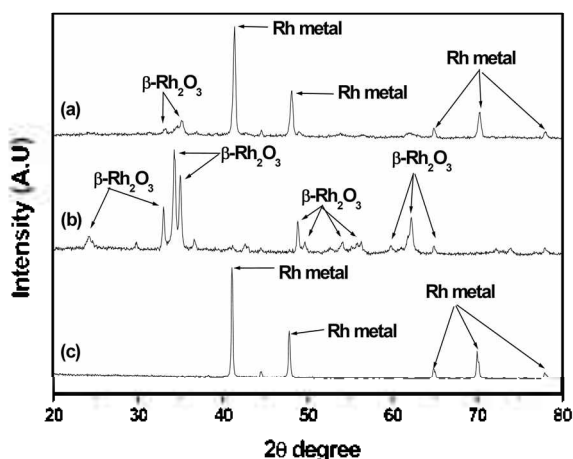


Figure 1. XRD patterns of rhodium black, as received (a); oxidation in air at 800 °C for 5 h (b); reduction under 96% N_2 /4% H_2 mixture gas at 900 °C for 5 h (c).

Results and Discussion

Characterization of rhodium black as received and intermetallic compounds. Figure 1 shows XRD patterns of rhodium black before and after reduction (96% N_2 /4% H_2 mixture gas, 900 °C, 5 h) or oxidation (in air, 800 °C, 5 h). The XRD pattern (a) reveals that rhodium black as received is partially oxidized, and rhodium black after oxidation completely transforms into the $\beta\text{-Rh}_2\text{O}_3$ compound as indicated in pattern (b). After reduction on rhodium black, the well crystallized rhodium metal is obtained as shown in pattern (c). It should be pointed out that the reduction process on rhodium black is necessary to form an intermetallic compounds (Mg_xRh_y) between magnesium and rhodium because the MgRh_2O_4 formed by the oxide ion source is scarcely dissolved in acids, even aqua regia.

Rhodium black powder was treated in a reduction atmosphere at 900 °C for 5 h using N_2/H_2 mixture gas, and subsequently verified as rhodium metal by XRD analysis. The mixed powder (200 mg-rhodium metal and 3 g- NaHSO_4 as the fusion agent) lodged in an alumina crucible was heated in air at 600 °C for 5 h, and then dissolved in 30 mL aqua regia for the preparation of ICP analysis solution. Table 1 represents the chemical composition of rhodium black (raw material) obtained by ICP analysis. As depicted in Table 1, the main impurities of rhodium black are Ag, Cu, Fe, Mg, and Zn. So, the purity of rhodium is estimated to be 78.80%.

Chemical vapour transport reaction between Mg and Rh. The boiling point of magnesium at 1 atm is 1107 °C and the heat of vaporization is 127.4 kJ/mol at 1 atm. The boiling point of Mg at 3.95×10^{-6} atm (in this work) is calculated by Clausius-Clapeyron equation and the estimated value is 378 °C. And also, based on the boiling point (3,760 °C) and heat of vaporization (494 kJ/mol) at 1 atm, the boiling point of Rh at 3.95×10^{-6} atm is estimated to be 1913 °C by Clausius-Clapeyron equation. Compared with the boiling points of two metals at working condition, it is reasonable

Table 1. Chemical compositions of Rhodium black

| Ag (ppm) | Cu (ppm) | Fe (ppm) | Mg (ppm) | Rh ^a (pm) | Zn (ppm) |
|----------|----------|----------|----------|----------------------|----------|
| 2.14 | 4.49 | 1.17 | 3.05 | 341.20 | 21.11 |

^aThe purity of Rhodium Black (ρ_0): 78.80

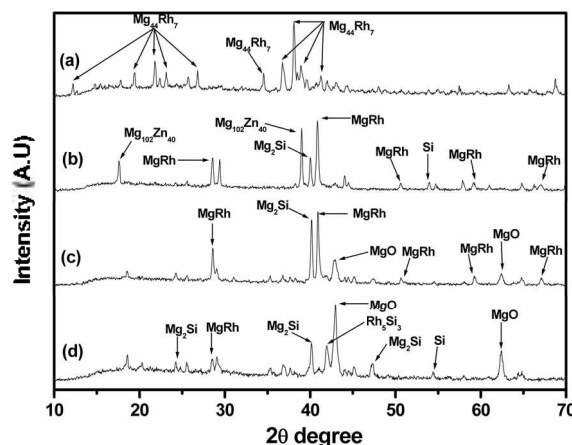


Figure 2. XRD patterns of powder samples after chemical vapour transport reactions in the silica ampoules under vacuum at various temperatures, 500 °C for 5 h (a); 600 °C for 5 h (b); 700 °C for 5 h (c); 800 °C for 5 h (d).

