Chemical Form of Precipitate by Coprecipitation with Palladium for Separation of Trace Elements in High-Purity Metals

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The reductive coprecipitation with palladium has been reported for separation and pre-concentration of trace elements in high-purity metals. In order to evaluate the chemical forms of precipitate by this method, precipitates from acidic solution containing Se, Te, Au, Ag and Pd (only or mixture) were produced under the condition of quantitative precipitation and measured by X-ray diffraction and electron diffraction. The precipitates from solutions including single element were confirmed by X-ray diffraction or electron diffraction. In measurement of Te and Pd precipitate, X-ray diffraction peaks of each element were increase as leaving time lengthens. In measurement of Se precipitate, no X-ray diffraction patterns were found independent of leaving time in the acidic solution. But when leaving time was 24 h, electron diffraction spots of Se were found. The precipitates from solutions including mutual elements (mixture of Pd and the other elements (Se, Te, Au and Ag)) were confirmed by X-ray diffraction or electron diffraction. In measurement of Pd–Au or Pd–Ag precipitate, these elements were respectively precipitated as elementary substance. However, in measurement of Pd–Se or Pd–Te precipitate, it was found that palladium selenide (Pd_xSe_y) or palladium telluride (Pd_xTe_y) was product.

1. Introduction

The technologies of production of high-purity metals and alloys have been developing and characters of them have been widely investigated.[1–5] In order to assess the purity, it is necessary to determine the trace elements included in them. For determination of trace elements in high-purity metals and alloys, it is often necessary to separate and pre-concentrate the trace elements before determination. Because the matrix elements cause adverse effects on determination of trace elements, the effects of the matrix elements on the determination of the trace elements have to be removed. The limit of detection can be decreased by these pre-concentration procedures and it is possible to sensitively and precisely determine the trace elements in high-purity metals and alloys.

The contaminations of high-purity metals with impurity elements have been decreased and the reported determination methods cannot be applied. Liquid-liquid extraction methods using harmful organic solvents have been employed for separation and pre-concentration.[6–9] Since such organic solvents might be hazardous to environment and humans, an analytical procedures without harmful reagents are needed and new techniques for determination of trace amounts of elements are required.

As a separation and pre-concentration method, the authors have reported a reductive coprecipitation with palladium method. This method can be applied to determination of trace amounts of selenium, tellurium,[10,11] gold and silver[12] in high-purity metals and alloys, or antimony, germanium and tin in high-purity iron.[13] These elements are determined by an electrothermal atomic absorption spectrometry (ET-AAS) after separation. The advantages of the proposed method are as follows:

(1) An analytical procedure is simple and easy.
(2) Multiple elements can be simultaneously separated.
(3) Determinations of trace elements are unaffected by matrix elements.
(4) The analytical trace elements can be high-sensitively determined by ET-AAS.

Palladium takes part in both the carrier of coprecipitation and the chemical modifier of determination by ET-AAS.

In order to elucidate the mechanism of precipitate production by this method, the authors have tried to evaluate the chemical form of the product precipitates by X-ray diffraction (XRD) and electron diffraction (ED).

2. Experimental

2.1 Apparatus

A RIGAKU Rotaflex RU-200B for XRD and a JEOL JEM-200FX for ED were employed for evaluation of precipitate and the operating conditions are listed in Table 1. The camera length for ED was decided by measurement of palladium standard sample. An Erlenmeyer flask with ground stopper for production of precipitate and a membrane filter (Nuclepore Polycarbonate, pore size 0.2 μm) for filtration were used.

Table 1 Instrumental and operating conditions.

