

Phases and Phase Relations of the System Pd-Sb

팔래듐-안티모니계의 化合物 및 相平衡 研究

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ABSTRACT : Phase relations of the Pd-Sb system were investigated using the sealed-capsule technique; the quenched run products were studied by reflected light microscopy, X-ray diffraction, and electron microprobe analysis. Eight binary phases were confirmed to exist in the system: Pd₂₀Sb₇, Pd₃₁Sb₁₂, Pd₅Sb₃ (mertieite II), Pd₅Sb₂, Pd₂Sb, Pd₅Sb₃, PdSb (sudburyite), and PdSb₂ (unnamed PdSb₂). The X-ray powder diffraction data of all the phases, except for Pd₅Sb₃, however, may be indexable on an orthorhombic cell, space group Cmc2, with a=3.362(1), b=17.484(7), c=6.934(2)Å. Some physical properties as well as re-determined cell parameters are newly established. A revised phase relations of the Pd-Sb system are presented.

요약 : 팔래듐-안티모니계의 상관계 규명을 위한 연구를 위해 고순도 석영관을 사용해 시료를 제작한 후 가열시켜, 그 반응물을 반사현미경, X선회절분석, 전자현미분석법을 통해 연구하였다. 그 결과 팔래듐-안티모니계에는 Pd₂₀Sb₇, Pd₃₁Sb₁₂, Pd₅Sb₃(mertieite II), Pd₅Sb₂, Pd₂Sb, Pd₅Sb₃, PdSb(sudburyite), PdSb₂(천연 PdSb₂) 등 8개의 二成分 化合物이 존재함이 밝혀졌다. Pd₅Sb₃를 제외한 모든 化合物의 X선회절분말자료는 이미 발표된 문헌자료와 일치함을 알 수 있었다. 그러나 Pd₅Sb₃의 X선분말회절 양상은 공간군 Cmc2인 사방정계의 a=3.362(1), b=17.484(7), c=6.934(2)Å 단위포로 격자지수화 할 수 있음이 밝혀졌다. 이 연구결과 각 化合物에 대한 보다 자세한 격자상수와 일부 물리적 특성자료가 도출되었다. 이 연구로부터 얻어진 실험적 자료를 토대로 팔래듐-안티모니계의 새 상변화도(phase diagram)가 제시되었다.

INTRODUCTION

A large number of platinum-group minerals have been reported from many parts of the world. Many of them are palladium antimonides and show extensive compositional variations, mainly due to substitution of Pd by Pt, Cu, Ni, etc. and Sb by Bi, Te, As, Sn, etc.. Complexity of their chemistry and difficulties in getting X-ray diffraction data cause a number of natural phases unnamed or unidentified. For this reason, the precise phase relations and phase chemistry of the binary compounds of the Pd-Sb system are of interest and

become essential. The Pd-Sb system, in fact, has been re-investigated in this study, as a part of the on-going Pd-Pt-Sb ternary research in our laboratory, because some discrepancies exist in number of phases and their composition between earlier reported data.

PREVIOUS STUDY

Phase relationships of the Pd-Sb system were first investigated by Sander (1912) and later by Grigorjew (1932). There is substantial agreement between their results. The phase diagram pre-

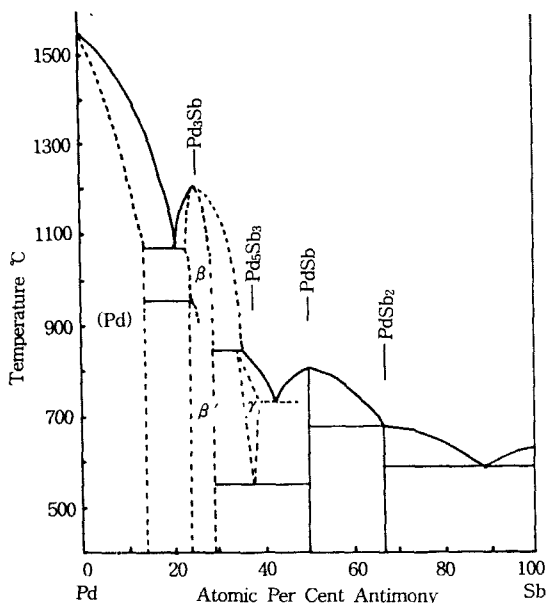


Fig. 1. Phase diagram of the Pd-Sb system by Hansen and Anderko (1958). A compromise between those of Sander (1912) and Grigorjew (1932)

