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New Data on the Synthetic $Pt_{34}Sb_7$ and Pt_3Sb Phases

合成化合物 $Pt_{34}Sb_7$와 Pt_3Sb에 對한 새로운 자료

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ABSTRACT : In the process of re-checking the phase relations of the Pt-Sb system the previously reported $Pt_{4+}Sb$ phase did not occur. Instead, $Pt_{34}Sb_7$ phase with an average chemical composition (wt%) Pt 89.3, Sb 11.4, total 100.7, has been newly found to exist, and the formula $Pt_{34}Sb_7$ has been tentatively assigned to it. It is pale brownish grey to yellowish grey under reflecting microscope and non-bireflectant. VHN_{100}=225 (206-243). X-ray powder patterns are ($d(I/I_0)$): 2.318(100), 2.293(100), 2.110(30), 1.440(50), 1.390(15), 1.283(5), 1.203(70) and 1.192(40)Å. They are indexable on the basis of tetragonal cell with a=3.948(3), c=16.85(1)Å. A question whether the tetragonal $Pt_{34}Sb_7$ is the new phase or a polymorph of the cubic $Pt_{4+}Sb$ phase remains unclear and awaits better X-ray diffraction, electron microprobe analysis and DTA for the $Pt_{4+}Sb$ phase.

The Pt_3Sb phase reported to be of tetragonal symmetry has been confirmed to exist. It is greyish yellow in air and in oil, very weakly bireflectant, and weakly anisotropic. VHN_{25}=216 (183-240). Its X-ray powder data have been successively indexed on a tetragonal cell with a=3.9455(7), c=16.959(5)Å.

要 約 : Pt-Sb成分系의 相平衡關係에 대한 확인실험과정에서 이미 보고된 바 있는 $Pt_{4+}Sb$가 존재하지 않음이 밝혀졌다. 그리고 화학성분(wt%)이 Pt 89.3, Sb 11.4이고 화학식이 $Pt_{34}Sb_7$인 새로운 合成體가 존재한다는 사실이 밝혀졌다. $Pt_{34}Sb_7$은 반사현미경하에서 회색을 띄며 多色性이 없다. 硬度는 VHN_{100}=225(206-243)이다. X선분말회절자료는 2.318(100), 2.193(100), 2.110(30), 1.440(50), 1.390(15), 1.283(5), 1.203(70), 1.192(40)Å이며 正方晶系로써 a=3.948(3), c=16.85(1)Å인 格子常數를 가지고 있다. $Pt_{34}Sb_7$가 成分이 비슷한 等軸格子의 $Pt_{4+}Sb$와 同質異像의 가능성을 규명하기 위해서는 정밀한 X선회절분석, 전자현미분석, 시차열분석등의 연구자료가 필요하다.

또한, Pt_3Sb가 존재하며 正方晶系의 결정구조를 갖는다는 以前의 보고는 이번 연구에서 확인되었다. 合成體 Pt_3Sb는 반사광하에서 옅은 노란색을 띄며 弱한 多色性과 異方性을 나타낸다. 硬度는 VHN_{25}=216(183-240)이다. 이번 연구에 의하면 Pt_3Sb는 正方晶系로써 格子常數가 a=3.9455(7), c=16.959(5)Å이다.

INTRODUCTION

Phases and phase relations of the Pt-Sb system that includes stumpflite (PtSb) and geversite ($PtSb_2$) were first investigated by Friedrich and Leroux (1909) and later by Nemilow and Woronow (1936). There is a substantial agreement between the two on the existence of the phases Pt_4Sb, PtSb and $PtSb_2$. However, the Pt_5Sb_2 phase reported by Friedrich and Leroux(1909) was not found by Nemilow and Woronow(1936).

Bhan *et al.* (1969) re-investigated the same system in the region 0~50 at.% Sb (Fig. 1) and confirmed the existence of the Pt_4Sb phase.