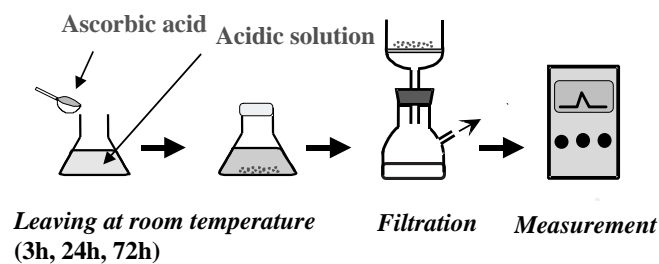| XRD	RIGAKU Rotaflex RU-200B
X-ray	Cu Kα
Voltage	40 kV
Current	150 mA
Measurement	
Method	θ-2θ
Area	25–85 degree
Scan rate	0.02 degree s^{-1}
TEM	JEOL JEM-2000FX
Voltage	200 kV
Camera length	97.75 cm
	(Measured by palladium)

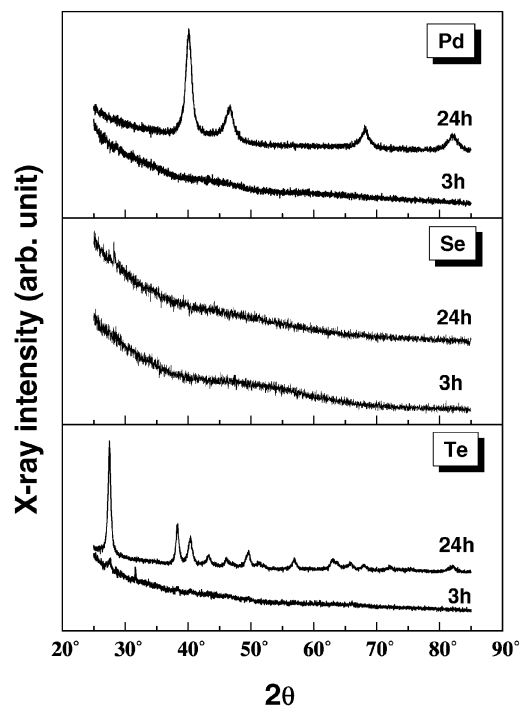Fig. 1   Outline of experimental procedure.

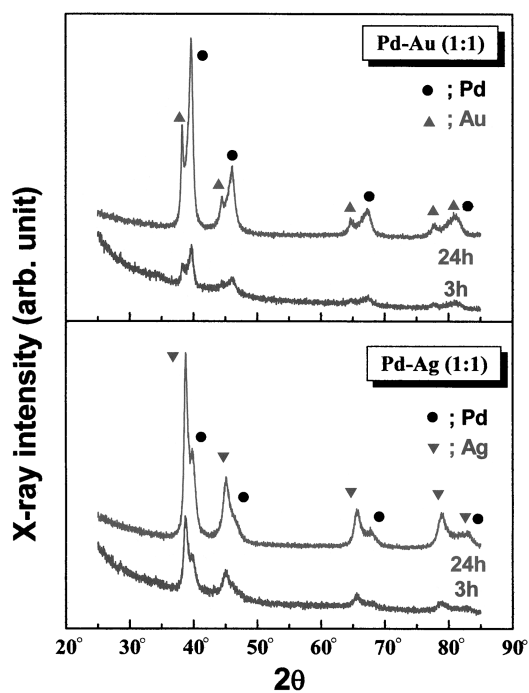Fig. 2   X-ray diffraction patterns of precipitate from Pd, Se and Te solution.

Fig. 3   X-ray diffraction patterns of precipitate from Pd–Au and Pd–Ag solution.
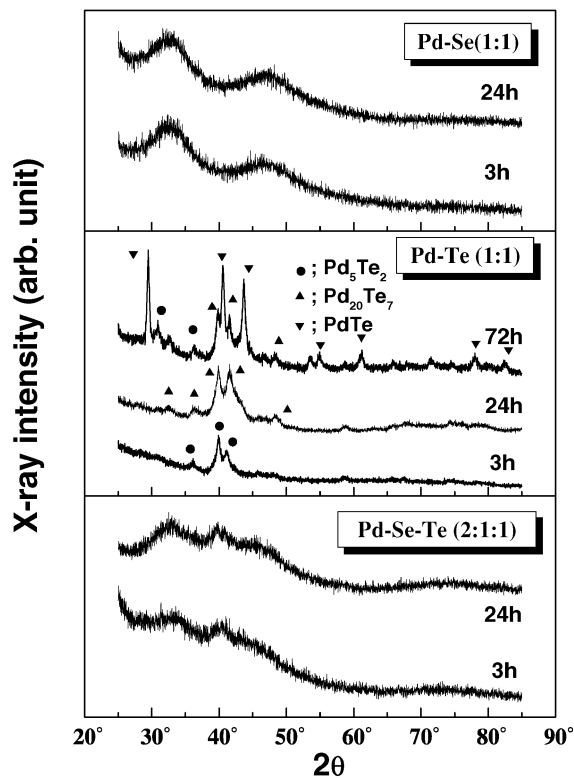

