Effective Alloying Treatment for Platinum Using Iron Chloride Vapor

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An effective alloying treatment for Pt using FeCl₂ (x = 2, 3) vapor was demonstrated towards developing a novel recovery process for platinum group metals (PGMs) in catalyst scrap. Suitable reaction conditions were discussed from the perspective of thermodynamics, and its validity was confirmed experimentally. When pure Pt samples were reacted with FeCl₂ vapor at 1200 K under the coexistence of metallic Fe, an Fe-Pt alloy showing ferromagnetism was easily formed, even though the samples were not in physical contact with the metallic Fe. On the basis of thermodynamic considerations, alloying of Pt mainly proceeds via the disproportionation of FeCl₂ vapor, with the gaseous phase containing FeCl₃ acting as the medium to transport Fe from the metallic Fe to the Pt samples. When the alloyed sample was kept under FeCl₃ vapor at 1200 K, Fe was removed and ferromagnetism was lost. Therefore, it is concluded that FeCl₂ vapor treatment under the coexistence of Fe is a feasible and useful technique for alloying Pt and forming a ferromagnetic Fe-Pt alloy. The results obtained in this study indicate that treatment with FeCl₂ vapor followed by magnetic separation has potential as an effective technique for concentrating PGMs directly from catalyst scrap. [doi:10.2320/matertrans.M-M2017844]

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1. Introduction

Pt and other platinum group metals (PGMs) are indispensable in various catalysts owing to their unique catalytic activities with excellent heat and corrosion resistance.¹–³ For example, the catalytic converter in automobiles, a device used for detoxifying automobile emissions, usually contains Pt, Pd, and Rh; in 2015, this application accounted for approximately 40% of the world’s consumption of Pt.⁴–⁵ PGM-based catalysts are also widely used in the petroleum refining industry.

The recovery of PGMs including Pt from spent catalysts has been actively carried out in many countries because they are costly to procure. It is notable that the mineral resources of PGMs are predominately localized in South Africa and Russia,¹–⁴ and that their extraction and subsequent treatment generates large quantities of waste and consumes a considerable amount of energy. Recycling PGMs is also important for ensuring their steady supply and for reducing the environmental burden.

Most catalyst scrap has a complicated structure, with Pt and other PGMs present as minor components. For example, automobile catalytic converters mostly consist of a honeycomb-structured ceramic substrate composed of cordierite or a similar chemically stable ceramic material. The substrate is coated with a porous catalyst layer consisting of various oxides such as alumina and ceria. PGMs are supported on the porous catalyst layer in the form of fine particles, with the total PGM concentration in the catalyst being approximately 500–5000 mass ppm.⁶–⁷ The low PGM concentrations and the complex scrap structure make the effective recovery of PGMs difficult. Furthermore, PGMs are chemically stable and do not react with most acids. The high chemical stabilities of PGMs also make their extraction difficult.

In typical commercial recycling processes, catalyst scraps are mechanically pulverized in order to evaluate the PGM content (i.e., the scrap value), and then subjected to a pyrometallurgical process to concentrate the PGMs.²,³ Subsequently, the enriched PGMs are dissolved using strong oxidizing acids, such as aqua regia (HCl/HNO₃) and hydrochloric acid with chlorine gas (HCl/Cl₂).¹–³,⁶ Finaly, the PGMs extracted into HCl solution are purified and separated using various hydrometallurgical techniques such as solvent extraction, precipitation, and ion exchange.¹–³,⁶,⁷ In the pyrometallurgical concentration process, catalyst scraps are smelted with a collector metal such as Cu or Fe; the PGMs are concentrated in the metallic phase, and the ceramic components of the scraps are removed as slag waste.¹–³,⁸,⁹ While the pyrometallurgical process is an effective upgrading technique for catalyst scraps, it requires large-scale equipment and is energy-intensive.

