

TRANSITION-METAL-CHALCOGEN SYSTEMS X: THE Pd-Te PHASE DIAGRAM

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Summary

The Pd-Te phase diagram has been studied in the composition range between 20 and 100 at.% Te using differential thermal analysis (DTA) and X-ray powder diffraction in combination with the results of an earlier thermodynamic investigation. In contrast with previous results by other authors it could be shown that the two phases PdTe and PdTe₂, with congruent melting points at 1019 K (55.0 at.% Te) and 1025 K (66.5 at.% Te), respectively, are separated by a two-phase field at all temperatures. The phase Pd₃Te₂ was shown to form peritectically at 780 K. The existence of four different phases was concluded for the composition range between 25 and 30 at.% Te from the DTA results: Pd₂₀Te₇ and "Pd_{2.5}Te", stable up to 1026 K and 768 K, respectively; Pd₉Te₄, stable between 741 and 878 K, and the high temperature phase ξ , stable between 835 K and its congruent melting point at 1183 K (27.8 at.% Te). The Pd₄Te phase was confirmed. Between about 20 and 25 at.% Te experimental results of the DTA measurements are reported without interpretation.

1. Introduction

The Pd-Te phase diagram, as it is reported in the literature [1 - 3], is characterized by the existence of a continuous solid solution between the limiting stoichiometric compositions PdTe and PdTe₂ at temperatures between 910 and 960 K, resembling the well known non-stoichiometric phase in the Ni-Te system [4, 5]. At lower temperatures a miscibility gap is shown separating the phases PdTe and PdTe₂ with rather limited homogeneity ranges which crystallize in the NiAs (B8₁) type and the CdI₂ (C6) type structure respectively. A recent thermodynamic investigation in our laboratory [6], however, revealed at once that the phase diagram as it was shown cannot be correct. This prompted us to continue the series of investigations of transition-metal-chalcogen systems [7, 8] with a study of the Pd-Te

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system using differential thermal analysis (DTA) and X-ray powder diffraction methods. The phase boundaries obtained from the results of the thermodynamic investigation [6] were also included to construct the complete phase diagram between about 20 and 100 at.% Te.

The first reports about the preparation of palladium tellurides, mostly by precipitation from aqueous solutions, are from Tibbals [9], Brukl [10], and Wöhler *et al.* [11]. Thomassen [12] prepared the two phases PdTe and PdTe₂ by direct reaction from the pure elements and determined their crystal structures to be of the NiAs- and the CdI₂-type respectively. Grønvold and Røst [13] performed the first systematic investigation of the entire system, and they discovered in addition to the two phases already known the cubic compound Pd₄Te as well as three more phases between 25 and 33 at.% Te which were designated Pd₃Te, Pd_{2.5}Te, and Pd₂Te. Owing to the rather complicated powder patterns their crystallographic identification turned out to be very difficult. Whereas Grønvold and Røst [13] did not detect any significant mutual solubility between PdTe and PdTe₂, Guggenheim *et al.* [14] reported that all samples with tellurium contents between 50 and 66.7 at.% were single phase (although no temperatures were specified).

A complete phase diagram was presented by Medvedeva *et al.* [2] for the composition range between 20 and 100 at.% Te based on the results of thermal analyses, X-ray measurements and measurements of the microhardness and the electrical conductivity. It showed the above mentioned solid solution between PdTe and PdTe₂ at higher temperatures which was confirmed by Kjekshus and Pearson [3] by high-temperature X-ray data. These authors determined also the phase boundaries of PdTe and PdTe₂ at lower temperatures from the composition dependence of the lattice parameters in samples quenched from different temperatures. Raub *et al.* [15] studied the occurrence of superconductivity in platinum group chalcogenides. From their lattice constant data they concluded a homogeneity range of about 50 to 52 at.% Te (at temperatures between 673 and 873 K) for PdTe, whereas the superconductivity results seemed to indicate that at the palladium-rich end the range extends to 48 at.% Te. An extremely narrow homogeneity range around 66.7 at.% Te was found for PdTe₂.