sented by Hansen and Anderko (1958), on the basis of the two sets of data, is shown in Fig. 1. Four binary phases were reported, namely, Pd_3Sb , Pd_5Sb_3 , PdSb , and PdSb_2 . Of these, PdSb had been identified earlier by Roessler (1985). Bälz and Schubert (1969) reported an additional phase, Pd_3Sb , which is stable at below 580°C and decomposes into PdSb_2 and Pd_5Sb_3 at about 580°C . El-Boragy et al. (1970) confirmed the Pd_5Sb_3 phase and reported an additional, structurally related, non-stoichiometric $\text{Pd}_{5+x}\text{Sb}_{2-x}$ phase equilibria in the region between 24 and 30 at.% Sb (Fig. 2) and reported a new phase, Pd_3Sb_3 . The same portion of the phase diagram was later revised by Wopersnow and Schubert (1977) as shown in Fig. 3.

Desborough et al. (1973) reported that they were unable to synthesize the Pd_3Sb phase which was shown by El-Boragy and Schubert (1971) to be stable over the temperature range $500\sim 800^\circ\text{C}$. Cabri et al. (1975) first recognized that the Pd:Sb ratio in the Pd_3Sb phase is closer to 2.9:1 rather than 3:1. This was confirmed by Wopersnow and

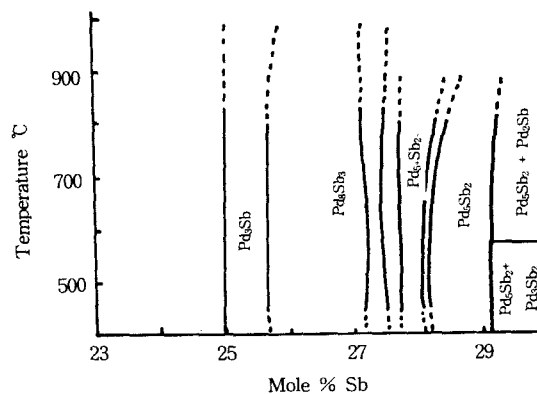


Fig. 2. Phase relations for the portion 23~30 at.% Sb of the Pd-Sb system (El-Boragy and Schubert, 1971).

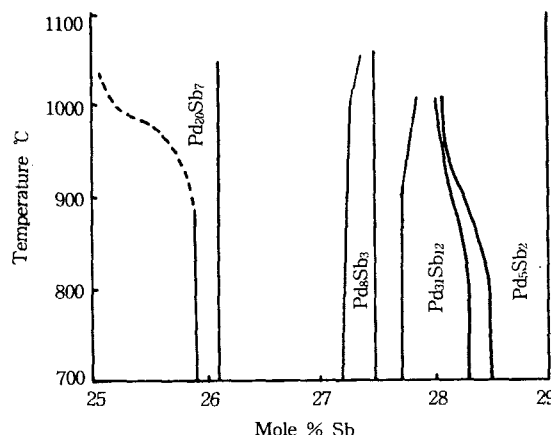


Fig. 3. Phase relations for the portion 25~29 at.% Sb of the Pd-Sb system (Wopersnow and Schubert, 1977).

Schubert (1977), who revised the formula of this phase to $\text{Pd}_{2.9}\text{Sb}_3$, and at the same time revised the formula for the $\text{Pd}_{5+x}\text{Sb}_{2-x}$ phase of El-Boragy et al. (1970) to $\text{Pd}_3\text{Sb}_{12}$. According to Fig. 3, compositions of the $\text{Pd}_{2.9}\text{Sb}_3$, Pd_5Sb_3 , $\text{Pd}_3\text{Sb}_{12}$, and Pd_3Sb_2 phases are 25.9~26.1, 27.2~27.5, 27.7~28.3, and 28.5~29.0 at.% Sb, respectively.

EXPERIMENTAL PROCEDURES

Starting materials were prepared from reagent grade palladium and antimony (all have 99.999% purity or better), and subsequently sealed in evac-

uated tubes of silica glass. The capsules were placed in a horizontal muffle furnace and heated at selected temperatures. To ensure homogeneity, most samples were opened, after initial heating, ground under acetone, pelletized and reloaded in the furnace for a further period of heating. The total heating period ranged from a few days to three months. Experimental runs were quenched by dropping the capsules in ice water.