In general, physical separation such as flotation and magnetic separation can be performed using simple and small-scale equipment with low energy consumption. Thus, some studies have been conducted on the enrichment process based on physical separation techniques. For example, magnetic separation after pulverization,¹⁰,¹¹ flotation after pulverization,¹¹,¹² selective grinding followed by size separation,¹³,¹⁴ and selective grinding after a heating/quenching treatment¹⁵ have been investigated for physically concentrating PGMs from spent automobile catalysts. Furthermore, physical concentration techniques involving chemical pretreatments, such as alloying, sulfurization, and electroless plating, have also been explored.¹⁶–⁲⁰ However, these techniques are still in the research stage or are not practical for industrial use. Nevertheless, they have potential for reducing the energy consumption and environmental burden of the existing recycling process. Furthermore, if a physical concentration pretreatment could sufficiently enrich the PGMs, they could be effectively extracted by acid dissolution without employing the pyrometallurgical concentration process.

In order to develop a novel physical concentration technique where the PGMs are efficiently concentrated by mag-
netic separation, the present authors have focused on the vapor-based alloying pretreatment for PGMs shown in Fig. 1. To the best of our knowledge, Okabe and Mitsui first proposed in a patent the basic concept of magnetic concentration involving alloying pretreatment.\textsuperscript{16} Notably, some of the alloys between Fe and PGMs show strong ferromagnetism close to room temperature. In addition, alloying with Fe can facilitate the acid dissolution of the PGMs.\textsuperscript{21} Thus, alloying with Fe is a valuable pretreatment for magnetically concentrating the PGMs from catalyst scrap. However, because PGMs are present on the scrap surface, which is inherently complex, it is quite difficult to alloy them directly by the reaction with solid Fe. Thus, in the alloying and magnetizing treatment shown in Fig. 1, FeCl\textsubscript{x} (x = 2, 3) vapor is used as the reactant. As shown in Fig. 2, FeCl\textsubscript{2} and FeCl\textsubscript{3} are highly volatile compared with Fe.\textsuperscript{22} This means that FeCl\textsubscript{x} vapor can be easily and effectively supplied to the PGMs on the scrap surfaces by heating.

Although alloying pretreatment using FeCl\textsubscript{1} vapor is attractive for the reasons given above, research on this technique is quite limited. In the patent by Okabe and Mitsui, for example, powder PGM samples (Pt, Pd, and Rh) were alloyed with Fe when heated under FeCl\textsubscript{3} vapor at 973–1273 K in a quartz chamber.\textsuperscript{16} However, the reported results included large uncertainties and were not reproducible. In our previous study,\textsuperscript{20} alloying and magnetization of PGMs (Pt, Pd, and Rh) was confirmed when thin wire samples were reacted with FeCl\textsubscript{2} vapor in a steel vessel maintained at 1200 K. However, the research was preliminary, and the alloying reaction mechanism was unclear. In this study, thermodynamic analyses and experiments were conducted on the FeCl\textsubscript{x}-vapor-based alloying treatment for Pt and the reaction system that effectively alloys Pt with Fe is clarified.

2. Thermodynamic Considerations

Alloying treatment of Pt is discussed at a reaction temperature of 1200 K. At this temperature, the stable phase of FeCl\textsubscript{2} is liquid. However, its vapor pressure (p\textsubscript{FeCl\textsubscript{2}}) is as high as 3.2 × 10\textsuperscript{-1} atm,\textsuperscript{22} as shown in Fig. 2, and it is possible to effectively supply FeCl\textsubscript{2} vapor on Pt. FeCl\textsubscript{3} is more volatile than FeCl\textsubscript{2}. FeCl\textsubscript{3} volatilizes mainly as a dimer at relatively low temperatures, but its monomeric gas becomes stable near 1200 K. It is also noteworthy that analogous preliminary experiments were performed at around this temperature in previous studies.\textsuperscript{16,20}

