Notes

New Convenient Dissolution of Iron-Rhodium Alloys Using Hydrochloric Acid Containing a Small Amount of Nitric Acid without Heating for an ICP-AES Analysis

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A new convenient dissolution method for Fe-Rh alloys has been developed. Aqua regia has been used for the dissolution of rhodium alloy samples. However, it is difficult to dissolve high-concentration rhodium (more than 50 mass%) in aqua regia, because a rhodium-passivity on the alloys surface occurs with nitric acid. By using hydrochloric acid containing a small volume of nitric acid, Fe-Rh (24 – 64 mass%) alloys could be completely decomposed and dissolved under mild experimental conditions. The principal advantages of this method are simplicity and time-saving compared with other dissolution methods.

Introduction

Because rhodium is difficult to dissolve in acid, many chemical dissolution methods for rhodium-containing alloys have been proposed. These include HCl assisted by the dropwise addition of H_2O_2 or mixed HCl and $HClO_4$ in a sealed tube at 573 K for U-Rh alloys,[1] heated aqua regia for Pt-Rh (7 to 35 mass%) alloys,[2-4] mixed HNO_3, HCl and HF for Rh (1 mass%)/SiO_2 catalyst,[5] and a mixture of H_2SO_4 and HNO_3 for RhI_3 catalyst.[6] Sodium hydrogensulfate ($NaHSO_4$) for $NdRh_xB_y(AlCu)$ alloys (60 mass% Rh)[7] and potassium tetrafluoroborate (KBF_4) for Pt-Rh (0.5 mass%) alloy[8] have been employed as a flux for a fusion method. Moreover, a procedure using an electrolysis reaction in mixed HCl and H_2O_2 at 1.2 – 1.5 A cm^{-2} has been applied for the decomposition of Pt-Rh (20 to 40 mass%) alloys.[9] However, it is difficult to dissolve high-concentration rhodium (more than 50 mass%) alloys by these methods. Moreover, a dissolution method with a sealed tube, fusion methods and the electrolysis method are not convenient.

Actually, though Fe-Rh alloys containing a small amount of Rh (24 and 30 mass%) could be dissolved into aqua regia, the decomposition and dissolution of Fe-Rh (50 and 64 mass%) alloy samples were difficult to be dissolved in aqua regia. Mixed HCl and H_2O_2 could not be applied to the dissolution of Fe-Rh (24 to 64 mass%). The quantitative analysis of major components in various alloy samples has been performed by an inductively coupled plasma–atomic emission spectrometry (ICP-AES). Therefore, suitable decomposition procedures for the complete dissolution of samples are required. In order to develop a new and simple procedure for the dissolution of Fe-Rh alloys, a dissolution method using hydrochloric acid containing a small volume of nitric acid was investigated under mild experimental conditions at ambient temperature and pressure.

Experimental

Apparatus

A Hitachi P-5200 dual monochromatic ICP emission analysis system was used; the operating conditions are given in Table 1. The selection of spectral lines was performed using mutual spectral interference coefficients obtained for 639 emission lines of 68 elements.[10,11]

Table 1   Instrument and experimental conditions

ICP source	Hitachi P-5200 ICP emission analysis system	
Plasma operating power	1.0 kW	
Frequency	27.12 MHz	
Argon flow rates		
Outer gas	12 L min^{-1}	
Intermediate gas	0.5 L min^{-1}	
Carrier gas	0.5 L min^{-1}	
Spectrometer		
Type	vertical dualmonochromator	
Mounting	Czerny-Turner type	
Focal distance	750 mm	
	spectrometer 1	spectrometer 2
Grating	3600 grooves mm^{-1}	1200 grooves mm^{-1}
Slit width	30 μm	30 μm
Slit height	10 mm	10 mm
Reciprocal linear dispersion		
(1st order)	0.29 nm mm^{-1}	1.06 nm mm^{-1}
Observation height	15 mm above load coil	
Optical path	in air	
Photomultiplier voltage	350 – 750 V	
Fixed-wavelength mode	integration time: 3 s × 3 times	

Spectral line used (nm)
Fe II 238.204   Rh I 343.489   Y II 371.030 (internal line)

Table 2　Solubility (%) with hydrochloric–nitric acid solvents to iron-rhodium alloys at ambient temperature

