Phase Equilibria of the System Pd-Sb-Te and Its Geological Implications

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ABSTRACT: Phase relations in the system Pd-Sb-Te were investigated at 1000°, 800°, and 600°C, using the sealed-capsule technique; the quenched products were studied by reflected light microscopy, X-ray diffraction, and electron microprobe analysis. At 1000°C, the solid phases Pd, $Pd_{20}Sb_7$, Pd_8Sb_3, $Pd_{31}Sb_{12}$, and Pd_5Sb_2 are stable with a liquid phase that occupies most of the isothermal diagram. Additional solid phases at 800°C are Pd_5Sb_3, PdSb, Pd_8Te_3, Pd_7Te_3, and a continuous $Pd_{20}Te_7$-$Pd_{20}Sb_7$ solid solution becomes stable. At 600°C, $PdSb_2$, $Pd_{17}Te_4$, Pd_9Te_4, PdTe, $PdTe_2$, Sb_2Te_3, and Sb and continuous PdSb-PdTe and $PdTe$-$PdTe_2$ solid solutions are stable.

All the solid phases exhibit solid solution, mainly by substitution between Sb and Te to an extent that varies with temperature of formation. The maximum substitution (at.%) of Te for Sb in the Pd-Sb phases is: 44.3 in Pd_8Sb_3, 52.0 in $Pd_{31}Sb_{12}$, 46.2 in Pd_5Sb_2 at 800°C; 15.3 in Pd_5Sb_3, 68.3 in $PdSb_2$ at 600°C. The maximum substitution (at.%) of Sb for Te in the Pd-Te phases is 34.5 in Pd_8Te_3 at 800°C, and 41.6 in Pd_7Te_3, 5.2 in $Pd_{17}Te_4$, 12.4 in Pd_9Te_4, and 19.1 in $PdTe_2$ at 600°C.

Physical properties and X-ray data of the synthetic Pd_9Te_4, PdTe, $PdTe_2$, Pd_8Sb_3, PdSb, and Sb_2Te_3 correspond very well with those of telluropalladinite, kotulskite, merenskyite, mertieite II, sudburyite, and tellurantimony, respectively. Because X-ray powder diffraction data consistently reveal a 310 peak (2.035Å), the $PdSb_2$ phase is most probably of cubic structure with space group $P2_13$. The X-ray powder pattern of a phase with PdSbTe composition, synthesized at 600°C, compares well with that of testibipalladite. Therefore, testibipalladite may be a member of the $PdSb_2$-$Pd(Sb_{0.32}Te_{0.68})$ solid solution series which is cubic and $P2_13$ in symmetry. Thus the ideal formula for testibipalladite, presently PdSbTe, must be revised to PdTe(Sb, Te). Borovskite(Pd_3SbTe_4) has not been found in the synthetic system in the temperature range 1000°-600°C.

INTRODUCTION

Palladium commonly occurs in nature as compounds with antimony and tellurium, which form important platinum-group minerals. In spite of this association, the only reference on phase relations in the system Pd-Sb-Te appears to be that of El-Boragy and Schubert (1971), who investigated the system at 400° C. Their phase diagram (Fig. 1) shows equilibria among the phases known in the related binary systems. Later phases and phase relations among the bounding binary joins were re-investigated by many investigators, as summarized below.

For the system Pd-Sb, Pd_3Sb, first reported by Sander (1912) and shown in the Pd-Sb join of the Pd-Sb-Te diagram of El-Boragy and Schubert, was found to have a Pd:Sb ratio of 2.9:1 (Cabri et al., 1975), and its formula was revised to $Pd_{20}Sb_7$ (Wopersnow and Schubert, 1977). The existence of $Pd_{20}Sb_7$, Pd_8Sb_3,

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$Pd_{31}Sb_{12}$, Pd_5Sb_2, Pd_5Sb_3, Pd_2Sb, PdSb and $PdSb_2$ was confirmed in the preliminary stages of this study.

For the phases in the system Pd-Te, the formula of the earlier-reported phases, Pd_4Te, Pd_3Te, and Pd_2Te, was revised to $Pd_{17}Te_4$ (Kim et al., 1990), $Pd_{20}Te_7$ (Wopersnow and Schubert, 1977) and Pd_9Te_4 (Matkovic and Schubert, 1978), respectively. The system also includes two new phases, Pd_8Te_3 (Cabri et al., 1979) and Pd_7Te_3 (Kim et al., 1990), which were not shown on the Pd-Te join of the Pd-Sb-Te diagram of El-Boragy and Schubert (1971). Kim et al. (1990) reported eight phases to exist in the system Pd-Te, namely: $Pd_{17}Te_4$, $Pd_{20}Te_7$, Pd_8Te_3, Pd_7Te_3, Pd_9Te_4, Pd_3Te_2, PdTe and $PdTe_2$. Pd_5Te_2 of Gronvold and Rost (1956) was not found by Kim et al. (1990), who considered it a mixture of Pd_8Te_3 and Pd_7Te_3.

The phase relations in the system Sb-Te remain unclear. Hansen and Anderko (1958) reported only one intermediate phase, Sb_2Te_3, in the system. Later, Abrikosov et al. (1959) proposed two additional phases β and γ, that exit in the range 0~60 at.% Te. Brown and Lewis (1962) suggested a phase (δ) with a homogeneity range from 11 to 60 at.% Te, and proposed that the β and γ phases of Abrikosov et al.

may have been products of nonequilibrium. Kim and Chao (1990) reconfirmed the existence of Sb_2Te_3. Below 520°C, they also found a problematic phase, related to the δ phase of Brown and Lewis (1962), whose compositional limit on the Sb-rich side is 12~13 at. % Te, and is uncertain on the Te-side owing to failure in obtaining equilibrium assemblages.

