백금-안티모니 系의 相平衡 및 化合物에 대한 硏究

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Phases and phase Equilibria of the Pt-Sb System

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요 약

백금-안티모니系의 상평형 및 안정 화합물에 대한 연구를 위해 합성실험을 실시하였다. 반응생성물은 반사현미경, X-선 회절분석, 전자현미분석 등으로 규명하였다. 백금-안티모니계에는 Pt_5Sb, Pt_3Sb, Pt_3Sb_2, PtSb, $PtSb_2$등 5종류의 화합물이 존재하며 Pt_5Sb_2는 존재하지 않는 것으로 밝혀졌다. Pt_5Sb는 처음 발견된 화합물로서 83at.%Pt의 화학성분을 가지며, 정방정계와 격자상수 a=3.948(3), c=16.85(1)Å를 가진다. Pt_3Sb의 X-선회절 분말자료는 a=3.9455(7), c=16.959(5)Å인 정방정계의 구조로 격자지수화가 가능하다. PtSb의 화학성분은 800℃까지 50at.% Pt이나 1000℃에서는 49at.% Pt이다. 백금속의 안티모니 고용한계는 1000°, 800°, 600℃에서 각각 7.5, 10.0, 6.1at.%이다. $PtSb_2$와 Sb를 잇는 액상곡선의 형태도 수정되었다.

Abstract

The phase diagram of the Pt-Sb system was reinvestigated, using the conventional sealed-capsule technique. The identification of phases present in the reaction products was made by reflected light microscopy, X-ray diffraction and electron microprobe analysis. The existence of compounds, Pt_5Sb, Pt_3Sb, Pt_3Sb_2, PtSb and $PtSb_2$ was confirmed. A new phase, Pt_5Sb with a composition of 83at.% Pt and tetragonal structure of the lattice parameters a=3.948(3), c=16.85(1)Å, was found. The X-ray powder data of Pt_3Sb may be indexable on a tetragonal cell with a=3.9455(7), c=16.959(5)Å. PtSb is stoichiometric up to 800℃ and becomes Pt-deficient as much as 1at.% at 1000℃. Solid solubility limits of Sb in Pt were determined to be 7.5, 10.0 and 6.1at.% at 1000°, 800° and 600℃, respectively. The earlier reported Pt_5Sb_2 was not found in this study. The liquidus curve between the $PtSb_2$ and Sb phases was revised.

INTRODUCTION

Phases and phase relations of the Pt-Sb system were first investigated by Friedrich and Leroux[1] and subsequently re-examined by Nemilow and Woronow[2]. The experimental results of the two authors showed a substantial agreement in the composition range from 50 to 100at.% Sb such that there exist the PtSb and $PtSb_2$ phases and a liq-

uidus line between $PtSb_2$ and Sb. However, there is a considerable difference in the 10-50at.% Sb region of the phase diagram. Friedrich and Leroux[1] placed the Pt_4Sb-PtSb eutectic at 33.6at.% Sb, 690° ±10℃, and reported that the Pt_5Sb_2 phase formed peritectoidally at 637°±8℃. In contrast, Nemilow and Woronow[2] placed the Pt_4Sb-PtSb eutectic at a lower temperature (633±8℃), but at the same composition. The latter investigators also reported that the Pt_4Sb and PtSb phases undergo polymorphic transformation at 671℃ and 660℃, respectively, and failed to confirm the existence of the Pt_5Sb_2 phase.

Bhan et al.[3] re-investigated this system in the region 0-50at.% Sb. They found 2 new phases Pt_3Sb and Pt_3Sb_2, and reported a eutectic reaction between Pt_3Sb and Pt_3Sb_2 at 633℃ and 31at.% Sb. Pt_3Sb phase melts incongruently to form Pt_4Sb and liquid of 30 at.% Sb at 682℃ and Pt_3Sb_2 melts incongruently at 732℃ forming PtSb and liquid of 33at.% Sb. Furthermore, Bhan and Schubert[4], based on their observation that the Pt content of the phase was greater than 80at.% Pt, proposed a new designation of $Pt_{4+}Sb$ for the formula of the phase previously known as Pt_4Sb.[1-3] The major discrepancies on the phases and phase relations existing in this binary can be summarized as shown in Table 1.