that the magnesium metal vapour transfers to the particulates of rhodium metal, which results in the intermetallic compounds of Mg_xRh_y , easily formed in the silica ampoules under vacuum at a certain temperature. Figure 2 represents XRD patterns after chemical vapour transport reactions between Rh metal and Mg metal in the silica ampoules under vacuum at various temperatures. The XRD pattern (a) reveals that the main phase is $\text{Mg}_{44}\text{Rh}_7$ one after thermal treatment at 500 °C for 5 h. At higher temperature (600 °C), the new phases, such as MgRh, $\text{Mg}_{102}\text{Zn}_{40}$, Mg_2Si , Si are formed as shown in the XRD pattern (b). It should be mentioned that Zn element comes from the impurity of Rh metal as depicted in Table 1 and Si element is due to the partially decomposed silica ampoules. The XRD pattern (c) after thermal treatment at 700 °C, are very similar to the XRD pattern (b) except the disappeared $\text{Mg}_{102}\text{Zn}_{40}$ and the newly formed MgO phase. After thermal treatment at 800 °C, the high temperature phases, such as Mg_2Si , MgRh, Rh_2Si_2 , Si, and MgO come into existence.

Rh dissolution in acid. The powders obtained from the crushed silica ampoules were dissolved using aqua regia at 60 °C and then filtered. In the dissolution using aqua regia,

Table 2. Concentration and recovery % of Rhodium as a function of temperature

| Condition | Rh (ppm) | Rh recovery% |
|--|----------|--------------|
| silica ampoule treated at 500 °C for 5 h | 300.54 | 87.79 |
| silica ampoule treated at 600 °C for 5 h | 307.33 | 95.45 |
| silica ampoule treated at 700 °C for 5 h | 268.97 | 83.53 |
| silica ampoule treated at 800 °C for 5 h | 320.86 | 99.75 |

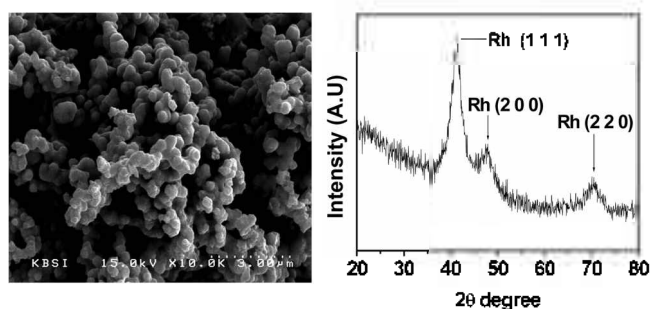


Figure 3. SEM image of the compound recovered by cementation (left) and its XRD pattern (right).

the color of the solution changed from clear yellow to rosy red, indicating that Rh dissolved in the solution. ICP analysis reveals the concentration (ppm) and recovery% of rhodium as shown in Table 2. The percentages of Rh recovery tend to increase as the temperature of silica ampoule is augmented. However at 700 °C, the lowest value is obtained, which is due to the formation of insoluble matters under aqua regia.

Rh recovery experiment. Rh dissolved aqua regia solution was then heated and dried to remove nitric acid. The dried compound was again dissolved in 2 M H₂SO₄ solution and then subjected to Rh recovery. The standard reduction potentials of impurities (Ag, Cu, Fe, Mg, and Zn) and Rh as shown in Table 1, are as followed;

$\text{Ag}^+/\text{Ag} = 0.799 \text{ V}$, $\text{Cu}^{2+}/\text{Cu} = 0.337 \text{ V}$, $\text{Fe}^{2+}/\text{Fe} = -0.440 \text{ V}$,
 $\text{Mg}^{2+}/\text{Mg} = -2.37 \text{ V}$, $\text{Zn}^{2+}/\text{Zn} = -0.762 \text{ V}$, $\text{Rh}^{3+}/\text{Rh} = 0.758 \text{ V}$.

Based on the standard reduction potentials, it is reasonable that the excess amount of Cu powder was added to the Rh dissolved 2 M H₂SO₄ solution at 50 °C. After keeping the solution containing the precipitate at 50 °C for 2 h, the black precipitate was recovered by centrifugation and treated with

6 N HNO₃ solution in order to remove Ag and residue Cu. This manipulation promises to be highly purified Rh metal. Figure 3(a) shows the SEM image of the compound recovered from the solution containing Rh by cementation using Cu powder. The recovered precipitate was observed as aggregated pseudo-spherical particles = 30 nm in diameter. Figure 3(b) indicates that the precipitate is mostly metallic Rh, and the impurity phases were not identified by XRD analysis. ICP analysis reveals that the purity of the recovered Rh is approximately 99.2%.

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