The phase relations in the system Pd-Sb-Te merit re-investigation on the grounds that (1) the system is now known to include at least 17 binary phases, and (2) approximately 40% of those phases are known to have natural equivalents, and substitution between Sb and Te is common in them.

Because palladium antimonides and tellurides are found in mineral assemblages of early crystallization from magma as well as in late-stage hydrothermal environments, the present investigation covers phase relations in the system Pd-Sb-Te at 1000°C, 800°C, and 600°C. According to the binary phase diagram of Pd-Sb (Hansen and Anderko, 1958; Wopersnow and Schubert, 1977; Kim and Chao, 1990), Pd-Te (Kim et al., 1990) and Sb-Te (Hansen and Anderko, 1958; Abrikosov et al., 1959; Brown and Lewis, 1962), only solid phases are stable below 400°C, implying that the ternary phase relations of the system Pd-Sb-Te below 400°C would be essentially the same as those at 400°C, as established by El-Boragy and Schubert (1971).

EXPERIMENTAL PROCEDURES

Mixes were prepared from palladium wire and sponge (purity, 99.999%) and spectrographically pure tellurium and antimony ingot, all purchased from Johnson-Matthey Chemicals Ltd., and subsequently sealed in evacuated 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 114.6 mm Gandolfi camera using Ni-filtered $CuK\alpha$ 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
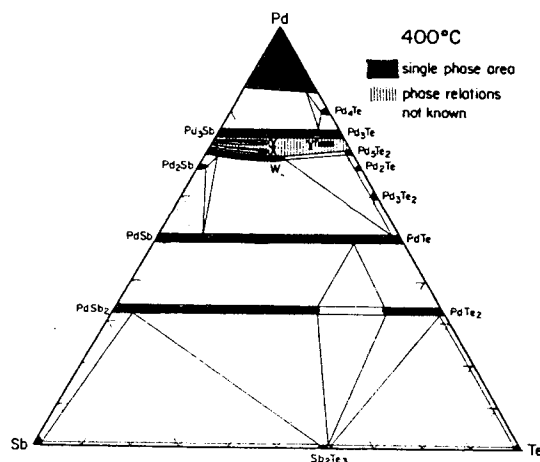

Fig. 1. Phase relations in the system Ps-Sb-Te at 400°C (El-Boragy and Schubert, 1971).

a Cambridge MK5 and a Jeol 733 electron-microprobe analyser using synthetic Pd-Te and Pd-Sb compounds and spectrographically pure Pd, Sb and Te elements as standards.

EXPERIMENTAL RESULTS

The experimental data, including starting bulk composition and compositions of phases identified, are omitted here because they are too big to tabulate here. However, the interpretation of the experimental results at 1000°C, 800°C and 600°C is presented diagrammatically in Figs. 2, 3, and 4, respectively.

The isothermal section at 1000°C (Fig. 2) is characterized by the presence of palladium, $Pd_{20}Sb_7$, Pd_8Sb_3, $Pd_{31}Sb_{12}$, Pd_5Sb_2 and a large field of liquid. Palladium contains up to 16.5 at.% Sb and 10.8 at.% Te in solid solution along the Pd-Sb and Pd-Te binary joins, respectively. The $Pd_{20}Sb_7$ phase has a homogeneity range of 24.6 to 26.0 at.% Sb. Tellurium substitution for Sb is 42 at.% in $Pd_{20}Sb_7$, 36~38 at.% in Pd_8Sb_3, 38.3 at.% in $Pd_{31}Sb_{12}$ and 16.5 at.% in Pd_5Sb_2. There are four 3-phase fields. Boundaries of one 3-phase assemblage are $Pd(Pd_{0.84}Sb_{0.14}Te_{0.02})+Pd_{20}Sb_7$ $(Pd_{20.17}Sb_{4.48}Te_{2.35})+liquid(Pd_{0.74}Sb_{0.13}Te_{0.13})$. It is not possible to determine accurate boundaries of other invariant fields, because (1) compositions of the solid phases involved are very similar, (2) the liquid phase coexisting with solid phases tends to separate into metastable phases during quenching, and (3) $Pd_{31}Sb_{12}$ and their structurally related Pd_5Sb_2 are nearly identical in optical properties and X-ray powder diffraction patterns. However, boundaries of remaining 3-
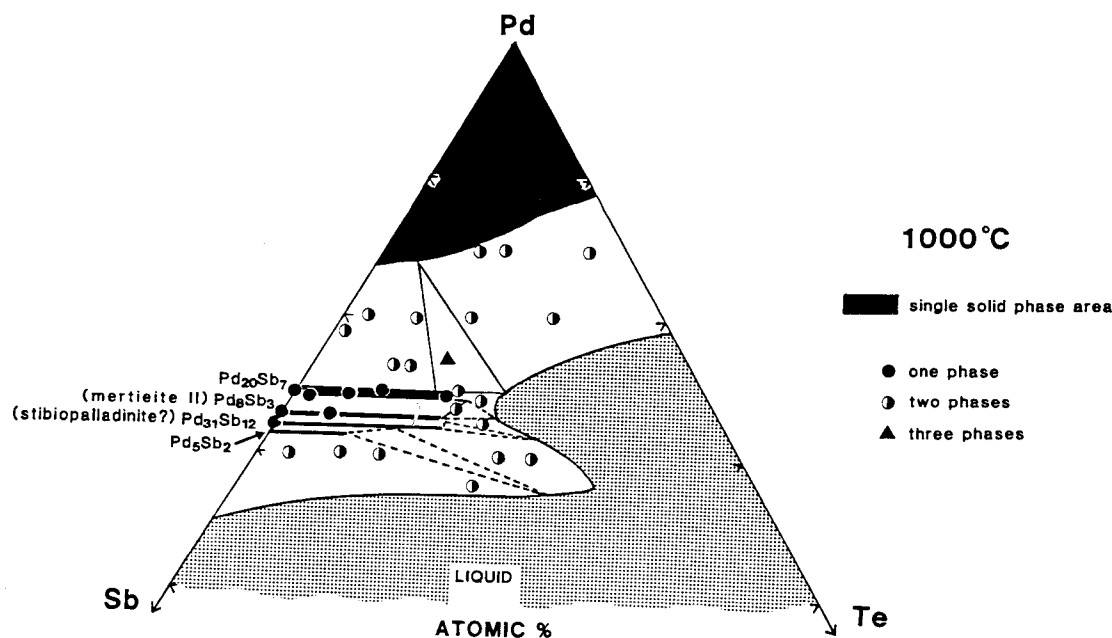
Fig. 2. Phase relations in the system Pd-Sb-Te at 1000℃.