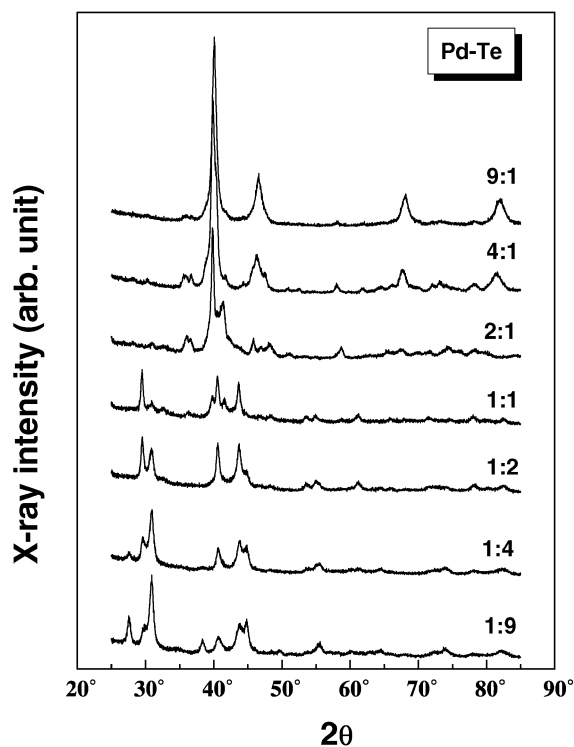Fig. 4   X-ray diffraction patterns of precipitates from Pd–Se, Pd–Te and Pd–Se–Te solution.

Fig. 5   X-ray diffraction patterns of precipitates from several Pd–Te solution; Leaving time is 72 h.

2.2   Reagents

Standard solutions of palladium, selenium, tellurium, gold and silver ($1 \, \text{kg m}^{-3}$) were prepared by dissolution of these metallic elements in acid.   All the used reagents were analytical-reagent grade and distilled water was used for all preparation procedures.

Table 2 X-ray diffraction patterns of precipitates from several Pd–Te solution; leaving time is 72 hours.

9:1 2θ		4:1 2θ		2:1 2θ		1:1 2θ		1:2 2θ		1:4 2θ		1:9 2θ	
										27.60	Te	27.56	Te
						29.60	PdTe	29.60	PdTe	29.56	PdTe	29.58	PdTe
						30.78	Pd_5Te_2						
								31.18	$PdTe_2$	31.16	$PdTe_2$	31.14	$PdTe_2$
				32.62	Pd_5Te_2	32.64	Pd_5Te_2						
36.00	$Pd_{20}Te_7$	36.00	$Pd_{20}Te_7$	36.04	$Pd_{20}Te_7$								
		36.68	$Pd_{20}Te_7$	36.66	$Pd_{20}Te_7$	36.64	$Pd_{20}Te_7$						
												38.34	Te
		39.86	$Pd_{20}Te_7$	39.82	$Pd_{20}Te_7$	39.84	$Pd_{20}Te_7$						
40.10	Pd	40.12	Pd										
						40.66	PdTe	40.66	PdTe	40.68	PdTe	40.70	PdTe
		41.52	$Pd_{20}Te_7$	41.52	$Pd_{20}Te_7$	41.54	$Pd_{20}Te_7$						
												43.36	Te
						43.78	PdTe	43.82	PdTe	43.82	PdTe	43.80	PdTe
		44.38	Pd_3Te										
								44.86	$PdTe_2$	44.86	$PdTe_2$	44.86	$PdTe_2$
		45.78	Pd_5Te_2	45.80	Pd_5Te_2								
46.66	Pd	46.64	Pd										
		47.68	Pd_3Te										
				48.34	Pd_5Te_2	48.36	Pd_5Te_2						
												49.80	Te
						53.62	PdTe	53.64	PdTe	53.640	PdTe		
						54.88	PdTe	54.86	PdTe	54.86	PdTe		
								55.60	$PdTe_2$	55.62	$PdTe_2$	55.60	$PdTe_2$
57.98	Pd_4Te	57.960	Pd_4Te										
				58.66	$Pd_{20}Te_7$								
						61.22	PdTe	61.24	PdTe				
				67.04	$Pd_{20}Te_7$					64.60	$PdTe_2$	64.58	$PdTe_2$
68.14	Pd	68.14	Pd										
						71.30	PdTe						
73.34	Pd_4Te	73.36	Pd_4Te							74.14	$PdTe_2$	74.16	$PdTe_2$
				74.70	$Pd_{20}Te_7$								
						78.04	PdTe	78.06	PdTe				
		78.30	Pd_4Te										
82.02	Pd	81.98	Pd							82.22	$PdTe_2$	82.22	$PdTe_2$
						82.50	PdTe						