Run products were studied by reflected light microscopy, X-ray powder diffraction and electron-microprobe analysis. X-ray diffraction patterns were obtained with a 114.6mm Gandolfi camera using Ni-filtered $\text{CuK}\alpha$ radiation. X-ray photographs were also taken in a Guinier-type focusing camera of 80mm diameter with filtered $\text{CoK}\alpha$ radiation. Where accurate X-ray data were required for calculation of the cell dimensions, a Philips automated X-ray diffractometer was used. Compositions of individual phases were determined with a Cambridge MK5 and a JEOL 733 electron-microprobe analyzers using synthetic Pd-Sb compounds and spectrographically pure Pd and Sb elements as standards.

EXPERIMENTAL RESULTS

Phase Relations

According to the phase diagrams of E1-Boragy and Schubert (1971, Fig. 2) and Wopersnow and Schubert (1977, Fig. 3), phase relations in the region 20~30 at.% Sb appear to be complicated due to the presence of phases with similar compositions. The present investigation was thus primarily to verify the phases previously reported, particularly in the region 0~50 at.% Sb.

Data on starting bulk composition of thirty nine runs prepared and their experimental results are given in Table 1. Runs, with starting compositions in the range 0~25 at.% Sb and quenched from 510~1000°C (runs 31, 39, 43, 50, 52 and 266) invariably yielded two phases, Pd and $\text{Pd}_{20}\text{Sb}_7$.

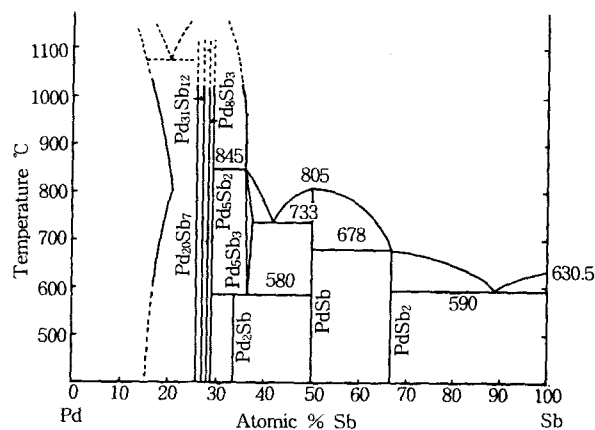


Fig. 4. Revised phase diagram of the Pd-Sb system.

Solid solubility of Sb in Pd is 21.0 at.% Sb at 800°C and 16.5 at.% Sb at 1000°C. These data differ considerably from those previously reported: approximately 14 at.% Sb (Sander, 1912), 16 at.% Sb (Grigorjew, 1932), and 17 at.% Sb (Pratt et al., 1968) with no temperature dependence up to 1000°C. The composition of the $\text{Pd}_{20}\text{Sb}_7$ phase coexisting with Pd is constant, within the analytical error, at 510~1000°C, ranging from 74.0~74.4 at.% Pd. It is clear that the Pd:Sb ratio is 2.88~2.85:1 rather than 3:1, supporting the correctness of the designation $\text{Pd}_{20}\text{Sb}_7$ for this phase. The Pd_5Sb_7 , Pd_3Sb_2 , and Pd_3Sb_7 phases were confirmed. The Pd_3Sb phase reported by Bälz and Schubert (1969) was also confirmed (Fig. 3). It is stable below 570°C and decomposes into Pd_3Sb_2 and Pd_3Sb_3 at between 570°C and 600°C, in agreement with the temperature of 580°C determined by Bälz and Schubert (1969). The Pd_3Sb_3 phase is confirmed to be stable at 600~800°C, and has a homogeneous range of less than 2 at.% at 700°C.

Run 60-5, quenched from 700°C, gave an assemblage of PdSb and a liquid of 66.2 at.% Sb. Run 60-6, quenched from 650°C, consisted of large crystals of Pd_3Sb_2 and very small amounts of liquid containing minute dendrites of Pd_3Sb_3 . Solid solubility of Pd in Sb at 510~520°C was negligible.

Revised phase relations established based on the

Table 1. Experimental results of the system Pd-Sb.