In view of the above controversies, the whole range of this system was re-investigated in this study to confirm the stable phases and their relations and to provide some mineralogical information on the existing phases.

MATERIALS AND EXPERIMENTAL METHOD

The platinum used was grade 1 wire and powder form of 99.9995% purity and the antimony was broken ingot of 99.9999% purity. Silica capsules were prepared from the transparent fused tubings with 5mm inside diameter and 1mm wall thickness. After loading the reagents into the tube, by difference method, a tightly fitting silica glass rod about 2cm long was placed on top of the mixture in order to keep the mix in place and to reduce the vapour volume on heating. The capsule was then evacuated and sealed off with a torch. The capsules were then placed into the horizontal and cylindrical electrical furnaces. All runs were heated for a period from a few days to 40 days until all the elements appeared to have been reacted thoroughly. To ensure homogeneous reaction most samples were opened and the contents were finely ground and pelletized for further reactions.

Quenched run products were identified and analysed by reflecting light microscopy, X-ray diffraction, and electron microprobe analysis. Micro-indentation hardness of the synthetic phases was determined, using a Leitz Durimet hardness tester.

Table 1. Comparison of phases of the Pt-Sb system.

	Friedrich and Leroux[1]	Nemilow and Woronow[2]	Bhan et al.[3]
Phases present	Pt_4Sb, Pt_5Sb_2, PtSb, $PtSb_2$	Pt_4Sb, PtSb($P6_3/mmc$), $PtSb_2$ (Pa3)	Pt_4Sb, (Cu_3Au-type str.) Pt_3Sb(distorted $ZrAl_3$-str.) Pt_3Sb_2 (Ibam), PtSb, $PtSb_2$
Eutectic reaction	Pt_4Sb-PtSb(33.6 at.% Sb, 690° ± 10℃)	Pt_4Sb-PtSb(33.6 at.% Sb, 633 ± 8℃)	Pt_3Sb-Pt_3Sb_2 (31 at.% Sb, 633℃)

RESULTS AND DISCUSSION

All the runs prepared for this system and individual phases identified from their reaction products are shown in Table 2.

Pt

Platinum contains Sb up to 7.5at.% in solid solution at 1000℃, 10.0at.% at 800℃ and 6.1at.% at 600℃. These values are comparable with those of 8at.% at 1000℃ and 10at.% at 800℃ given by Fri-

Table 2. Experimental results of the Pt-Sb system.

Run no.	Bulk composition(at.%) Pt	Sb	Temp. (℃)	Heating period(days) 1h	2h	3h	Phases identified	Composition(at.%) Pt	Sb
1	85.00	15.00	600	5	14	14	Pt	93.9	6.1
							Pt_5Sb	83.0	17.0
2	77.49	22.51	600	5	14	14	Pt_5Sb	82.9	17.1
							Pt_3Sb	75.1	24.9
3	72.96	27.04	600	6	14	13	Pt_3Sb	75.2	24.8
							Pt_3Sb_2	60.1	39.9
4	62.03	37.97	600	5	14	14	Pt_3Sb	75.3	24.7
							Pt_3Sb_2	60.1	39.9
5	39.90	60.10	600	5	14	14	PtSb	50.0	50.0
							$PtSb_2$	33.5	66.5
6	24.99	75.01	600	5	14	14	$PtSb_2$	33.5	66.5
							Sb	0.0	100.0
7	79.97	20.03	650	8	12	20	Pt_5Sb	82.9	17.1
							Pt_3Sb	75.0	25.0
8	74.99	25.01	600	8	20	10	non-equilibrium		
9	59.97	40.03	600	8	20		Pt_3Sb_2	60.0	40.0
10	50.00	50.00	800	8	8		PtSb	50.0	50.0
11	33.33	66.67	1000	5	7		$PtSb_2$	33.3	66.7
12	55.04	44.96	600	10	8		Pt_3Sb_2	59.9	40.1
							PtSb	50.0	50.0
13	55.00	45.00	800	6	4		PtSb	50.1	49.9
							L		
14	82.98	17.02	600	10	8	8	non-equilibrium		
15	55.99	44.01	800	9	5		PtSb	50.1	49.9
							L		
16	54.02	45.98	1000	9	10		PtSb	49.5	50.5
							L		
17	48.99	51.01	1000	10	8		PtSb	48.8	51.2
18	63.00	37.00	800	8	6		PtSb	49.9	50.1
							L		
19	42.95	57.05	800	2	6		PtSb	49.5	50.5
							$PtSb_2$	33.3	66.7
20	57.96	42.04	1000	4	10		L		
21	60.00	40.00	1000	4	10		L		
22	50.00	50.00	1000	6	15		PtSb	49.1	50.9
							L		
23	50.00	50.00	600	5	20		PtSb	50.0	50.0
24	14.98	85.02	800	4	10		$PtSb_2$	33.1	66.9
							L	0.1	99.9
25	79.84	20.16	800	5	14		Pt	90.0	10.0
							L		
26	71.01	28.99	800	6	8		non-equilibrium		
27	68.95	31.05	800	7	5		L	68.8	31.2
28	63.94	36.06	800	7	11		non-equilibrium		
29	20.09	79.71	1000	3	15		$PtSb_2$	33.3	66.7
							L	0.4	99.6
30	84.55	15.45	1000	4	4		Pt	92.5	7.5
							L		
31	5.00	95.00	1000	3	12		$PtSb_2$	33.1	66.9
							L	0.4	99.6