Figure 3(a) shows the phase diagram of the Fe-Pt system.\textsuperscript{23–25} Pure Pt has a face-centered cubic (fcc) structure and forms a fcc solid solution (γ-(Fe,Pt)) with Fe. Besides a disordered fcc phase, three stable ordered phases are present (i.e., γ\textsubscript{1}-Fe\textsubscript{3}Pt with an L1\textsubscript{2} structure, γ\textsubscript{2}-FePt with an L1\textsubscript{0} structure, and γ\textsubscript{3}-FePt\textsubscript{3} with an L1\textsubscript{2} structure). In addition, a stable region of the solid solution with a body-centered cubic (bcc) structure (α-(Fe,Pt)) is present at the Fe-rich region below 1185 K. γ-(Fe,Pt), γ\textsubscript{1}-Fe\textsubscript{3}Pt, and γ\textsubscript{2}-FePt exhibit ferromagnetism at ordinary temperatures (∼298 K).

As shown in Fig. 3(a), with an increase in the Fe concentration at 1200 K, the stable phase changes from Pt-rich γ-(Fe,Pt) to γ\textsubscript{1}-Fe\textsubscript{3}Pt, to γ\textsubscript{2}-FePt, and then to Fe-rich γ-(Fe,Pt). The reported phase boundaries relating to the ordered phases differ somewhat in the literature.\textsuperscript{23,24,26–28} However, Fig. 3(a) shows that γ\textsubscript{2}-FePt or Fe-Pt alloys con-
taining γ2-FePt (i.e., a mixture of γ2-FePt3 and γ2-FePt) and a mixture of γ2-FePt and Fe-rich γ-(Fe,Pt) become stable at an Fe concentration of approximately 35–65 mol%. γ2-FePt is ferromagnetic at room temperature, and its formation allows us to effectively recover the Pt from scrap by magnetic separation. When the Fe concentration exceeds approximately 65 mol% at 1200 K, the Fe-rich γ-(Fe,Pt) phase becomes stable. This Fe-rich phase can be converted into Fe-Pt alloys with ferromagnetic properties at room temperature (i.e., α-(Fe,Pt), γ1-Fe3Pt, and/or γ2-FePt) during cooling or by annealing at intermediate temperatures. For the efficient recovery of Pt from catalyst scrap by magnetic separation, it is necessary to convert Pt into γ2-FePt and/or Fe-rich γ-(Fe,Pt) in the alloying reaction at 1200 K.

Fredriksson and Seetharaman measured the activities of Fe (αFe) in some Fe-Pt alloys (their compositions are denoted by open circles in Fig. 3(a)) by the solid-electrolyte galvanic cell method in the temperature range of 1073–1273 K.25) Based on this study, αFe was evaluated at 1200 K and shown in Fig. 3(b). In the evaluation of αFe, the standard state of Fe was defined to be its pure solid state. Overall, the αFe values show negative deviation from ideality due to the strong affinity of Fe with Pt. The αFe value under the γ-(Fe,Pt)/γ2-FePt equilibrium was estimated to be $\frac{-5 \times 10^{-1}}{1}$, based on the αFe values of points b and c. Meanwhile, the αFe value under the γ2-FePt/γ1-Fe3Pt equilibrium was $4 \times 10^{-2}$, as represented by the αFe values of point d. In terms of equilibrium, Pt can be converted into γ2-FePt when the αFe of the reaction system is higher than $4 \times 10^{-2}$. Furthermore, when the αFe of the reaction system is higher than $5 \times 10^{-1}$, Fe-rich γ-(Fe,Pt) can form at 1200 K.

Figure 4 shows the chemical potential diagram for the Fe-Cl-O system. The diagram was calculated at 1200 K using thermodynamic data22) based on the assumption that the activity of all chemical species is unity (the standard state of gaseous species is 1 atm). The axes correspond to the logarithms of αFe, the partial pressure of chlorine (pCl2), and the partial pressure of oxygen (pO2). The most stable phases are represented as faces, whereas the phase equilibria are indicated by the intersections between these faces.