Sample No.	Composition (at.%)		Temp.(°C)	Heating Period (days)			Phases present	Composition (at.%)	
	Pd	Sb		1h	2h	3h		Pd	Sb
31	79.98	20.02	510	20	36		Pd		
							Pd ₂ Sb ₇	74.0	26.0
32	73.18	26.82	510	12	13	14	Pd ₂ Sb ₇		
							Pd ₃ Sb ₃	72.8	27.2
33	67.03	32.97	510	16	14	18	Pd ₃ Sb ₂	71.1	28.9
							Pd ₂ Sb	66.7	33.3
34	63.16	36.84	510	14	14	18	Pd ₃ Sb	66.7	33.3
							PdSb	50.0	50.0
35	60.03	39.97	510	17	10	18	Pd ₃ Sb	66.7	33.3
							PdSb	49.9	50.1
36	54.06	45.94	510	16	10	18	Pd ₂ Sb	66.5	33.5
							PdSb	50.0	50.0
37	47.98	52.02	510	16	10	15	PdSb	49.9	50.1
							PdSb ₂	33.4	66.6
38	30.00	70.00	510	20	12	14	PdSb ₂	33.7	66.3
							Sb	0.0	100.0
39	79.99	20.01	600	13	20	19	Pd		
							Pd ₂ Sb ₇	74.2	25.8
40	66.67	33.33	500	22	19	22	Pd ₂ Sb	66.7	33.3
41	33.33	66.67	600	22	19	20	PdSb ₂	33.3	66.7
42	50.00	50.00	600	22	19	20	PdSb	50.0	50.0
43	74.95	25.05	600	19	19	20	Pd		
							Pd ₂ Sb ₇	74.4	25.6
44	72.73	27.27	600	19	19	20	Pd ₃ Sb ₃	72.7	27.3
45	71.43	28.57	600	19	19	20	Pd ₃ Sb ₂	71.4	28.6
46	62.50	37.50	600	19	19	20	Pd ₃ Sb ₃	62.9	37.1
							PdSb	52.0	48.0
47	72.00	28.00	800	14	14		Pd ₃ Sb ₁₂	72.0	28.0
48	67.96	32.04	800	13	14		Pd ₃ Sb ₂	71.8	28.2
							Pd ₃ Sb ₃		
49	4.98	95.02	520	21	27		PdSb ₂	33.3	66.7
							Sb	0.0	100.0
50	79.97	20.03	800	6			Pd		
							Pd ₂ Sb ₇		
51	67.96	32.04	800	6	12		Pd ₃ Sb ₂	71.1	28.9
							Pd ₃ Sb ₃	63.9	36.1
52	79.92	20.08	1000	7			Pd	83.3	16.7
							Pd ₂ Sb ₇	74.4	25.6
53	68.01	31.99	1000	7			Pd ₃ Sb ₂	71.4	28.6
							L	63.8	36.2
54	62.47	37.53	800	5			Pd ₃ Sb ₃	63.7	36.3
							L		
55	57.00	43.00	800	5			L		
56	58.01	41.99	570	30	10		Pd ₂ Sb	66.3	33.7
							PdSb	50.0	50.0
57	58.00	42.00	620	21	20		Pd ₃ Sb ₃	62.7	37.3
							PdSb	50.0	50.0

Table 1. (continued)

Sample No.	Composition (at.%)		Temp.(°C)	Heating Period (days)			Phases present	Composition (at.%)	
	Pd	Sb		1h	2h	3h		Pd	Sb
58	57.99	42.01	700	22	12		Pd ₃ Sb ₃	62.1	37.9
							PdSb	50.0	50.0
59	67.80	32.20	700	22	19		Pd ₃ Sb ₂	71.4	28.6
							Pd ₃ Sb ₃	62.8	37.2
60	74.00	26.00	800	8	10		Pd ₂ Sb ₇	74.0	26.0
61-1	68.01	31.99	600	21	15		Pd ₃ Sb ₂	71.5	28.5
							Pd ₃ Sb ₃	63.6	36.4
60-2	74.00	26.00	1000	2	10		Pd ₂ Sb ₇	74.2	25.8
60-3	72.79	27.21	1000	2	10		Pd ₃ Sb ₃	72.8	27.4
60-4	62.50	37.50	700	4	10		Pd ₃ Sb ₃	62.4	37.6
60-5	44.79	55.21	700	4	10		PdSb	49.4	50.6
							L	33.8	66.2
60-6	29.99	70.01	650	10			PdSb ₂	33.6	66.4
							L		
60-7	10.99	89.01	650	10			L	11.0	89.0
266	78.94	21.06	800	16			Pd	79.0	21.0
							Pd ₂ Sb ₇		
573	66.80	33.20	1000	2			Pd ₃ Sb ₂	71.2	28.8
							L		

Abbreviation: L=liquid, 1h=initial heating, 2h=second heating, 3h=third heating.

interpretation of present experimental results are shown in Fig. 4.