Abbreviations: L: liquid, 1h=initial heating; 2h=second heating, 3h=third heating, after grinding and pelletizing.

edrich and Leroux[1] and Nemilow and Woronow[2], but are much higher than the values of 3at.% at 1000℃ and 4at.% at 800℃ derived from the phase diagram of Bhan et al.[3] The composition of liquid phases coexisting with Pt at 800℃ and 1000℃ could not be determined due to the separation of solids from the former liquids during quenching. The refined cell parameters, using the present X-ray powder data, are a=3.9226(2)Å for pure platinum. Micro-indentation hardness measurements gave VHN_{100}=113.8(107-120).

Pt_5Sb

In this investigation neither Pt_4Sb phase nor Pt_4Sb phase was observed. Instead, a phase having a composition of $Pt_{83}Sb_{17}$ was newly encountered to exist at 600℃ and 650℃ and the chemical formula Pt_5Sb is thus assigned to it. Microscopic examinations of the Pt_5Sb phase show that under reflected light it is pale brownish grey or yellowish grey in air and in oil, showing no bireflectance. Micro-indentation hardness of this new phase was VHN_{100}=225(206-243). An attempt to synthesize the single phase Pt_5Sb was not successful, even after repeated heating and grinding of the mixes. This is apparently due to slow reaction rate at the lower temperature range, as evidenced by the presence of unreacted Pt in the run product. The X-ray powder pattern (Table 3), obtained from Pt_5Sb coexisting with Pt_3Sb at 600℃, cannot be indexed according to the cubic cell with a=3.99Å, given by Bhan and Schubert[4] for the Pt_4Sb phase. However, the X-ray powder data are successfully indexable on a tetragonal cell with a=3.948(3), c=16.85(1)Å, as shown in Table 3. Composition identity of Pt_5Sb with structurally different Pt_4Sb and Pt_4Sb[1-3] is not confirmed, because the previous authors did not present the chemical composition of their phases. Assuming the Pt_5Sb and Pt_4Sb are of compositionally identical, the structural differences in the phases might be resolved in terms of polymorphic transformation. For further clarification, a careful differential thermal analysis for the Pt_5Sb seems necessary.

Table 3. X-ray powder diffraction data of synthetic Pt_5Sb

Tetragonal a=3.948(3) c=16.85(1) Å					
h	k	l	d_{cal}(Å)	d_{obs}(Å)	I/I_o
1	1	4	2.327	2.318	100
1	0	6	2.288	2.293	100
0	0	8	2.106	2.110	30
2	0	8	1.440	1.440	50
2	2	1	1.391	1.390	15
2	0	10	1.281	1.283	5
0	0	14	1.203	1.203	70
3	0	6	1.191	1.192	40

Pt_5Sb coexisting with Pt_3Sb at 650℃. CuKα radiation (λ=1.5418Å), 114.6mm Gandolfi camera.