phase fields may be postulated on the basis of the known tie-line of the neighboring 2-phase fields: $Pd_{20}Sb_7(Pd_{74.0}Sb_{15.1}Te_{10.9}) + Pd_8Sb_3(Pd_{72.3}Sb_{17.9}Te_{9.8}) + $ liquid; $Pd_8Sb_3(Pd_{72.3}Sb_{17.9}Te_{9.8}) + Pd_{31}Sb_{12}$ $(Pd_{72.1}Sb_{17.2}Te_{10.7}) + $ liquid; and $Pd_{31}Sb_{12}$ $(Pd_{72.0}Sb_{20.7}Te_{7.3}) + Pd_5Sb_2(Pd_{71.6}Sb_{23.7}Te_{4.7}) + $ liquid.

At 800℃, a few additional phases become stable (Fig. 3): Pd_5Sb_3 and PdSb on the Pd-Sb join, and $Pd_{20}Te_7$, Pd_8Te_3 and Pd_7Te_3 on the Pd-Te join. There is a complete solid solution between $Pd_{20}Sb_7$ and $Pd_{20}Te_7$, which are isostructural (Wopersnow and Schubert, 1977). The palladium solid solution field is determined by joining the solubility limits, 21 at.% Sb on the Pd-Sb join and 14.8 at.% Te on the Pd-Te join. Limits of tellurium substitution for Sb in Pd_8Sb_3, $Pd_{31}Sb_{12}$, Pd_5Sb_2, Pd_5Sb_3 and PdSb are 44.3, 52.0, 46.2, 4.5 and 4.0 at.%, respectively. Limits of antimony substitution for Te in Pd_8Te_3 and Pd_7Te_3 are 34.5 at.% and 36.3 at.%, respectively. The three 3-phase fields determined are $Pd(Pd_{84.6}Sb_{6.6}Te_{8.8}) + Pd_{20}(Te, Sb)_7$ $(Pd_{73.6}Te_{21.8}Sb_{4.6}) + $ liquid (1), $Pd_5Sb_2(Pd_{70.8}Sb_{15.7}Te_{13.5}) + Pd_7Te_3(Pd_{71.5}Sb_{10.3}Te_{18.4}) + $ liquid, and $Pd_5Sb_2(Pd_{71.0}Sb_{28.7}Te_{0.3}) + Pd_5Sb_3(Pd_{64.4}Sb_{34.0}Te_{1.6}) + $ liquid. Phase relations in the areas between Pd_8Sb_3 and Pd_8Te_3 solid solution end-members and between $Pd_{31}Sb_{12}$ and Pd_8Te_3 solid solution end-members are not clear owing to difficulties in identification of the optically and compositionally similar phases.

In the isothermal section at 600℃ (Fig. 4), more solid phases become stable, namely: $PdSb_2$, $Pd_{17}Te_4$, Pd_9Te_4, PdTe, $PdTe_2$, Sb_2Te_3, and Sb. The liquid fields exist only as thin strips near the three binary joins. Phase relations in the shaded area in Fig. 4 are not known because of the same difficulties in identification of the phases in the quenched products. Five 3-phase assemblages determined are $Pd(Pd_{89}Te_8Sb_3) + Pd_{17}Te_4(Pd_{81}Te_{18}Sb_1) + Pd_{20}(Te, Sb)_7(Pd_{74.3}Te_{22.0}Sb_{3.7})$, $Pd_5Sb_2(Pd_{69.8}Sb_{29.8}Te_{0.4}) + Pd_5Sb_3(Pd_{62.2}Sb_{32.0}Te_{5.8}) + PdSb_2(Pd_{32.9}Sb_{34.8}Te_{32.3}) + Sb_2Te_3(Sb_{40.4}Te_{59.6}) + $ liquid (68 at.% Te), and $PdSb_2(Pd_{33.5}Sb_{39.2}Te_{27.3}) + Sb_2Te_3(Sb_{40.4}Te_{59.6}) + $ liquid(54 at.% Te).