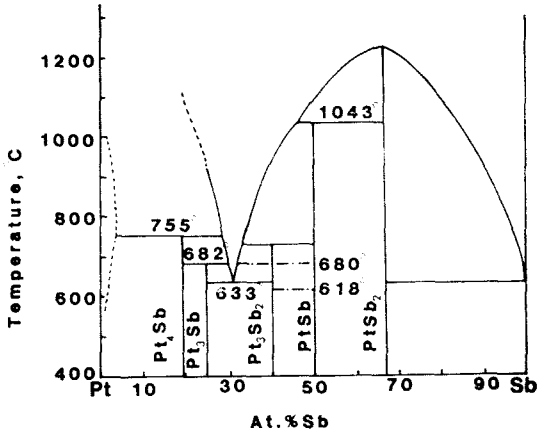

Fig. 1. Phase diagram of the Pt-Sb system(Bhan *et al.*, 1969). Dotted lines indicate uncertainty and broken lines metastable compounds.

Pt_5Sb_2 did not occur, instead 2 new phases Pt_3Sb and Pt_3Sb_2 existed as stable phases. Bhan and Schubert (1969) revised the formula for the phase previously known as Pt_4Sb to $Pt_{4+}Sb$ because Pt-content of the phase was about 81 to 82 at.% Pt.

In the course of reviewing the phase relations of the system, a phase $Pt_{34}Sb_7$, compositionally similar but structurally different to $Pt_{4+}Sb$, was encountered. The purpose of this contribution is to present new crystallographic and mineralogical data for the $Pt_{34}Sb_7$ and Pt_3Sb phases and to interprete these in the light of the previous studies.

EXPERIMENTAL

The platinum used was grade 1 wire, 99.9995% purity with Fe, Ca, Ag, Si, Cu, Mg all less than 0.0005%. The antimony was broken ingot of 99.9999% purity with only Bi and Si of 0.0001%. Experiments were performed in sealed evacuated silica glass tubings with tightly fitted glass rods on top of the mixtures. The horizontal and electrical furnaces were used and then the platinum thermocouples used were calibrated against the melting point of cadmium chloride(568°C). Temperatures within the furnaces were checked daily and found to be constant within ±2°C. All runs were heated for a period from a few days to 40 days until all the elements appeared to have been reacted thoroughly. Quenched run products were identified and analysed by ore microscopy, X-ray diffraction, and electron microprobe analysis. All the microprobe analyses were carried out at an accelerating voltage of 25KV and a specimen current of 50nA. The X-ray lines measured were $L\alpha$ for Pt and Sb, using the following standards: spec. pure Pt, synthetic Pt_3Sb_2 and spec. pure Sb.

RESULTS AND DISCUSSION

The overall experimental results, although not shown completely in this paper, have shown that the phase diagram of Bhan *et al.* (1969) is essentially correct and only minor revisions are necessary: the liquidus curve over much of the range between $PtSb_2$ and Sb must be somewhere above 1,000°C. Experimental results selected for the present purpose are tabulated in Table 1.

A phase having a composition $Pt_{83}Sb_{17}$ has been encountered at 600° and 650°C. Microprobe analyses made on it are listed in Table 2. Its Pt : Sb atomic ratio is clearly not 4 : 1 but closer to 4.85 : 1, and therefore the formula $Pt_{34}Sb_7$ is tentatively assigned to the phase. Its compositional deviation from 4 : 1 stoichiometry is comfirmed from the run 7 which gives 2-phase product consisting of $Pt_{34}Sb_7$ and Pt_3Sb.

Microscopic examinations of the $Pt_{34}Sb_7$ show that under the reflected light it is pale brownish grey to yellowish grey in air and in oil, and non-bireflectant. The micro-hardness VHN_{100}, based on 6 indentations, is in the range 206–243.

Table 1. Experimental data.

Run No.	Bulk Composition (at%)			Heating Period(days)	Phases Present
	Pt	Sb	Temp.(°C)		
1	85.00	15.00	600	33	Pt $Pt_{34}Sb_7$
2	77.49	22.51	600	33	$Pt_{34}Sb_7$ Pt_3Sb
3	72.96	27.04	600	34	Pt_3Sb Pt_3Sb_2
4	62.03	37.97	600	33	Pt_3Sb Pt_3Sb_2
7	80.00	20.00	650	28	$Pt_{34}Sb_7$ Pt_3Sb
15	80.00	20.00	800	5	Pt Liquid
21	83.00	17.00	600	26	non-equilibrium
23	75.00	25.00	600	40	non-equilibrium

Table 2. Electron microprobe analyses for $Pt_{34}Sb_7$ and Pt_3Sb.