2.3 Procedure

The outline of experimental procedure is shown in Fig. 1. The standard solutions of these elements (single or mutual) and $10\,cm^3$ of $18\,kmol\cdot m^{-3}$ sulfuric acid were transferred into an Erlenmeyer flask and the solution was heated to fumes. After cooling to room temperature, the solution was diluted with $90\,cm^3$ of water. 3.0 g of ascorbic acid was added, and the solution was left at room temperature with ground stopper. The product precipitate was collected by filtration and measured by XRD and ED. The employed leaving times were adopted 3 h, 24 h, and 72 h. Weight of the precipitate was 10 mg. In spite of leaving time length, these elements in standard solutions were quantitatively precipitated by the procedure described above.

3. Results and Discussion

3.1 Evaluation by X-ray diffraction
3.1.1 Single element precipitate

Pd, Se and Te precipitate was respectively measured by XRD and these XRD patterns are shown in Fig. 2. No diffraction patterns were found in leaving for 3 h in measurement of Pd and Te precipitate. Diffraction patterns of each element were found in leaving for 24 h. In measurement of Se precipitate, no diffraction patterns were found in spite of leaving time length.

3.1.2 Precipitate from Pd–Au and Pd–Ag solution

Precipitate samples from a mixed Pd and Au (1:1), and a mixed Pd and Ag (1:1) solution were respectively evaluated by XRD and these XRD patterns are shown in Fig. 3. In measurement of both samples, diffraction peaks were increased as leaving time lengthens.

In measurement of the Pd–Au precipitate, diffraction peaks

Table 3   Electron diffraction patterns of precipitates from Pd–Se and Pd–Se–Te solution.