Figure 4 shows that FeCl2(l) equilibrates with Fe(s) and FeO(s) at the potential point α: αFe = 1, pCl2 = $1 \times 10^{-6}$ atm, and pO2 = $1 \times 10^{-17}$ atm. This indicates that when the amounts of Fe(s) and FeCl2(l) are present in sufficient quantities in the reaction system, its chemical potential can be maintained close to point α (i.e., a high αFe condition). From the viewpoint of equilibrium, alloying Pt with Fe proceeds until the αFe of the Fe-Pt alloy equals the αFe of the reaction system. As mentioned earlier, FeCl3(l) equilibrates with FeCl2(s) with a partial pressure of $3.2 \times 10^{-1}$ atm at 1200 K. Therefore, the reaction with FeCl3 vapor under the coexistence with Fe(s) and FeCl2(l) has the potential to convert Pt into γ2-FePt and/or Fe-rich γ-(Fe,Pt).

Figure 4 also indicates that FeCl3(g) is stable under low αFe and high pCl2 conditions. FeCl3(g) cannot coexist with Fe(s) and equilibrates with FeCl2(l) and Fe2O3(s) at the potential point β: αFe = $1 \times 10^{-3}$, pCl2 = $1 \times 10^{-2}$ atm, and pO2 = $3 \times 10^{-5}$ atm. The αFe region where FeCl3(g) is stable is much lower than the αFe in γ2-FePt (αFe) and Fe-rich γ-(Fe,Pt). This means that Pt cannot be converted into γ2-FePt and/or Fe-rich γ-(Fe,Pt) by reacting with FeCl3 vapor.

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**Fig. 3** (a) Phase diagram for the Fe-Pt system22,24) and (b) activities of Fe estimated at 1200 K. The Fe activities at the composition and temperature denoted by open circles were evaluated based on the reported data.25

**Fig. 4** Chemical potential diagram for the Fe-Cl-O system at 1200 K. Thermodynamic data in reference22) was used. The potential point α and β corresponds to the Fe/FeCl2/FeO and FeCl3/FeCl2/Fe2O3 equilibria, respectively.
at 1200 K. In other words, if the γ₂-FePt or Fe-rich γ-(Fe,Pt) is kept under FeCl₃ vapor, dealloying would proceed as follows:

\[ \text{Fe}(s, \text{in Pt}) + 2\text{FeCl}_3(g) \rightarrow 3\text{FeCl}_2(l) \]  
\[ \text{Fe}(s) + 2\text{FeCl}_3(g) = 3\text{FeCl}_2(l) \]  
\[ \Delta G^{\circ}(2) = -160 \text{ kJ at 1200 K}^{22} \]

where \( \Delta G^{\circ}(2) \) is the standard Gibbs energy of reaction (2).

When Pt is reacted with FeCl₂ vapor under the coexistence of Fe, two types of alloying reactions can be expected. One of them is a disproportionation of FeCl₂ vapor. As shown in Fig. 5(a), when the disproportionation of FeCl₂ vapor proceeds on the surface of Pt, Pt is alloyed with Fe, and FeCl₃ vapor is generated as a by-product.

\[ 3\text{FeCl}_2(g) \rightarrow \text{Fe}(s, \text{in Pt}) + 2\text{FeCl}_3(g) \]  
\[ 3\text{FeCl}_2(g) = \text{Fe}(s) + 2\text{FeCl}_3(g) \]  
\[ \Delta G^{\circ}(4) = 126 \text{ kJ at 1200 K}^{22} \]

The FeCl₃ generated by the disproportionation diffuses in the gas phase and then reacts with Fe, which regenerates FeCl₂.

\[ \text{Fe}(s) + 2\text{FeCl}_3(g) \rightarrow 3\text{FeCl}_2(g) \]  
\[ \Delta G^{\circ}(7) = 194 \text{ kJ at 1200 K}^{22} \]