Phases and Their Properties

Palladium

Pure element Pd examined in this study is white with yellowish tinge under reflected light. It is isotropic and takes a good polish. Micro-indentation hardness tests give $VHN_{100} = 116.3$ (109-123) for 5 measurements. X-ray powder pattern compares very well with that of earlier reported data (JCPDS CARD 5-681). Refined cell parameter, $a = 3.8881(5)\text{Å}$, is very similar to $a = 3.8898\text{Å}$ of PDF 5-681 and $a = 3.890\text{Å}$ of Raub(1959). Solid solubility of Sb in the pure Pd is 16.5 at.% at 1000°C, 21.0 at.% at 800°C, and 0.2 at.% at 510°C.

Pd₂Sb₇

Wopersnow and Schubert (1977) determined the structure of Pd₂Sb₇ to be rhombohedral, space group R3, with $a = 11.734(1)$, $c = 11.021(2)\text{Å}$. The melting point of the Pd₃Sb phase was reported to

be 1220°C (Sander, 1912) and 1185°C (Grigorjew, 1932). No further data for this phase have been published. A natural analogue of synthetic Pd₂Sb₇ is not yet known. Although the formula Pd₂Sb was originally given for stibiopalladinite by Adam (1927), it was later revised to Pd_{5+x}Sb_{2-x} ($x = 0.05$) by Cabri and Chen (1976).

The Pd₂Sb₇ phase synthesized in the present study has a compositional range of 74.0~74.5 at.% Pd between 510°C and 1000°C. Under reflected light, Pd₂Sb₇ is yellowish white in air and creamy yellow in oil, showing no birefractance. Anisotropy is very weak in air, brownish grey to bluish grey, and it is slightly enhanced in oil. Micro-indentation hardness measurements gave $VHN_{100} = 516$ (488-548) for 5 indentations.

The refined cell dimensions of the Pd₂Sb₇ phase, quenched from 1000°C, 800°C, and 600°C, and obtained by indexing on hexagonal axes, are $a = 11.717(3)$, $c = 11.011(8)\text{Å}$; $a = 11.715(2)$, $c = 11.008(5)\text{Å}$; and $a = 11.712(2)$, $c = 11.013(2)\text{Å}$, respectively.

Pd₃Sb₃

Pd₃Sb₃ was reported to be rhombohedral, with $a = 7.57(9)$, $c = 42.80(3)$ Å (El-Boragy and Schubert, 1971). Cabri et al. (1975) confirmed the phase and determined the cell dimensions of their synthetic Pd₃Sb₃ to be $a = 7.60(1)$, $c = 42.904(1)$ Å, which are in good agreement with those reported by El-Boragy and Schubert (1971). Wopersnow and Schubert (1976) determined the space group of the Pd₃Sb₃ to be R3c, and gave the cell dimensions as $a = 7.6152(7)$, $c = 43.032(7)$ Å. Micro-indentation hardness was reported by Cabri et al. (1975) to be $VHN_{30} = 516$ (501-545).

The group II mertieite (mertieite II) from Goodnews Bay, Alaska described by Desborough et al. (1973), is now generally accepted as the natural analogue of the synthetic Pd₃Sb₃ phase (Cabri, 1981). Mertieite II was originally thought to have the approximate formula (Pd, Cu)_{5+x}(Sb, As)_{2-x}, where $x = 0.1-0.2$. Cabri et al. (1975) restudied two grains of the type material and found mertieite II to be stoichiometric Pd₃(Sb, As)₃. They also showed by X-ray single crystal and powder diffraction work that the mineral is rhombohedral, with $a = 7.546(2)$, $c = 43.18(1)$ Å.

Pd₃Sb₃ was synthesized in this study between 600 and 1000°C. It is creamy yellow, under reflected light, and non-pleochroic. The phase is moderately anisotropic, showing brownish grey to almost extinction. It is optically identical to these of mertieite II. However, the micro-indentation hardness value of the synthetic Pd₃Sb₃, $VHN_{30} = 324$ (241-349), is significantly lower than $VHN_{30} = 516$ (501-545) of the synthetic Pd₃Sb₃ of Cabri et al. (1975) and $VHN_{30} = 544$ (511-588) of mertieite II (Cabri, 1981).