| Pd–Se, 24 h			Pd–Se–Te, 3 h			Pd–Se–Te, 24 h		
R (cm)	d (nm)		R (cm)	d (nm)		R (cm)	d (nm)	
0.760	0.3228	$Pd_{17}Se_{15}$	0.765	0.3207	$Pd_{17}Se_{15}$	0.755	0.3250	$Pd_{17}Se_{15}$
0.860	0.2853	$Pd_{17}Se_{15}$, Pd_7Se_4	0.855	0.2870	$Pd_{17}Se_{15}$, Pd_7Se_4	0.850	0.2887	$Pd_{17}Se_{15}$, Pd_7Se_4
0.895	0.2741	Pd_7Se_4						
			0.950	0.2583	Pd_9Te_4	0.945	0.2596	Pd_9Te_4
0.975	0.2516	$Pd_{17}Se_{15}$	0.995	0.2466	$Pd_{17}Se_{15}$, Pd_3Te_2	0.990	0.2504	$Pd_{17}Se_{15}$, Pd_3Te_2
			1.065	0.2304	Pd_9Te_4, Pd_2Te, Pd_3Te_2	1.070	0.2293	Pd_9Te_4, Pd_2Te, Pd_3Te_2
1.185	0.2071	$Pd_{17}Se_{15}$, Pd_7Se_4	1.185	0.2071	$Pd_{17}Se_{15}$, Pd_7Se_4	1.180	0.2079	$Pd_{17}Se_{15}$, Pd_7Se_4
1.265	0.1940	$PdSe$	1.285	0.1909	$PdSe$, Pd_2Te	1.285	0.1909	$PdSe$, Pd_2Te
1.315	0.1866	$Pd_{17}Se_{15}$						
1.380	0.1778	$PdSe$	1.390	0.1765	$PdSe$	1.385	0.1772	$PdSe$
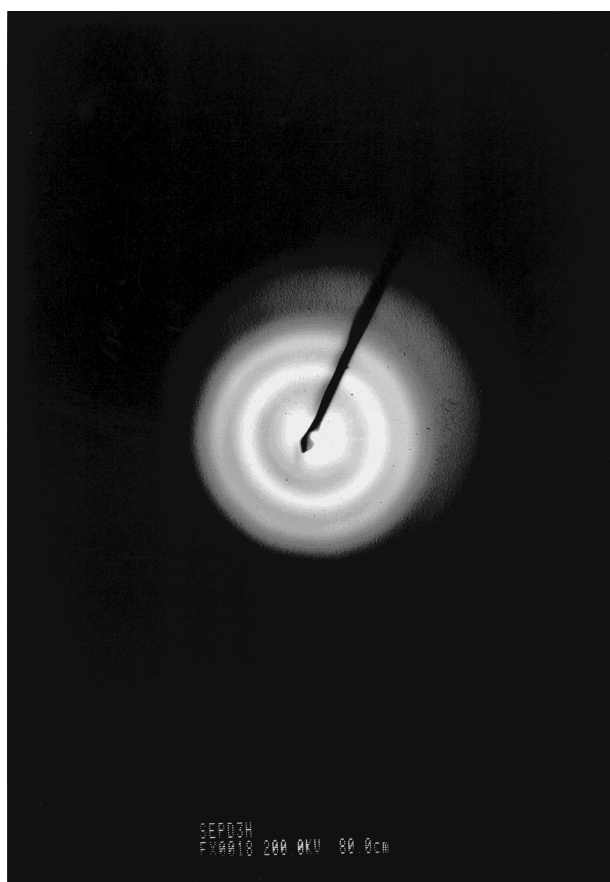
Fig. 6   Electron diffraction of precipitate from Pd–Se solution; Leaving time is 3 h.
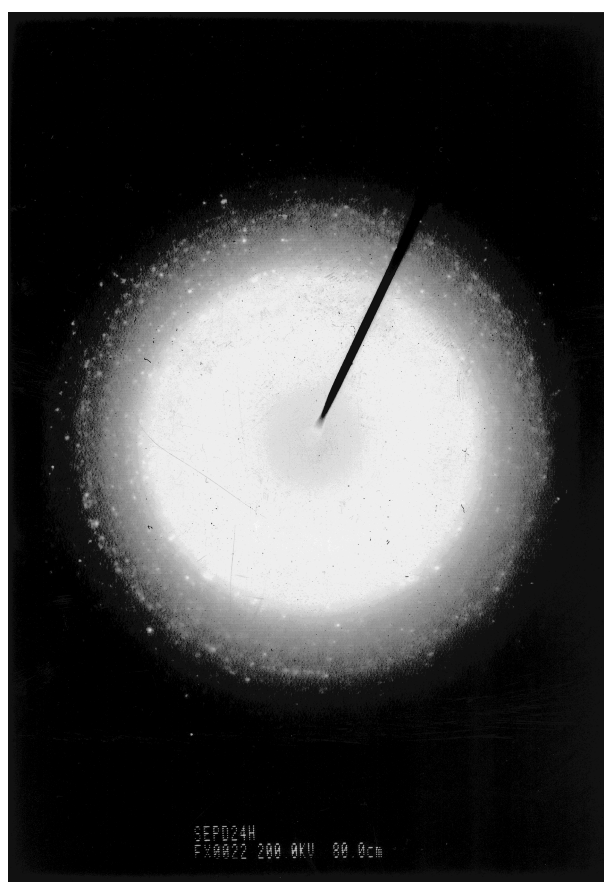