In addition to $Pd_{20}Sb_7$-$Pd_{20}Te_7$ solid solution, there is one more complete solid solution: PdSb-PdTe (hexagonal, $P6_3/mmc$). The PdSb-PdTe solid solution shows a slight depletion in Pd (approximately 1 at.%) on the Te-rich side. The PdSb-PdTe solid solution is stable to at least 670℃ and may persist to the melting temperature of PdTe at 746℃, as measured by Ipser and Schuster(1986). The cell parameters of the $Pd_{20}Sb_7$-$Pd_{20}Te_7$ and PdSb-PdTe solid solutions measured in this study (Tables 1, 2 and Figs. 5, 6) show good linear correlations with Te content.

Run products with bulk compositions $Pd_{40}Sb_5Te_{55}$, $Pd_{39}Sb_{10}Te_{51}$, and $Pd_{37.4}Sb_{12.6}Te_{50.0}$, all quenched from 600℃, yielded a "perthitic" intergrowth of PdTe and $PdTe_2$ solid solutions. The texture strongly indicates
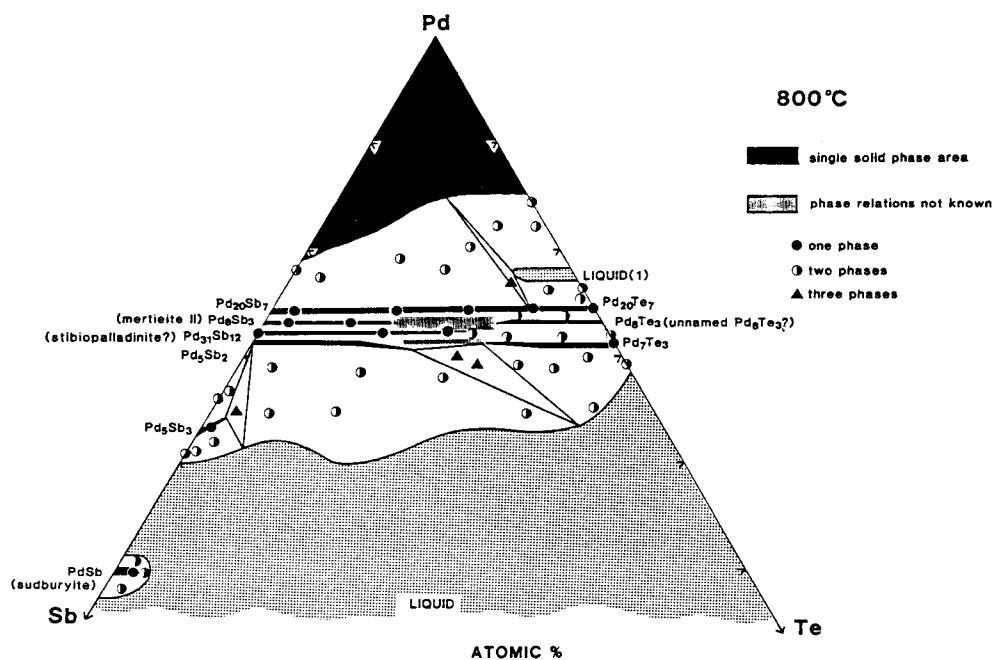
Fig. 3. Phase relations in the system Pd-Sb-Te at 800°C.

that the phases in the intergrowths are exsolution products from an originally homogeneous solid-solution, and supports the interpretation of Kim et al. (1990) that there is a complete solid solution between PdTe (NiAs-type structure) and $PdTe_2$ [$Cd(OH)_2$-type structure]. The solid solution is apparently not quenchable, and exsolution occurs somewhere below 600°C. This 2-phase exsolution area is shown in Fig. 4 (shaded).

$PdSb_2$ shows an extensive solid-solution from pure $PdSb_2$ to $Pd(Sb_{0.32}Te_{0.68})_2$, but does not form a complete solid solution with the structurally different $PdTe_2$. A similar extension of the $PdSb_2$-$Pd(Te, Sb)_2$ solid solution also was observed at 400°C (El-Boragy and Schubert, 1971). $PdSb_2$ was reported to have a pyrite structure, with a cell parameter of 6.439Å (Thomassen, 1928, Table 3), 6.4584(5)Å (Furuseth et al.,1965), and 6.460Å (Pratt et al., 1968). However, X-ray powder data (Table 3), obtained by powder diffractogram as well as by Guinier and Gandolfi camera methods with approximately 6~8 hour exposure time, consistently reveal a very weak reflection, with a d of 2.035 Å, which can be indexed as 310. The 310 reflection is prohibited in the Pa3 pyrite structure but is consistent with a $P2_13$ ullmannite (NiSbS) structure. The refined a parameter 6.4626(3)Å for $PdSb_2$ synthesized at 600°C in this study is in good agreement with

Table 1. Cell dimension of the $Pd_{20}(Sb, Te)_7$ solid solution series.

Run No.	Composition (at.%)			Temp.	Cell parameters	
	Pd	Sb	Te	(°C)	a(Å)	c(Å)
43	74.4	25.6	–	600	11.717(3)	11.011(8)
1001	74.2	15.2	10.6	600	11.754(2)	11.061(3)
1002	74.1	10.1	15.8	600	11.765(2)	11.094(2)
1003	74.0	5.1	20.9	600	11.779(1)	11.135(1)
78	74.0	–	26.0	600	11.797(3)	11.150(4)

$CuK\alpha_1$ radiation (λ=1.54059Å), automated X-ray diffractometer.

Table 2. Cell dimension of the synthetic sudburyite-kotulskite solid solution series.