Another alloying reaction expected to proceed is the thermal decomposition of FeCl₂ vapor, as shown in Fig. 5(b). In this case, Cl₂ gas is generated as a by-product of the alloying reaction.

\[ \text{FeCl}_2(g) \rightarrow \text{Fe}(s, \text{in Pt}) + \text{Cl}_2(g) \]  
\[ \text{FeCl}_2(g) = \text{Fe}(s) + \text{Cl}_2(g) \]  
\[ \Delta G^{\circ}(8) = 194 \text{ kJ at 1200 K}^{22} \]

Subsequently, the Cl₂ gas generated by the thermal decomposition regenerates FeCl₂ by reacting with metallic Fe.

\[ \text{Fe}(s) + \text{Cl}_2(g) \rightarrow \text{FeCl}_2(g) \]  
\[ \Delta G^{\circ}(9) \]

In either case, FeCl₂ vapor acts as a transport medium for Fe and is not consumed in the overall reaction:

\[ \text{Fe}(s) \rightarrow \text{Fe}(s, \text{in Pt}) \]

Given the dominant alloying reaction in the FeCl₂ vapor treatment between disproportionation (reaction (3)) and thermal decomposition (reaction (6)), the equilibrium partial pressures of FeCl₃ and Cl₂ \( (p_{\text{FeCl}_3} \text{ and } p_{\text{Cl}_2}, \text{ respectively}) \) on the Fe-Pt alloy were calculated at 1200 K using thermodynamic data.\(^{22} \)

Figure 6 shows the \( a_{\text{Fe}} \) dependence of the \( p_{\text{FeCl}_3} \) and \( p_{\text{Cl}_2} \) when the \( p_{\text{FeCl}_2} \) is \( 3.2 \times 10^{-1} \) atm. The \( p_{\text{FeCl}_3} \) and \( p_{\text{Cl}_2} \), equilibrating with the Fe-Pt alloy and FeCl₂ vapor decrease with an increase in \( a_{\text{Fe}} \). As shown in Fig. 6, the \( p_{\text{FeCl}_3} \) is orders of magnitude greater than the \( p_{\text{Cl}_2} \). For example, when the \( a_{\text{Fe}} \) is \( 1 \times 10^{-1} \) (γ₂-FePt is stable), the \( p_{\text{FeCl}_3} \) is \( 1 \times 10^{-3} \) atm, but the \( p_{\text{Cl}_2} \) is as low as \( 1 \times 10^{-8} \) atm. Thus, it
is reasonable to consider that the alloying of Pt by the thermal decomposition of FeCl₂ is negligible. In the proposed FeCl₂ vapor treatment (see Fig. 5), alloying of Pt with Fe should proceed mainly by the disproportionation of FeCl₂ vapor.

3. Experimental

3.1 Reaction with FeCl₂ vapor under the coexistence of Fe

Alloying of Pt using FeCl₂ vapor was demonstrated using the experimental apparatus shown in Fig. 7 (Exp. no. 170201_Fe-PGM_exp1). The quartz container, which is composed of four L-shaped units welded to the center unit, was used as the reaction chamber. The four L-shaped units contained either micron-sized Pt powder (99.95%; gray color; Tanaka Kikinzoku Kogyo K.K.; cf. Figure 10(a)) or thin Pt wire (99.99%; diameter (ϕ) = 0.5 mm; length (l) = approximately 20 mm; Tanaka Kikinzoku Kogyo K.K.); their abbreviations and masses of Pt samples are listed in Table 1. A mixture of Fe powder (4.01 g; >95%; Wako Pure Chemical Industries, Ltd.) and FeCl₂ powder (0.51 g; 99.9%; Kojundo Chemical Laboratory Co., Ltd.) was placed at the bottom of the center unit. To avoid the adsorption of water from ambient air, a mixture of Fe and FeCl₂ powders were loaded in the quartz chamber inside a glove box under a high-purity N₂ atmosphere. The chamber was then sealed in vacuum. The internal volume of the quartz ampoule was approximately 23 mL. In the quartz ampoule, the Pt samples were not in physical contact with the metallic Fe.