Pt_3Sb

The Pt_3Sb phase[4] is confirmed. Pt_3Sb is pale greyish yellow in air with very weak bireflectance. It is weakly anisotropic, varying from brownish grey to greyish brown in air. Micro-indentation hardness tests gave VHN_{25}=216(183-249). Electron microprobe analyses of Pt_3Sb coexisting with Pt_5Sb or Pt_3Sb_2 show that it is stoichiometric in composition. The X-ray powder pattern (Table 4) of Pt_3Sb was taken from the specimen containing an additional Pt_3Sb_2 phase, and are indexed in this study on the basis of a tetragonal cell. It is noted that there remains two unindexable, weak X-ray reflections (2.482 and 2.450A) which apparently do not belong to Pt_3Sb_2. Using the present X-ray diffraction data and also ignoring the aforementioned 2 X-ray lines the lattice parameters were determined to be a=3.9455(7), c=16.959(5)Å, being in good agreement with the previous results of a=3.94, c=16.99Å[3]. In this connection, it should be mentioned that Bhan et al.[3] also repeatedly observed a few weak X-ray reflections(their d-valuse not specified) in their Guinier film and stated that Pt_3Sb has very weak lines only in-

Table 4. X-ray powder diffraction data of synthetic Pt_3Sb

Tetragonal a=3.9455(7) c=16.959(5) Å					
h	k	l	d_{cal}(Å)	d_{obs}(Å)	I/I_o
1	0	5	2.572	2.570	35
				2.482*	5
				2.450*	5
1	1	4	2.330	2.328	100
0	0	8	2.119	2.115	45
2	0	0	1.972	1.970	50
2	1	1	1.755	1.753	20
2	0	6	1.617	1.616	2
2	0	8	1.444	1.444	65
2	2	0	1.394	1 394	30
2	1	9	1.288	1.287	10
1	1	12	1.260	1.261	45
3	1	4	1.196	1.197	50
2	2	8	1.165	1.165	15
3	1	6	1.141	1.141	5

Pt_3Sb coexisting with Pt_3Sb_2 at 600℃ CuKα radiation (λ=1.5418Å), 114.6mm Gandolfi camera.
* unidentified.

dexable on a tetragonal cell by doubling the a-axis. They suggested that the small difference of this tetragonal structure from the $ZrAl_3$-type structure might have been resulted from slight distortion of the structure. However, it is not certain whether the problematic weak X-ray lines mentioned by Bhan et al.[3] are identical to those found in the present study, mainly because the earlier investigators have not presented the X-ray powder pattern nor specified the X-ray lines.

Pt_3Sb_2

Pt_3Sb_2[3] is confirmed to exist. This phase, synthesized at 600℃ in this study, is pale brownish pink or creamy yellow under reflected light and possesses a weak bireflectance from cream to pale greenish yellow. Anisotropism is moderate in air from greyish brown to bluish green, and strong in oil from pale yellow to greenish blue. The Micro-indentation hardness value is VHN_{100}=275(240-306). The X-ray powder diffraction data (Table 5) of Pt_3Sb_2, quenched from 600℃, do not agree well with those of Bhan et al.[3] The discrepancies involve the magnitude of the relative intensities and missing reflections which seem to be due to the different method in recording the data. The cell parameters indexed on an orthorhombic cell

Table 5. X-ray powder data of synthetic Pt_3Sb_2.