Run No.	Composition (at.%)			Temp.	Cell parameters	
	Pd	Sb	Te	(°C)	a(Å)	c(Å)
42	50.0	50.0	–	600	4.0753(4)	5.5910(5)
1004	50.0	40.0	10.0	670	4.0955(4)	5.6015(6)
1005	49.4	24.9	25.7	670	4.1152(1)	5.6186(2)
1006	48.7	11.7	39.6	670	4.1293(2)	5.6357(3)
820	48.6	–	51.4	600	4.130 (3)	5.661 (5)

$CuK\alpha_1$ radiation (λ=1.54059Å), automated X-ray diffractometer.
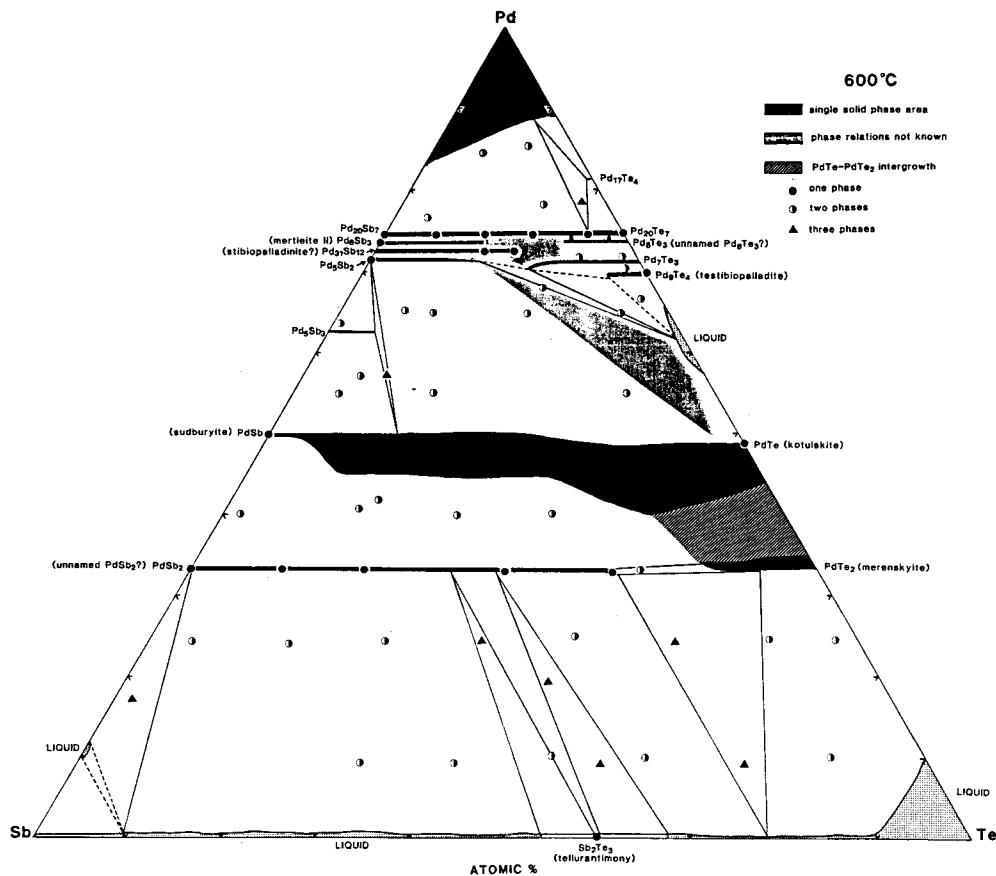
Fig. 4. Phase relations in the system Pd-Sb-Te at 600°C.

6.460Å given by Pratt et al. (1968). The X-ray powder patterns of single-phase products on the PdSb₂-Pd $(Te_{0.68}Sb_{0.32})_2$ solid solution also reveal a weak 310 reflection, indicating the absence of structural break in the solid solution. Fig. 5 shows a positive correlation of the cell dimension of the $PdSb_2$ solid solution with Te content.

All the phases, except for $Pd_{17}Te_4$, Sb_2Te_3, and Sb, exhibit extensive solid solution. Palladium contains 17 at.% Sb on the Pd-Sb join and 11 at.% Te on the Pd-Te join. Pd_5Sb_2, Pd_5Sb_3 and $PdSb_2$ contain as much as 39.8, 15.3, and 68.3 at.% Te, respectively, in substitution for Sb. The extent of antimony substitution for Te in $Pd_{17}Te_4$, Pd_7Te_3, Pd_9Te_4 and $PdTe_2$ is 5.2, 41.6, 12.4, and 19.1 at.%, respectively.

The Pd-Sb-Te phase diagram at 400°C (Fig. 1) proposed by El-Boragy and Schubert (1971) shows some similarities to that of this study (Fig. 4), especially for the 33.3~100 at.% Pd region, although the designation of some phases on the Pd-Te join of their diag-

ram differs from ours.

Pd-Sb-Te MINERALS IN RELATION TO SYNTHETIC PHASES

Many of the synthetic phases in the system occur in nature. These are telluropalladinite (Pd_9Te_4), kotulskite (PdTe), merenskyite ($PdTe_2$), mertieite II (Pd_8Sb_3), sudburyite (PdSb), and tellurantimony (Sb_2Te_3). Physical properties and X-ray powder data of these minerals correspond very well with those of the synthetic phases and are going to be published elsewhere.