Phase	Weight percent			Atomic percent	
	Pt	Sb	total	Pt	Sb
$Pt_{34}Sb_7$	89.2	11.3	100.5	83.1	16.9
	88.1	11.5	99.6	82.8	17.2
	88.7	11.6	100.3	82.7	17.3
	88.5	11.5	100.0	82.8	17.2
	88.3	11.2	99.5	83.1	16.9
Pt_3Sb	83.1	17.3	100.4	75.0	25.0
	83.3	17.1	100.4	75.3	24.7
	83.2	17.3	100.5	75.0	25.0
	83.1	17.4	100.5	74.9	25.1
	83.3	17.2	100.5	75.1	24.9

Table 3. X-ray powder diffraction data for synthetic $Pt_{34}Sb_7$.

k	k	l	d_{cal}(Å)	d_{obs}(Å)	I/I_0
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

X-ray powder pattern was obtained from a mixture of $Pt_{34}Sb_7$ and Pt_3Sb quenched from 600°C. CuK_α radiation (λ=1.5418Å), 114.6mm Gandolfi camera.

Single-crystal X-ray diffraction data could not be obtained because an attempt to grow a single-phased $Pt_{34}Sb_7$ was failed. Thus the X-ray powder pattern (Table 3) was obtained from a mixture of $Pt_{34}Sb_7$ and Pt_3Sb on a 114.6mm Gandolfi camera with Ni-filtered $CuK\alpha$ radiation. Indexing of the X-ray reflection lines is carried out by "try and error" method. They are indexable successfully with a tetragonal, primitive cell as shown in Table 3. The refined cell parameters, calculated by a least squares method, are a=3.948(3), c=16.85(1)Å.

$Pt_{34}Sb_7$ is very similar to $Pt_{4+}Sb$ in composition, when considering the statistical error of 1% for the electron microprobe analyser. The structure of $Pt_{4+}Sb$, previously known as Pt_4Sb, was reported to be cubic (Cu_3Au-structure), with a=3.99Å (Bhan and Schubert, 1969). Since X-ray powder data for $Pt_{4+}Sb$ (and Pt_4Sb) have not been published by previous authors, confirmation on the identity between $Pt_{34}Sb_7$ and $Pt_{4+}Sb$ has been attempted in the following way. Assuming $Pt_{4+}Sb$ and $Pt_{34}Sb_7$ are an identical phase, the X-ray powder reflection lines for the $Pt_{34}Sb_7$ phase must be indexable, at least, according to the cubic cell as suggested by Bhan

and Schubert(1969). Based on the equation:

$$a^2/d^2_{hkl}=h^2+k^2+l^2=n, \quad (n=\text{integer})$$

interplanar lattice spacing for 111 must be 2.30. There are 2 distinct and strongest X-ray lines whose average value would be close to it (2.30): 2.318(100) and 2.293(100). Other reflection lines do not satisfy well to the proposed cubic cell of Bhan and Schubert(1969) since the a^2/d^2_{hkl} valus for them are not integer except one: 2.110 (3.57), 1.440(7.68), 1.390(8.23), 1.238 (9.67), 1.203(11.00), 1.192(11.20). It is thus apparent that $Pt_{34}Sb_7$ is not structurally identical to $Pt_{4+}Sb$, based upon the X-ray diffraction data available at present. However, possibility that $Pt_{34}Sb_7$ being a polymorph of $Pt_{4+}Sb$ is not totally dismissed, although the phase diagram (Fig. 1) does not show any indication for it. In order to verify whether $Pt_{4+}Sb$ and $Pt_{34}Sb_7$ are of an identical composition with different structures careful DTA experiment should be performed for the phase. If $Pt_{34}Sb_7$ undergoes phase transformation below 755°C, the structural difference found in $Pt_{34}Sb_7$ and $Pt_{4+}Sb$ may be explained. If it does not, $Pt_{34}Sb_7$ may be a new phase and the existence of $Pt_{4+}Sb$ is questionable.

As the $Pt_{4+}Sb$ phase has shown structural discrepancy when compared with the data obtained in this study, the crystallographic data for Pt_3Sb is subsequently subjected to reinvestigation.