Fig. 7   Electron diffraction of precipitate from Pd–Se solution; Leaving time is 24 h.

of Pd and Au were respectively found. Similarly, diffraction peaks of Pd and Ag were respectively found in measurement of the Pd–Ag precipitate. Therefore, when Au or Ag was precipitated together with Pd, these elements were respectively precipitated as an elementary substance.

3.1.3   Precipitate from Pd–Se, Pd–Te and Pd–Se–Te solution

Precipitate samples from a mixed Pd and Se (1:1), a mixed Pd and Te (1:1), and a mixed Pd, Se and Te (2:1:1) solution were respectively evaluated by XRD and these XRD patterns are shown in Fig. 4. In measurement of Pd–Se and Pd–Se–Te precipitate, no diffraction patterns were found in spite of leaving time length and chemical forms of these precipitates could not be evaluated.

In measurement Pd–Te precipitate, diffraction patterns of palladium telluride were found and these elements were precipitated as compounds. The chemical forms of precipitates were different as difference of leaving time length. It is considered that a chemical form of precipitate is changed or a different compound is accidentally produced. But the reason is unknown for this phenomenon.

3.1.4   Precipitate from several ratio of Pd–Te solution

Precipitate samples from several ratios of mixed Pd and Te solutions were evaluated by XRD. The samples were produced from solutions, which the ratio of Pd and Te was changed from 9:1 to 1:9 in leaving for 72 h and measured by

XRD, respectively. These XRD patterns are shown in Fig. 5. When the Pd–Te ratio was changed, several different diffraction patterns were found.

These evaluation results are listed in Table 2. Palladium and some palladium telluride compounds were simultaneously produced when the Pd–Te ratio was 9:1 or 4:1. Tellurium and some palladium telluride compounds were simultaneously produced when the Pd–Te ratio was 1:9. In the other Pd–Te ratios samples, several palladium telluride compounds were respectively produced. The chemical forms of product precipitates were different when the ratio of palladium and tellurium was changed.

3.2 Evaluation by electron diffraction
3.2.1 Precipitate from Se, Pd–Se and Pd–Se–Te solution

Because XRD patterns could not be found in measurement of the Se, Pd–Se and Pd–Se–Te precipitates, the chemical forms of these precipitates were evaluated by using ED. The ED picture of Pd–Se precipitate in leaving for 3 h is shown in Fig. 6, and that for 24 h is shown in Fig. 7. No diffraction spots were found in leaving for 3 h. But diffraction spots could be found in leaving for 24 h. Therefore, it is considered that the precipitate in leaving for 3 h is amorphous state and the crystallization of precipitate progressed as the leaving time lengthens. Similar results were obtained in measurement of Se precipitate. In measurement of Se–Te–Pd precipitates, diffraction spots were found in spite of leaving time length.

The evaluation results of ED measurement are listed in Table 3. Several palladium selenide compounds were produced in Pd–Se precipitate and Palladium selenide and palladium telluride were simultaneously and respectively produced in Pd–Se–Te precipitate.

In spite of leaving time length and chemical forms, these elements were quantitatively precipitated.

4. Conclusions

The chemical forms of product precipitates by the reductive coprecipitation were evaluated by using X-ray diffraction and electron diffraction. As a result, crystallization of the precipitate in acidic solution progressed as leaving time lengthens. The chemical forms of the precipitates were evaluated as follows: Palladium selenide was produced when Se was precipitated with Pd. Palladium telluride was product when Te was precipitated with Pd. Moreover, palladium selenide and palladium telluride were respectively produced when Se and Te were simultaneously precipitated with Pd. However, when gold or silver was precipitated with Pd, the compounds were not produced but these elements were precipitated as the elementary substance, respectively.

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