The X-ray powder pattern of $Pd_{31}Sb_{12}$ synthesized in this study is very similar to that of $Pd_{5+}Sb_{2-}$ (later revised to $Pd_{31}Sb_{12}$) of El-Boragy et al. (1970) and that of the stibiopalladinite from Potgietersrust, South Africa (Cabri and Chen, 1976). The parameters of the hexagonal cell of stibiopalladinite, established by single-crystal X-ray diffraction, are a=7.598(2)Å, c=
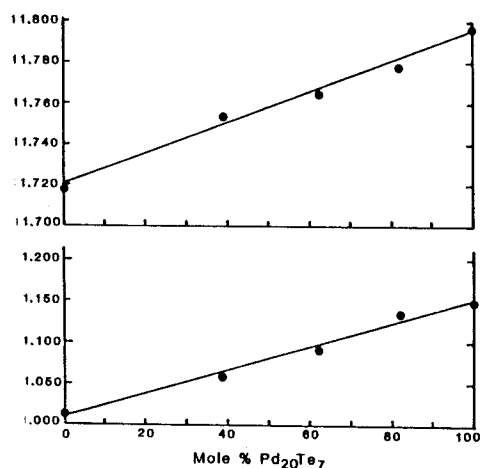
Fig. 5. Cell dimension versus composition of $Pd_{20}Sb_7$-Pd_{20} Te_7 solid solution.

Fig. 6. Cell dimension versus composition of synthetic sudburyite-kotulskite solid solution.

28.112(9)Å (Cabri and Chen, 1976). The X-ray pattern of $Pd_{5+}Sb_{2-}$ of El-Boragy et al. (1970), which contains additional weak lines, must be indexed on a larger hexagonal cell with a=7.6006(1)Å, c=41.945 (8)Å. The X-ray powder pattern of $Pd_{31}Sb_{12}$ from this study, however, may be indexed on both cells. Thus, the mineral stibiopalladinite and the synthetic phase $Pd_{31}Sb_{12}$ of El-Boragy et al.(1970) and of this study are, clearly, structurally related but their true relationship can only be estabilished by further single-crystal study of the synthetic material.

Telargpalite (Pd, Ag)$_{4+}$Te, cubic with an a=12.60 (2)Å,from Oktyabr deposit, U.S.S.R. (Kovalenker et al., 1974), was considered by Berlincourt et al. (1981) as the natural equivalent of the synthetic Pd_4Te phase of Gronvold and Rost (1956). Although Pd_4Te (presently proposed to be $Pd_{17}Te_4$; Kim et al., 1990) also is cubic, with an a=12.67Å, its powder pattern is not identical with that of telargpalite.

The Pd : Te ratio in keithconnite, $Pd_{3-x}Te$ (0.14< x<0.43),from the Stillwater Complex, Montana, was reported to be between 2.571 and 2.714,that is, between $Pd_{20}Te_7$ and Pd_7Te_3 (Cabri et al., 1979). Although the X-ray powder pattern of keithconnite is vaguely similar to that of $Pd_{20}Te_7$, a phase identical to keithconnite has not been found in this study.

Cabri (1981) reported an unnamed Pd_8Te_3 mineral in heavy-mineral concentrates from the Stillwater Complex, Montana. The X-ray powder pattern of the unnamed Pd_8Te_3 mineral is, however, not identical to either of the two synthetic forms of Pd_8Te_3 (Kim et al., 1990), although it bears some similarity to the X-ray powder pattern of the lower-temperature form
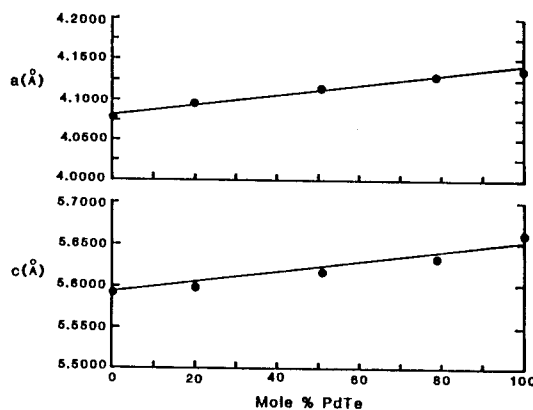
quenched from 500°C.

Another unnamed mineral, with the composition $Pd_{1.0}(Sb_{1.9}Fe_{0.04}Cu_{0.03})$ and an ideal formula $PdSb_2$, was reported by Graham (1978) from the Nairne pyrite deposit, South Australia. The mineral is optically isotropic and is probably the natural equivalent of the synthetic $PdSb_2$ phase. However, there are insufficient data, especially in X-ray data, on the natural phase to substantiate its identity with synthetic $PdSb_2$.

The mineral testibiopalladite from China (P.M.M. R.G., 1974; Fleischer et al., 1976) was given a chemical formula of Pd(Sb, Bi)Te based on the assumption that Bi substitutes for Sb. The formula of testibiopalladite was later idealized to PdSbTe (Cabri, 1981), which implies that the mineral is an ordered 1 : 1 : 1 compound. The structure of stibiopalladite (Table 3) was considered to be of Pa3 pyrite type, but later corrected to P2$_1$3 ullmannite type by analogy to michenerite (Institute of Geochemistry, Chinese Academy of Science, 1981). The X-ray powder pattern of a phase with PdSbTe composition, synthesized at 600°C, compares well with that of testibiopalladite given by P.M.M.R.G. (1974). The cell dimension a of the synthetic PdSbTe is 6.5483Å (Table 3), close to the value of 6.533Å reported by Hulliger (1963) but smaller than the value (6.557~6.581Å) reported for the natural phases (P.M.M.R.G., 1974). It is probably due to the presence of impurities, Ni and Bi, in the natural mineral that the cell parameter of the natural phases is larger than that of the synthetic phase. From the phase diagram at 600°C (Fig. 4), it is clear that PdSbTe is a member of the $PdSb_2$-PdTe ($Sb_{0.64}Te_{0.36}$) solid solution and not an ordered 1 : 1 : 1 compound. Consequently, the definition of testibiopalladite should perhaps be modified to cover the