The quartz ampoule shown in Fig. 7(b) was kept for 1 h in an electric furnace preheated at 1200 K. After the heat treatment, the ampoule was removed from the furnace and cooled in water. Fig. 7(c) shows the quartz ampoule after the heat treatment. Processed Pt samples were recovered by breaking the ampoule using a hammer. When the quartz ampoule was broken, Pt samples in the form of powder were scattered, and only a fraction of the samples was recovered. The recovered Pt samples were rinsed with distilled water, ethanol, and then acetone before they were dried in air.

After the FeCl₂ vapor treatment, the magnetic properties of the powder and wire samples were verified using a small round neodymium magnet (Nd-Fe-B alloy; diameter, ϕ = 7 mm; height, h = 5 mm). For the powder samples, the microstructures and crystalline phases were analyzed by scanning electron microscopy (SEM) using a JSM-6510LV (JEOL) system and by X-ray diffraction (XRD) using a D2 PHASER (Bruker Corporation, Cu-Kα radiation), respectively. Furthermore, the average compositions of the processed powder samples were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). For these experiments, a fraction of the powder sample (approximately 0.1 g) was dissolved completely using aqua regia at approximately 333 K. After the solution had evaporated completely, the resulting salt was dissolved again in 50 mL of 2 M HCl. Then, the solution was diluted by 50 times using 2 M HCl to prepare the sample solution. The Fe and Pt concentrations in the sample solution were analyzed using a SPS3520UV (SII NanoTechnology Inc.).

Regarding the wire samples after processing, one of them (Pt-W-1) was subjected to cross-sectional observation. The wire sample was embedded in resin, and SEM and energy-dispersive X-ray spectroscopy (EDS) using a JSM-6510LV (JEOL) were used to analyze the microstructure and composition of the cross-section. Another wire sample (Pt-W-2) was used as a feed material in the experiment described in Section 3.2.

3.2 Reaction with FeCl₃ vapor under the coexistence of FeCl₂

The instability of Fe-Pt alloy under FeCl₃ vapor was confirmed experimentally using the apparatus shown in Fig. 8 (Exp. no. 170213_Fe-PGM_exp4). The Pt wire (Pt-W-2) after alloying treatment using FeCl₂ vapor (cf. Section 3.1) was held in a quartz ampoule with a mixture of FeCl₂ powder (0.15 g; 99.9%; Kojundo Chemical Laboratory Co., Ltd.), FeCl₃ powder (0.026 g; 99%; Kojundo Chemical Laboratory Co., Ltd.), and Fe₂O₃ powder (0.15 g; >95%; Kanto Chemical Co., Ltd.). The internal volume of the quartz ampoule was approximately 22 mL. Since iron chlorides are hydroscopic, the FeCl₂/FeCl₃/Fe₂O₃ mixture was treated and loaded in the quartz chamber inside a glove box under a high-purity N₂ atmosphere. Furthermore, the chamber was sealed in vacuum immediately after its removal from the glove box.

The quartz ampoule containing the samples was heated to 1200 K at a heating rate of 1.8 K min⁻¹ in an electric furnace and then maintained at 1200 K for 4 h. After the heat treatment, the ampoule was removed from the furnace and cooled in water. Figures 8(b) and 8(c) show the quartz ampoule before and after the heat treatment, respectively. The wire sample was recovered by breaking the quartz ampoule, and its surface was then rinsed with ethanol. The magnetic property of the wire sample was tested using a handheld neodymium magnet, and cross-sectional SEM/EDS analyses were performed.