The X-ray powder diffraction pattern of Pd₃Sb₃ quenched from 600°C is well compared with earlier data in the literature. The cell parameters of the Pd₃Sb₃ phases synthesized in this study were refined by a least-squares method using powder diffraction data indexed on hexagonal axes. The refined cell parameters of these phases, $a = 7.604(1)$, $c = 42.943(4)$ Å, are well within the range of

those reported by other authors for synthetic Pd₃Sb₃ and mertieite II. It is shown in this study that the temperature at which the phase is synthesized has little effect on the cell parameters. Mertieite II has a smaller a -parameter and a larger c parameter as compared with the synthetic phases, perhaps due to compositional difference.

Pd₃₁Sb₁₂

According to El-Boragy et al. (1970), Pd₃₁Sb₁₂ is rhombohedral with $a = 7.6_{13}$, $c = 42.2_{40}$ Å, structurally related to Pd₃Sb₂ which is also rhombohedral with $a = 7.6_6$ and $c = 13.86_3$ Å. The c parameter of Pd₃₁Sb₁₂ is approximately three times of that of Pd₃Sb₂. The X-ray powder diffraction patterns of Pd₃₁Sb₁₂ and Pd₃Sb₂ are also quite similar. Optical and physical data of Pd₃₁Sb₁₂ are non-existent in the literature.

Pd₃₁Sb₁₂ was synthesized in this study at 800°C and its X-ray powder diffraction pattern is essentially identical to that of Pd₃₁Sb₁₂ given by El-Boragy et al., except for minor discrepancies in designating relative intensities and d -values of some lines. The refined cell parameters are $a = 7.6006(1)$ and $c = 41.945(8)$ Å, in good agreement with those given by El-Boragy et al. (1970). The compositional range of this phase given by Wopersnow and Schubert (1977) was not confirmed in this study.

Under reflected light Pd₃₁Sb₁₂ is yellowish white in air and pale yellow in oil, showing no birefractance. It is moderately anisotropic from brownish grey to greenish grey in air and in oil. Micro-indentation hardness measurements give $VHN_{30} = 467$ (423-494) and $VHN_{100} = 463$ (437-498) for four indentations each.

The mineral stibiopalladinite is closely related to the synthetic Pd₃₁Sb₁₂ phase. Stibiopalladinite was originally thought to be Pd₃Sb but later analysis (Desborough et al., 1973; Clark et al., 1974) on material from Potgietersrust, South Africa suggested the formula to be more accurately Pd₃Sb₂. Subsequent detailed study by Cabri and Chen

(1976) of the mineral from the locality of its original description, with electron microprobe analysis using synthetic standards, showed the composition of the mineral to be either $\text{Pd}_{5+x}\text{Sb}_{2-x}$ with $x=0.05$ or $\text{Pd}_{8-x}\text{Sb}_{3+x}$ with $x=0.065$. They chose the formula $\text{Pd}_{5+x}\text{Sb}_{2-x}$ because of its close relationship to synthetic $\text{Pd}_{5+x}\text{Sb}_{2-x}$ (presently $\text{Pd}_3\text{Sb}_{12}$) of El-Boragy et al. (1970).

According to Desborough et al. (1973), the symmetry of stibiopalladinite is either hexagonal or orthorhombic, but they excluded the hexagonal symmetry on the basis of their optical data. They gave the parameters of the orthorhombic cell with P22₂ space group as $a=12.80$, $b=15.04$, $c=11.36$ Å. However, the stibiopalladinite studied by Cabri and Chen (1976) is hexagonal, P6₃/mmc, P6₃mc, or P62c, with $a=7.607(2)$ and $7.598(2)$, $c=28.220(6)$ and $28.112(9)$ Å. The discrepancy was attributed to possible twinning in the crystals used by Desborough et al. (1973) or polytypism in the mineral.

The close relationship between Cabri and Chen's stibiopalladinite and synthetic $\text{Pd}_3\text{Sb}_{12}$ is substantiated by the fact that a direct comparison of the Gandolfi X-ray diffraction patterns of the two substances shows an excellent accordance with minor difference, in the back reflection region and in relative intensities of some lines. Most of the lines in the X-ray powder pattern of $\text{Pd}_3\text{Sb}_{12}$ may be indexed on the basis of the stibiopalladinite cell of Cabri and Chen (1976) with $a=7.604(4)$ and $c=28.09(1)$ Å.