Table 3. X-ray powder data of synthetic PdSb₂, PdSbTe and testibiopalladite.

h	k	l	Syn. PdSb₂(1) a=6.439Å d₀(Å)	I/I₀	Syn. PdSb₂(2) a=6.4626(3)Å d_c(A)	d₀(Å)	I/I₀	testibiopalladite(3) a=6.572Å D₀(Å)	I/I₀	Syn. testibiopalladite(4) a=6.5483(3)Å d_c(A)	d₀(Å)	I/I₀
1	1	1			3.731	3.733	5			3.780	3.784	2
2	0	0			3.231	3.232	28	3.28	50	3.274	3.276	50
2	1	0	2.889	4	2.890	2.890	100	2.940	100	2.928	2.930	100
2	1	1	2.626	4	2.638	2.639	78	2.680	80	2.673	2.674	88
2	2	0	2.273	2	2.284	2.284	20	2.325	40	2.315	2.315	28
3	1	0			2.043	2.035	81	2.088	5	2.070	2.062	1
3	1	1	1.942	7	1.948	1.948	74	1.983	90	1.974	1.974	94
2	2	2			1.865	1.865	11	1.895	10	1.890	1.890	7
3	2	0	1.790	3	1.792	1.792	27	1.825	50	1.816	1.816	28
3	2	1	1.725	5	1.717	1.727	37	1.755	70	1.750	1.750	51
4	0	0			1.615	1.616	7	1.642	10	1.637	1.637	12
330,		411	1.522	1				1.550	10			
4	2	0	1.442	2	1.445	1.445	11	1.470	30	1.464	1.464	18
4	2	1	1.408	5	1.410	1.410	20	1.435	50	1.428	1.429	22
3	3	2	1.375	1	1.377	1.378	8	1.397	30	1.396	1.396	86
4	1	2	1.317	3	1.319	1.319	5	1.340	30	1.336	1.336	5
511,		333	1.241	7	1.2437	1.2439	18	1.267	60	1.2602	1.2605	32
520,		432	1.197	6	1.2000	1.2000	15	1.221	50	1.2159	1.2159	19
5	2	1	1.177	5	1.1799	1.1801	10	1.198	40	1.1955	1.1957	14
4	4	0	1.140	7	1.1424	1.1425	15	1.162	60	1.1575	1.1577	20
600,		442			1.0771	1.0770	4	1.096	20	1.0913	1.0914	83
6	1	0			1.0624	1.0625	3	1.081	40	1.0765	1.0764	6
5	3	2			1.0483	1.0484	8	1.066	70	1.0622	1.0622	12
6	2	0			1.0218	1.0219	5	1.041	20	1.0353	1.0353	3

(1); Thomassen (1928). 57.65 mm camera, FeKα radiation (λ=1.934Å). (2); This study. Run 41, quenched from 600°C. CuKα₁ radiation (λ=1.54059Å), automated diffractometer. (3); JCPDS Card No. 29-961. (4); This study. Run 1012, quenched from 600°C, CuKα₁ radiation (λ=1.54059Å), automated diffractometer.

Te-rich members of the PdSb₂-PdTe(Sb, Te) solid solution. The ideal formula of testibiopalladite may then be written as PdTe (Sb, Te), with the general formula PdTe (Sb, Te, Bi), because up to 0.5 atom of Bi has been found to substitute for Sb or Te in the (Sb, Te) site in natural phases (Institute of Geochemistry, Chinese Academy of Science, 1981).

Fine intergrowths of the mineral analogue of PdTe (kotulskite) and PdTe₂ (merenskyite) have been observed in deposits in the Stillwater Complex, Montana (Cabri and Pickwick, 1974) and the Merensky Reef, South Africa (Kingston, 1966). The same fine intergrowths are also observed from the run products whose bulk compositions fall in between the two mineral compositions.

The mineral borovskite (Yalovoi et al., 1973; Fleischer, 1974) has an ideal composition of Pd₃SbTe₄. However, an ordered compound of this composition has not been found in the temprature range investigated here. An attempt to synthesize borovskite at 600°C from the bulk composition Pd₃₇.₄Sb₁₂.₆Te₅₀.₀ yielded fine intergrowths of PdTe solid solution (Pd₄₀.₈Te₄₄.₅
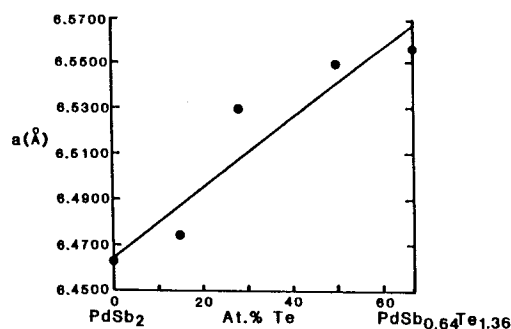

Fig. 7. Cell dimension versus composition of PdSb₂ solid solution.