4. Results and Discussion

4.1 Alloying of Pt by the reaction with FeCl₂ vapor

After the reaction with FeCl₂ vapor at 1200 K for 1 h in the quartz ampoule, the resultant powder samples (Pt-P-1 and Pt-P-2) were attached to a magnet, as shown in Figs. 9(a) and 9(b), respectively, and metallic Fe remained at the bottom of the center unit (see Fig. 7(c)). Figure 10 shows the SEM images of the Pt-P-1 powder sample before and after the experiment. The particle size of Pt increased somewhat following the FeCl₂ vapor treatment. Figure 11 shows the XRD patterns of the powder samples. It is clear that Pt was effectively alloyed with Fe and that γ₂-FePt, which exhibits ferromagnetism at room temperature, was formed. In the case of Pt-P-1, all diffraction peaks can be rationalized in terms of γ₂-FePt. However, Pt-P-2 contained a small amount of γ₃-FePt₃ as a secondary phase. The results of ICP-AES of the obtained powder samples are listed in Table 1. The average compositions of Pt-P-1 and Pt-P-2 were Fe₀.₄₆P₀.₅₄ and Fe₀.₄₆P₀.₆₀, respectively. In the binary phase diagram shown in Fig. 3, the average composition of Pt-P-1 occurs at the single-phase region of γ₂-FePt. Meanwhile, that of Pt-P-2 occurs near the boundary between
Table 1  Abbreviations and masses of pure Pt samples reacted with FeCl₂ vapor at 1200 K for 1 h. Average compositions of the powder samples after processing are also summarized.

<table>
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<tr>
<th>Exp. no.</th>
<th>Processed Pt sample</th>
<th>Mass of sample after exp., ( w_{\text{after}}/\text{g} )</th>
<th>Results of ICP-AES</th>
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<td>Name</td>
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<td></td>
<td>Pt-W-2</td>
<td>Wire (^b)</td>
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</tr>
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</table>

\(^{a}\): 99.95%; micron-sized as shown in Fig. 10(a).
\(^{b}\): 99.99%; \( \phi = 0.5 \) mm; \( l = 20 \) mm.
\(^{c}\): Due to experimental difficulties, not all of the processed samples were recovered.
\(^{d}\): \( N_{\text{Fe}} = 100 \cdot (C_{\text{Fe}}/55.85)/(C_{\text{Pt}}/195.1) \).
\(^{e}\): \( N_{\text{Pt}} = 100 \cdot (C_{\text{Pt}}/195.1)/(C_{\text{Fe}}/55.85 + C_{\text{Pt}}/195.1) \).
the $\gamma_2$-FePt/$\gamma_3$-FePt$_3$ binary-phase region and the $\gamma_2$-FePt single-phase region. The average compositions determined by ICP-AES are consistent with the XRD results. The small difference in the alloying behavior between Pt-P-1 and Pt-P-2 is probably related to the difference in weight between the processed samples.

After the experiment, the wire samples (Pt-W-1 and Pt-W-2) also became magnetized, as shown in Fig. 9(c). As reported in Table 1, the masses of the wire samples increased by several percent. Figure 12 shows the results of SEM/EDS for the Pt-W-1 cross-section after the reaction. The area from the surface to a depth of approximately 15 $\mu$m was alloyed with Fe. The Fe concentration was approximately 80 mol% at the outermost surface and decreased as the depth increased. The Fe concentration in the near-surface area was high enough to form $\gamma_2$-FePt.

The experimental results clearly show that the reaction with FeCl$_2$ vapor at 1200 K under the coexistence of Fe is an effective technique for alloying Pt and forming a ferromagnetic Fe-Pt alloy. Sufficient amounts of Fe and FeCl$_2$ were present in the quartz ampoule. Thus, the chemical potential in the reaction system is close to the potential point $\alpha$ shown in Fig. 4. In this study, the reaction time was only 1 h. Nevertheless, the Pt samples were sufficiently alloyed with Fe.
Fe to exhibit ferromagnetism. As discussed in Section 3, the alloying of Pt samples can be understood in terms of the disproportionation of FeCl₂ vapor and the ability of gaseous phase to serve as an effective transport medium for Fe (see Figs. 5 and 6).