Pt_3Sb was reported to be tetragonal ($ZrAl_3$ structure), a=3.94, c=16.96Å (Bhan *et al.*, 1969). Its X-ray powder diffraction data, however, have not been published. An attempt to synthesize single-phase Pt_3Sb was again unsuccessful in the present study. Microprobe analyses of Pt_3Sb coexisting with either $Pt_{34}Sb_7$ or Pt_3Sb_2 are shown in Table 2. It is stoichiometric without showing apparent compositional range. The Pt_3Sb phase under the reflecting microscope is pale greyish yellow in air with very weak bireflectance. It is weakly anisotropic, ranging from brownish grey to greyish brown in air. Micro-indentation hardness tests give VHN_{25}= 216 (183~240) for 6 measurements. The X-ray powder pattern shown in Table 4 was obtained from Pt_3Sb coexisting with Pt_3Sb_2, using a 114.6mm Gandolfi camera. The X-ray reflection lines are attempted to be indexed on the basis of a tetragonal cell as reported by Bhan *et al.* (1969) and the result is shown in Table 4. The refined cell parameters, calculated by the least-squares method using the present X-ray data, are a=3.9455(7), c=16.959(5)Å and are in excellent agreement with those of Bhan *et al.*. It is noted that there are 2 unindexable, weak reflections (2.482 and 2.450Å) that apparently do not belong to Pt_3Sb_2. Bhan and Schubert (1969) also noted a few weak X-ray reflections

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

h	k	l	d_{cal}(Å)	d_{obs}(Å)	I/I_0
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

X-ray powder pattern was obtained from a mixture of Pt_3Sb and Pt_3Sb_2, quenched from 600°C. CuK_α radiation (λ=1.5418Å), 114.6mm Gandolfi camera. X-ray reflection lines indexed on the basis of a tetragonal cell.

(their d-values not specified) in the Guinier film that did not fit well to the $ZrAl_3$ structure. Bhan *et al.* (1969) reported that Pt_3Sb has very weak X-ray lines indexable on a tetragonal cell by doubling the *a*-axis. They suggested that this small discrepancy from the $ZrAl_3$ 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 and Schubert (1969) and Bhan *et al.* (1969) are identical to those found in the present study, mainly because the earlier investigators have not specified the X-ray lines.

CONCLUSION

(1) $Pt_{34}Sb_7$, compositionally $Pt_{83}Sb_{17}$, has been encountered at 600° and 650°C in the present study. It is compositionally similar but structurally different to the previously reported $Pt_{4+}Sb$ phase.

The $Pt_{34}Sb_7$ phase is under reflected light pale browish grey to yellowish grey in air and in oil and non-bireflectant. Micro-indentation measurements give VHN_{100}=225 (206~243) for 6 indentations. Its X-ray powder data are indexable on a tetragonal cell with a=3.948(3) and c=16.85(1)Å.

(2) Identity of $Pt_{34}Sb_7$ with $Pt_{4+}Sb$ which did not occur in this study is still pending mainly because the X-ray powder patterns of the $Pt_{4+}Sb$ phase were not reported. If $Pt_{34}Sb_7$ and $Pt_{4+}Sb$ are identical in composition the structutal discrepancy in them may be explained in terms of polymorphism.

(3) Pt_3Sb is greyish yellow in air, very weakly bireflectant and weakly anisotropic. Micro-indentation hardness tests give VHN_{25}=216 (183~240) for 6 measurements. The X-ray powder patterns except for 2.482 and 2.450 lines for the Pt_3Sb phase can be indexable on a tetragonal cell. The refined cell parameters are a=3.9455 (7), c=16.959(5)Å, in excellent agreement to those reported by Bhan *et al.* (1968).

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REFERENCES

Bhan, Y.C., Godecke, T. and Schubert, K. (1969) Konstitution einiger Mischungen des Platins mit B-Elementen (B=Sn, Sb, Te). Jour. Less-Common Metals, 19, 121-140.

Bhan, S. and Schubert, K. (1969) Über die Struktur von Phasen mit Kupfer Unterstruktur in einigen T-B Legierungen (T=Ni, Pd, Pt; B=Ga, In, Tl, Pb, Sb, Bi). Jour. Less-Common Metals, 17, 73-90.

Friedrich, K. and Leroux, A. (1909) Über das Schmelzdiagramm der Platin-Antimonlegierungen. Metallugie, 6, 1-3.

Moffatt, W.G. (1979) The Handbook of Binary Phase Diagrams, 3 vol., and the Index to Binary Phase Collections, 1st ed.. General Electric Company, Schenectady, New York.

Nemilow, W.A. and Woronow, N.M. (1936) Über Platins mit Antimon. Z. Anorg. Chem., 226, 177-184.