Sb₁₄.₇) and PdTe₂ solid solution (Pd₃₄.₁Te₅₃.₃Sb₁₂.₆) in approximately 1:1 ratio. The composition of borovskite is, therefore, either unquenchable or unstable in the pure system. The presence of Pt in substitution for Pd and Bi in substitution for Sb and Te may have played an important role in stabilizing the mineral.

Natural analogues of the PdSb-PdTe solid solution are demonstrated by the assemblages found by Watkinson and Hak(pers. comm., 1989) in sulfide-rich ores from the Expo Ungava deposit, Quebec, the Shebandowan deposit, Ontario, and the Birchtree deposits, Manitoba. The composition of sudburyite and kotulskite grains in these assemblages ranges from $(Pd_{0.92}Ni_{0.05}Fe_{0.01}Co_{0.01})$ $(Sb_{0.82}As_{0.09}Bi_{0.08}Te_{0.01}S_{0.01})$ to $(Pd_{0.89}Fe_{0.03})$ $(Te_{0.61}Sb_{0.27}Bi_{0.15}As_{0.04})$, and thus covers a large portion of the PdSb-PdTe solid solution. As synthetic PdSb shows very limited solid solution, up to $Pd_{50}Sb_{48}Te_2$ at $800°C$, the mineral assemblages in these deposits must have been formed at a lower temperature, perhaps below $746°C$, the melting temperature of PdTe, as determined by Ipser and Schuster (1986).

ACKNOWLEDGMENTS

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팔라듐-안티몬-테루르 系의 相平衡과 地質學的 意義

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요   약 : 자연에는 팔라듐을 주성분으로 하는 백금족광물이 다수 산출되고 있다. 그 중 일부 광물은 독립된 광물로서 결정학적·광물학적 연구가 잘 되어 있는 반면 아직도 광물로서의 특성이 완전하게 규명되지 못한 경우도 상당수가 있다. 따라서 이 연구에서는 팔라듐-안티몬-테루르 성분계를 택해 이 3성분계에서의 상관계를 1000℃, 800℃, 600℃ 에서 각각 연구하고 이들 연구결과를 천연광물을 보다 체계적으로 규명·보완하는데 적용시키는 것을 그 연구 목적을 두었다.

합성실험을 위해 순수한 원소물질을 정량적으로 혼합시킨 후 실리카 튜브에 넣고 진공상태에서 밀봉하였다. 전기 고온로에서 가열반응시킨 시료는 얼음물을 이용해 급냉시켰으며 반응물은 반사현미경, 전자현미분석, X선 회절법 등으로 분석하였다. 1000℃ 에서 안정한 고체로는 Pd, Pd₂₀Sb₇, Pd₈Sb₃, Pd₃₁Sb₁₂, Pd₅Sb₂가 있다. 800℃ 에서는 Pd₅Sb₃, PdSb, Pd₈Te₃, Pd₇Te₃, Pd₂₀Te₇-PdSb₇ 완전고용체가 추가로 존재한다. 600℃ 에서는 PdSb₂, Pd₁₇Te₄, Pd₉Te₄, PdTe, PdTe₂, Sb₂Te₃, Sb, 그 밖에 PdSb-PdTe와 PdTe-PdTe₂ 고용체가 다시 안정한 고체 화합물로 추가된다.

모든 고체 화합물이 Sb와 Te간의 원소치환에 의해 고용체를 이루고 있으며 그 고용한계의 범위는 생성온도에 따라 변한다. Pd-Sb화합물에서 안티몬(Sb)를 치환하는 테루르(Te) 최대 치환범위(at.%)는 Pd₈Sb₃에서 44.3, Pd₃₁Sb₁₂에서 52.0, Pd₅Sb₂에서 46.2이며 그 최대 치환현상은 800℃ 에서 일어난다. Pd₅Sb₃와 PdSb₂에서의 최대 치환은 600℃ 에서 일어나며 그 정도는 각각 15.3, 68.3이다. Pd-Te화합물에서 Te를 치환하는 Sb의 최대치(at.%)는 Pd₈Te₃가 800℃ 에서 34.5, Pd₇Te₃, Pd₁₇Te₄, Pd₉Te₄, PdTe₂는 600℃ 에서 각각 41.6, 5.2, 19.1로 나타난다.

Pd₉Te₄, PdTe, PdTe₂, Pd₈Sb₃, PdSb, Sb₂Te₃는 각각 tellurantimony와 일치하며 광학적·결정구조적 성질이 매우 잘 일치한다. 지금까지 등축정계의 Pa3구조를 가지고 있는 것으로 알려진 PdSb₂화합물은 Gandolfi camera와 Guinier camera법에 의해 310으로 격자 지수화할 수 있는 2.035Å peak가 일정하게 기록이 되므로 P2₁3공간군에 속하는 것으로 재평가된다. Testibiopalladite의 성분을 가지는 PdSbTe성분의 화합물을 합성하여 X선 회절분석을 실시하면 testibiopalladite의 X선 회절양상과 일치함을 알 수 있다. 이 사실은 testibiopalladite가 등축정계이며 동시에 P2₁3공간군에 속하는 PdSb₂-Pd(Sb₀.₃₂Te₀.₆₈)고용체의 일부분에 속하는 광물임을 알 수 있게 한다. 따라서 현재의 testibiopalladite의 이상화학식인 PdSbTe는 PdTe(Sb, Te)로 바뀌어져야 할 것으로 믿어진다. Pd₃SbTe₄로 표현되는 borovskite는 1000°~600℃ 의 온도범위에서는 존재하지 않음을 알 수 있다.