The proposed FeCl₂ vapor treatment followed by magnetic separation has potential as a novel process that can effectively concentrate PGMs directly from catalyst scrap. It is expected that other PGMs, such as Pd and Rh, can also be alloyed and magnetized by the reaction with FeCl₂ vapor demonstrated in this study. In order to develop this recycling process further, the applicability of the treatment process to other PGMs and the reactivity of the ceramic components in catalyst scraps (e.g., cordierite and alumina) during the vapor treatment must be considered in future studies.

In principle, magnetic concentration using the proposed alloying pretreatment does not require a large-scale plant or a long processing time. Thus, if this recycling process is well developed and put to practical use, the material flow of PGM recycling can be changed as shown in Fig. 13. Catalyst scraps containing Pt and other PGMs, such as spent automobile catalysts, are generated and collected all over the world; they are often transported to refinery by ships and/or by ground transportation methods for extracting and refining PGMs. The proposed magnetic concentration process can be carried out at scrap collecting sites. If the proposed method is adopted for concentrating PGMs, the obtained PGM concentrate, which is highly valuable and has a significantly lower volume than untreated scrap, can be transported by air to refineries for further treatment. In this new recycling route, refined PGMs can be obtained quickly.

4.2 Dealloying of Fe-Pt alloy by the reaction with FeCl₃ vapor

The Pt wire (Pt-W-2) whose surface was significantly alloyed with Fe (see Fig. 9(c) and 12) was placed in a quartz ampoule with a mixture of FeCl₂, FeCl₃, and Fe₂O₃, as shown in Fig. 8, and then heated at 1200 K for 4 h. After the heat treatment, Pt-W-2 did not attach to a magnet, as shown in Fig. 9(d). Furthermore, the weight of Pt-W-2 decreased from 0.0861 g to 0.0852 g during the heat treatment. The sample weight after the heat treatment coincides with that before the alloying treatment using FeCl₂ vapor (i.e., the initial weight of Pt-W-2 listed in Table 1). Fig. 14 shows the microstructure and composition profile of a Pt-W-2 cross-section after the experiment. The Fe concentration in the surface area was <10 mol%. Clearly, Fe was removed from the Pt wire during the heat treatment.

During the heat treatment, the wire sample was surrounded by FeCl₂/FeCl₃ vapor, and it is reasonable to consider that the chemical potential of the reaction system was maintained close to the potential point $\beta$ shown in Fig. 4. The dealloying of the Fe-Pt alloy can be explained by its reaction with FeCl₃ vapor (i.e., reaction (1)). As predicted on
the basis of the thermodynamic considerations given in Section 3, the Fe-Pt alloy showing ferromagnetism was unstable in FeCl\textsubscript{2} vapor. Thus, the results indicate that the reaction with FeCl\textsubscript{3} vapor under the coexistence of FeCl\textsubscript{2} cannot be used as the alloying and magnetizing treatment for Pt.

5. Conclusions

An FeCl\textsubscript{3} (x = 2, 3) vapor treatment that can effectively convert Pt into Fe-Pt alloy exhibiting ferromagnetism was examined using a combination of thermodynamic analyses and experiments. When reacted with FeCl\textsubscript{2} vapor at 1200 K for 1 h under the coexistence of metallic Fe, pure Pt samples were effectively alloyed with Fe, resulting in formation of the γ\textsubscript{2}-FePt ferromagnetic phase. Thermodynamic considerations indicate that alloying of Pt proceeded mainly via the disproportionation of FeCl\textsubscript{2} vapor and that the gaseous phase indicates that alloying of Pt proceeded mainly via the FeCl\textsubscript{2}, but it cannot be achieved using FeCl\textsubscript{3} vapor. The results obtained in this study indicate that alloying treatment with FeCl\textsubscript{2} vapor followed by magnetic separation has the potential to be a novel process that can effectively concentrate PGMs directly from catalyst scrap.

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