Solvent	Rh (mass%)/thickness (mm)			
	24/0.4	30/0.1	50/0.4	64/0.5
A (10 ml HCl–10 ml HNO$_3$)	100% after 4 h	100% after 4 h	27% after 12 d	0.08% after 12 d
B (10 ml HCl–10 ml HNO$_3$–20 ml H$_2$O)	100% after 3 d	100% after 3 d	0.02% after 12 d	0.01% after 12 d
C (15 ml HC–l5 ml HNO$_3$)	100% after 4 h	100% after 4 h	100% after 6 h	19% after 9 d
D (15 ml HC–l5 ml HNO$_3$–20 ml H$_2$O)	100% after 3 d	100% after 3 d	0.01% after 12 d	0.02% after 12 d
E (18 ml HCl–2 ml HNO$_3$)	100% after 5 h	100% after 5 h	100% after 1 d	0.50% after 9 d
F (19 ml HCl–1 ml HNO$_3$)	100% after 1 d	100% after 1 d	100% after 1 d	98% after 9 d
G (19.5 ml HCl–0.5 ml HNO$_3$)	100% after 1 d	100% after 1 d	100% after 2 d	100% after 1 d
H (19.6 ml HCl–0.4 ml HNO$_3$)	100% after 1 d	100% after 1 d	100% after 2 d	100% after 1 d
I (19.7 ml HCl–0.3 ml HNO$_3$)	100% after 1 d	100% after 1 d	100% after 3 d	100% after 2 d
J (19.8 ml HCl–0.2 ml HNO$_3$)	100% after 2 d	100% after 2 d	100% after 3 d	100% after 2 d
K (19.9 ml HCl–0.1 ml HNO$_3$)	100% after 3 d	100% after 3 d	100% after 11 d	100% after 10 d

Table 3　Analytical results of iron-rhodium alloys ($n = 3$)

Sample	Nominal alloying composition (mass%)		Found (mass%)		
	Fe	Rh	Fe	Rh	Total
Alloy A	75.5	24.5	75.96 ± 0.11	24.14 ± 0.08	100.10 ± 0.14
Alloy B	68.5	31.5	69.53 ± 0.10	30.33 ± 0.02	99.86 ± 0.10
Alloy C	50.2	49.8	50.47 ± 0.05	49.71 ± 0.11	100.18 ± 0.13
Alloy D	35.2	64.8	36.18 ± 0.07	64.06 ± 0.05	100.24 ± 0.10

Reagents

A standard rhodium solution (1000 μg ml^{-1} in 2 M HNO$_3$) was made by Wako Pure Chemical Industries Ltd. All of the reagents used were of analytical-grade. Distilled water was used for all preparations of samples.

Procedure
Sample preparation. A 30 mg sample in a slightly stoppered 100 ml volumetric flask was dissolved in a mixed solution of 19.5 ml of HCl and 0.5 ml of HNO$_3$ at ambient temperature. After dissolution, 3.5 ml of HNO$_3$ was added to prepare the HNO$_3$ concentration by a standard rhodium solution (1000 μg ml^{-1} in 2 M HNO$_3$) and an iron standard solution (2.5 mg ml^{-1} in 1.328 M HNO$_3$), and 10 ml of a yttrium solution (1 mg ml^{-1} in 0.133 M HNO$_3$) was exactly added as an internal standard for an ICP measurement. Finally, the solution was diluted to 100 ml with water after adding water to 80 – 90 ml and warming up in 1 – 2 h at 353 – 363 K in water bath. The sample solutions were sprayed into ICP and the spectral intensities were measured.
Preparation of individual analyte solutions for calibration curves. A standard rhodium solution was transferred into volumetric flasks, stepwise. Next, 19.5 ml of HCl, HNO$_3$ prepared in order to obtain 4 ml, and 10 ml of the yttrium solution were added to the Rh solutions. Finally, the solutions were exactly diluted to 100 ml with water. Iron solutions for calibration curve were prepared by an iron standard solution in the same manner as the Rh solutions.

Results and Discussion

When the volume ratio of HCl–HNO$_3$ was changed, the effects of the dissolution of Fe-Rh (24 to 64 mass%) alloys on the volume ratio were investigated. The results are summarized in Table 2. Low rhodium (24 and 30 mass%) alloys were dissolved in not only a 1:1 mixture, but also in HCl containing a small amount of HNO$_3$. However, the high rhodium (50 and 64 mass%) alloys were dissolved in HCl containing a small amount of HNO$_3$. As shown in Table 2, the dissolubility of the rhodium alloys with the acid mixture decreased with the addition of water. It is considered as follows:
1) Since insoluble passivity, which is M$_x$Rh$_y$O$_z$ (M: metal) or Rh$_Y$O$_Z$, on the surface of higher rhodium alloys occurred with HNO$_3$ in excess (or with heating), the dissolution of rhodium is interfered.
2) Generated chlorine gas with a reaction between HCl and HNO$_3$ can attack rhodium alloys.
3) The generation of chlorine from acid mixtures is suppressed by the addition of water.

Based on the factors described above, the authors established a new convenient dissolution method for Fe-Rh (24 to 64 mass%) alloys with a mixture of 19.5 ml of HCl and 0.5 ml of HNO$_3$ at ambient temperature.

Analytical results obtained by the recommended procedure and the sequential correction method[12] for Fe-Rh alloys are given in Table 3. As a conclusion, Fe-Rh (24 to 64 mass%) alloys could be completely dissolved in HCl containing a small amount of HNO$_3$ without heating. The principal advantages of this method are simplicity and time-saving compared with other dissolution methods. Therefore, the proposed method is suitable for routine analysis.

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