Pd_3Sb_2

The Pd_3Sb_2 was first observed by Bälz and Schubert (1969) as a decomposition product of Pd_2Sb , and was later confirmed by El-Boragy et al. (1970), Cabri and Chen (1976), and Wopersnow and Schubert (1977). According to El-Boragy et al. (1970) and Cabri and Chen (1976), the Pd_3Sb_2 phase is hexagonal, space group P6₃cm, with $a=7.60_6$ and $c=13.86_3$ Å. According to the Pd-Sb phase diagram of Wopersnow and Schubert (1977), Pd_3Sb_2 has a compositional range of 28.5~

29.0 at.% Sb. The physical properties of Pd_3Sb_2 were not reported. A natural analogue of the synthetic Pd_3Sb_2 is not yet known.

The Pd_3Sb_2 phase was synthesized in this study between 1000 and 510°C. The phase has a narrow composition range of about 1.5 at.% in terms of Pd (run 51 and run 53, Table 1). It is white with a creamy tint under reflected light in air, with no visible birefractance. It is weakly anisotropic from brownish grey to greenish grey in air. Micro-indentation hardness measurements give $\text{VHN}_{100}=522$ (483-560) for four indentations. The X-ray powder diffraction data of Pd_3Sb_2 compare well with those given by El-Boragy et al. (1970) and Cabri and Chen (1976), as do the cell parameters, $a=7.608(2)$, $c=13.861(1)$ Å, calculated from the powder data of this study.

Pd_3Sb_3

Pd_3Sb_3 was reported to be hexagonal (NiAs-type structure), with $a=4.45$ and $c=5.83$ Å on the basis of X-ray powder diffraction data (Schubert et al., 1953). There is no X-ray powder diffraction pattern nor physical properties reported for this phase in the literature.

Pd_3Sb_3 synthesized between 600 and 800°C has a narrow composition range of about 2 at.% in terms of Pd. Below 570°C, bulk compositions of the Pd_3Sb_3 composition produce PdSb and Pd_2Sb . Thus, the lower thermal stability limit of Pd_3Sb_3 must be somewhere between 570 and 600°C. The temperature 580°C, the upper stability limit of Pd_2Sb at which it decomposes into Pd_3Sb_3 and Pd_2Sb_2 (Bälz and Schubert, 1969), is tentatively accepted as the lower stability limit of Pd_3Sb_3 .

Under reflected light Pd_3Sb_3 is pale yellowish pink in air and in oil, showing no birefractance. It is weakly anisotropic, from brown to brownish pink in air and from brownish pink to greenish pink in oil. The micro-indentation hardness value is $\text{VHN}_{100}=394$ (339-433) for five indentations.

The X-ray powder diffraction data of Pd_3Sb_3 do not fit on the hexagonal cell given by Schubert et

al. (1953). However, comparison of the X-ray powder pattern of Pd₃Sb₃ with that of Pd₂Sb shows an excellent accordance, except for a minor difference in the back reflection region. Therefore, the X-ray powder data of Pd₃Sb₃ were re-indexed according to the Pd₂Sb cell (orthorhombic, space group Cmc2₁). The cell parameters refined by a least-squares method, using the present X-ray data, are $a = 3.362(1)$, $b = 17.484(7)$, $c = 6.934(2)$ Å.

Pd₂Sb

Bälz and Schubert (1969) reported Pd₂Sb to be orthorhombic, space group Cmc2₁, with $a = 3.356$, $b = 17.44$, $c = 6.90$ Å. The Pd₂Sb phase was reported to decompose at 580°C into Pd₃Sb₃ and Pd₂Sb₂. No further information is given about this phase, and no natural analogue of the synthetic Pd₂Sb is known.

The Pd₂Sb phase was synthesized in this study at 500 and 570°C. Under reflected light Pd₂Sb is white with a creamy tint in both air and oil and is weakly bireflectant. Anisotropism is strong, from brownish grey to greenish blue in air and from yellowish pink to dark greenish blue in oil. The micro-indentation hardness test gives $VHN_{100} = 293$ (242–322) for four indentations. The X-ray powder diffraction data of Pd₂Sb are comparable with those given by Bälz and Schubert (1969), except that the d-values obtained in the present study are consistently larger. The cell parameters calculated by a least-squares method are $a = 3.366(1)$, $b = 17.523(3)$, $c = 6.929(2)$ Å.