	Pt_3Sb_2(1) a=6.446, b=10.939, c=5.319Å			Pt_3Sb_2 (This study)(2) a=6.410(8), b=10.939(7), c=5.29(1) Å		
h k l	d_o(Å)	I/I_o		d_c(Å)	d_o(Å)	I/I_o
1 0 0						
0 2 0	5.447	m-		5.471	5.470	89
1 2 1	3.282	vw				
2 0 0	3.221	vw				
1 3 0	3.173	m		3.169	3.172	87
2 2 0	2.778	m				
0 4 0	2.735	w		2.734	2.731	85
2 1 1	2.675	m+		2.659	2.658	15
0 0 2	2.661	m-				
112, 022	2.400	st				
1 4 1	2.277	m		2.272	2.276	30
2 3 1	2.200	m				
3 1 0	2.109	m-				
2 4 0	2.086	w+				
1 5 0	2.073	m-		2.070	2.070	100
2 0 2	2.053	m				
0 4 2	1.907	st		1.901	1.907	30
3 2 1	1.874	m				
0 6 0	1.826	vw-				
2 5 1	1.715	vw				
1 6 1	1.669	vw				
1 2 3	1.632	vw				
2 1 3	1.539	w				
1 7 0	1.520	w		1.518	1.519	7
0 6 2				1.501	1.501	8
1 4 3				1.444	1.444	4
0 8 0				1.367	1.364	21
2 7 1				1.357	1.358	15
1 8 1				1.2966	1.2979	24
5 3 2				1.1000	1.1002	6
3 6 3				1.0904	1.0898	10

(1) Bhan et al.[3] Guinier camera using CuKα radiation. w:weak, m:medium, st:strong.
(2) Run 109, quenched from 600℃. CuKα, radiation (λ=1.54059Å), automated diffractometer.

are a=6.410(8), b=10.939(7), c=5.29(1)Å.

No natural analogue of the Pt_3Sb_2 phase is known. However, an unnamed mineral $(Pt_{1.76-1.78}Pd_{1.24-1.22})_{3.00}Sb_{2.05-2.09}$ or $Pt_{1.69}Pd_{1.18}Sb_{1.96}Bi_{0.06}Sn_{0.09}As_{0.015}$ from the Driekop mine, South Africa, suggested by Cabri et al.[6] to be a possible Sn-bearing, Rh-free variety of genkinite $(Pt,Pd)_4Sb_3$, may rather be the natural analogue of the synthetic Pt_3Sb_2 phase.

PtSb

The PtSb phase[1-3] is confirmed to exist in this study. PtSb is cream under reflected light, weakly bireflectant and strongly anisotropic. Vicker's hardness tests gave VHN_{100}=424(376-464). Electron microprobe analyses for the phase indicate that it is stoichiometric at least up to 800℃ and has a slight deficiency of Pt(about 1at.%) at 1000℃. Hexagonal symmetry of the phase is confirmed and the cell parameters of the PtSb phase vary slightly depending on temperatures from which the phase was quenched: a=4.1318(6), c=5.483(1)Å at 800℃ and a=4.1420(5), c=5.486(1)Å at 1000℃. They compare well with the hexagonal cell of a=4.130(4), c=5.472(5)Å suggested by Thomassen[7] for the phase slowly cooled to room temperature from 600℃. Stumpflite[8] is a natural analogue of the synthetic PtSb phase. The physical properties of the synthetic PtSb phase are virtually identical to those of stumpflite, $Pt(Sb_{0.73}Bi_{0.27})$, first established as a new species by Johan and Picot.[9]

$PtSb_2$

$PtSb_2$ was synthesized at 600°-1000℃ in the present study. It is white with yellowish tinge in air under reflected light. Micro-indentation hardness value for the synthetic $PtSb_2$ phase is VHN_{100}=701(681-724). $PtSb_2$, synthesized at 1000℃, has a cubic cell with a=6.4373(2)Å, in good agreement with that (a=6.4400Å) reported by Kjekshus.[10] Geversite, the natural analogue of synthetic $PtSb_2$, first found from the Driekop mine, South Africa, was characterized as a new mineral by Johan and Picot.[9] The physical properties of geversite reported by Tarkian and Stumpfl[5] are in excellent agreement with those of $PtSb_2$.

Sb

Antimony is white with yellowish shade under reflected light. It is weakly bireflectant and weakly to moderately anisotropic from olive grey to brownish grey. Micro-indentation hardness measurements gave VHN_{100}=69.9(62.0-78.5). The X-ray diffraction results agreed well with those previously reported by Swanson and Fuyat.[11] Antimony is rhombohedral and the refined cell parameters, indexed on the hexagonal axes, are a=4.3056(8), c=11.250(3)Å. Solid solubility of Pt in Sb is negligible.