PdSb

PdSb was first reported by Sander (1912) to melt congruently at 805°C, and later at 800°C by Grigorjew (1932). The structure was determined by Thomassen (1928) and confirmed by Pratt et al. (1968) to be of NiAs-type hexagonal, space group P6₃/mmc with $a = 4.076$, $c = 5.591$ Å. Cabri and Laflamme (1974) re-determined the cell parameters as $a = 4.079(3)$, $c = 5.587(3)$ Å.

The PdSb phase was synthesized in the temper-

ature range of 500~700°C. The X-ray powder diffraction patterns and the cell parameters, $a = 4.0753(4)$, $c = 5.5910(5)$ Å, of this synthetic phase compare well with those reported for PdSb by Cabri and Laflamme (1974).

Pure PdSb is stoichiometric up to its melting point, but Te substitution for Sb causes the phase to become slightly deficient in Pd relative to total (Sb, Te).

Under reflected light synthetic PdSb is creamy yellow in air and in oil. Bireflectance is weak from creamy yellow to pale greenish yellow in air and moderate from greyish purple to dark greyish purple in oil. It is strongly anisotropic from dark greyish green to greyish pink in air and in oil. Micro-indentation hardness measurements give $VHN_{25} = 291$ (270–306) and $VHN_{100} = 294$ (279–302) for 4 indentations each.

Sudburyite, ideally PdSb, first described from Sudbury, Ontario (Cabri and Laflamme, 1974), is the natural analogue of the synthetic PdSb phase. The mineral contains Ni in substitution for Pd, ranging from 2 to 2.9 at.%. Its X-ray powder diffraction pattern and physical properties compare well with those of the synthetic phase, except that the mineral is less anisotropic, perhaps due to a composition difference.

PdSb₂

PdSb₂ has been reported as cubic, space group Pa3 (Thomassen, 1928; Furuseh et al., 1965), with $a = 6.439$ Å (Thomassen, 1928), $6.4584(5)$ Å (Furuseh et al., 1965), and 6.460 Å (Pratt et al., 1968). The melting point of PdSb₂ was measured to be 677~680°C by Sander (1912) and by Grigorjew (1932). Neither optical nor micro-indentation hardness data of this phase are reported.

PdSb₂ was synthesized between 510 and 650°C. Within the temperature range the compound has a stoichiometric composition. The PdSb₂ phase is creamy white, under reflected light, with no bireflectance both in air and oil. Micro-indentation hardness measurements give $VHN_{100} = 484$

Table 2. Electron microprobe analyses of the Pd-Sb phases.

Phases	Composition (wt.%)			Run No.	Temp. (°C)
	Pd	Sb	Total		
Pd ₃ Sb ₇	71.8	28.4	100.2	39	510
	71.5	28.8	100.3	60	800
	71.8	28.2	100.6	52	1000
	71.4	28.5	99.9	60-2	1000
Pd ₃ Sb ₃	70.1	30.0	100.1	32	510
	69.6	29.9	99.5	44	600
	69.8	30.0	99.8	60-3	1000
Pd ₃ Sb ₁₂	68.8	31.0	99.8	47	800
Pd ₃ Sb ₂	69.3	31.6	100.9	60-1	600
	68.7	31.6	100.3	59	700
	68.0	31.6	99.6	51	800
	69.5	31.6	101.4	53	1000
PdSb	64.3	36.8	101.1	33	510
	64.0	36.6	100.6	34	510
	63.7	36.4	100.1	36	570
PdSb ₃	60.4	39.6	100.0	60-1	600
	59.6	40.2	99.8	46	600
	59.9	40.6	100.5	59	700
	59.6	41.0	100.6	58	700
PdSb	46.6	53.5	100.1	58	700
	46.0	54.6	100.6	60-5	700
	46.7	53.5	100.2	36	510
	46.3	54.5	100.8	37	510
PdSb ₂	30.6	70.0	100.6	37	510
	30.7	69.4	100.1	38	510

(464-503) for 5 indentations. Kim and Chao (1991) re-investigated the PdSb₂ phase by Guinier camera method and found a reflection, with a d for 2.035 Å which can be indexed as 310. However, the 310 reflection is prohibited in the Pa3 structure but is consistent with a P2₃ structure. The refined cell parameter a is 6.4626(3) Å.

Electron microprobe analyses of the palladium antimonides confirmed to exist in this system and selected to show compositional variation are shown in Table 2.

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