Liquidus Curve

In the region between $PtSb_2$ and Sb, run 24, quenched from 800℃, yielded $PtSb_2$ in equilibrium with a liquid phase of $Pt_{0.1}Sb_{99.9}$ composition. Run 29, quenched from 1000℃, showed an assemblage of $PtSb_2$ and liquid of $Pt_{0.4}Sb_{99.6}$. While the reaction product of run 31 consisted of $PtSb_2$ and a liquid whose composition could not be determined accurately due to the separation of minute dendrites of $PtSb_2$ composition from an original liquid during quenching. Nevertheless, all the observation above indicate that the liquidus curve over much of the range between $PtSb_2$ and Sb must be somewhere above 1000℃ and almost vertical at near the Sb composition.

Pt_5Sb_2

Pt_5Sb_2, reported by Friedrich and Leroux[1], was not observed in this study.

The Pt-Sb Phase Diagram

The presently known Pt-Sb phase diagram of Bhan et al.[3] appeared to need revision owing to

the new findings. Thus, a new phase diagram is suggested in Fig. 1, based on the experimental data from this study.

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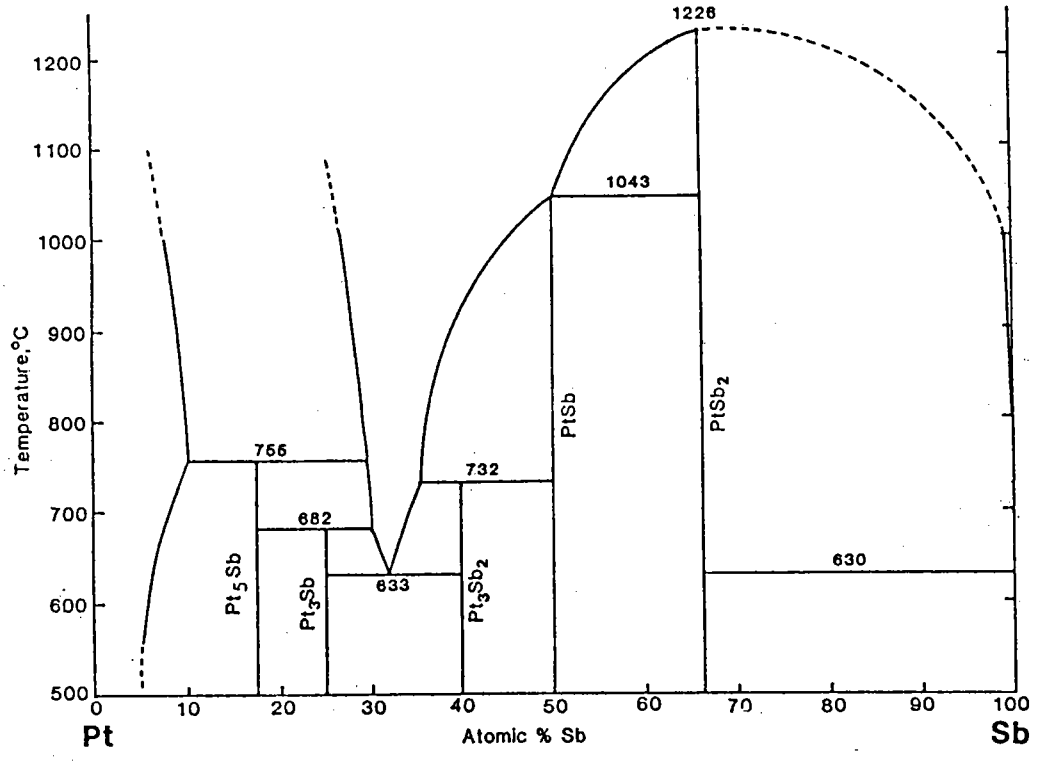

Fig. 1. Revised phase diagram of the Pt-Sb system