Kharkin *et al.* [16] investigated Pd-Te alloys obtained as thin films and determined the crystal structure of the Pd₄Te phase (which actually should be Pd₈₄Te₂₄, i.e. Pd_{3.5}Te, according to their results) from its electron diffraction pattern in one of these preparations [17]. Schubert and co-workers finally determined the crystal structures of three phases between 25 and 40 at.% Te, i.e. Pd₂₀Te₇, Pd₉Te₄, and Pd₃Te₂ [18 - 20].

2. Experimental details

The starting materials for most of the samples were tellurium (Asarco, New York, U.S.A.; purity, 99.99%) and palladium sponge (Ögussa, Vienna, Austria; purity, 99.9%); some alloys were prepared using palladium foil

(0.025 mm; Engelhardt Industries, Inc., New York, U.S.A.; purity, 99.95%) which had also been employed in the thermodynamic investigation [6]. Calculated amounts of the elements (total mass, 0.6 g) were weighed on a semi-microbalance to within ± 0.05 mg. Quartz ampoules were filled with the material, evacuated to 10^{-1} - 10^{-2} Pa, flushed several times with titanium-gettered argon and finally sealed under vacuum. The mixtures were usually annealed at 675 K for about 3 days, then slowly heated to 1075 K (1275 K for palladium-rich samples) in one week and kept at this temperature for 3 more days. Then they were cooled in the furnace. The samples for the X-ray measurements were finely powdered and annealed at temperatures between 650 and 850 K for periods between 1 and 4 weeks. A number of palladium-rich samples (No. 24 - 30) were prepared in little graphite crucibles which were placed inside the quartz ampoules to avoid any possible reaction between the palladium and SiO_2 . However, no significant differences could be detected in the results of the measurements.

The thermal analyses were performed using a commercial thermal analyser (DTA 404S/3; Netzsch, Selb, F.R.G.) with samples of about 0.5 g sealed under vacuum in special quartz containers. The heating rate was usually 2 K min^{-1} ; pure chromium was used as reference material. The Pt/Pt10%Rh thermocouples were calibrated at the melting points of high purity zinc, antimony and gold. DTA samples were frequently annealed for periods of 1 - 2 weeks at appropriate temperatures to ensure thermodynamic equilibrium before the measurements were started.

The X-ray investigations were carried out in Debye-Scherrer cameras of diameter 57.3 mm using filtered $\text{Co K}\alpha$ radiation. For some of the palladium-rich samples a larger camera was used with a diameter of 114.5 mm to obtain a better resolution of the complicated powder patterns. Lattice parameters were calculated by linear regression and extrapolation to zero using the function $\frac{1}{2}\{(\cos^2 \theta / \sin \theta) + (\cos^2 \theta / \theta^4)\}$.

3. Results

The results of DTA measurements for 36 samples are listed in Table 1. Usually the temperatures of the thermal effects are those evaluated from the heating curves; only for the liquidus both values, obtained on heating and on cooling, are given to allow an estimate of the upper and the lower limit of the true liquidus temperature. Generally the upper value is thought to be more reliable since the liquidus effect is frequently found to be affected by considerable supercooling. Table 2 contains the phase boundaries obtained from the breaks in the isopiestic "equilibrium curves" in the thermodynamic investigation (*cf.* ref. 6, Fig. 1). The complete phase diagram between about 15 and 100 at.% Te based on the results of the present investigation is shown in Fig. 1. The data points in the central part of the diagram are omitted for the sake of clarity. This part (20 - 70 at.% Te), including the actual experimental points, is shown separately in Fig. 2. For reasons discussed below no

19	64.0	1003			1020	1010
23	66.0			1012	1024	1010
20	70.0	721			1017	1005
34	75.0	721			1004	994
21	80.0	721			983	965
35	85.0	721			965	948
22	90.0	720			929	912
36	94.9	718			874	845

Compositions are the nominal values and are estimated to be correct within ± 0.1 at. %.

^aSamples not in equilibrium.

^bWeak effect in the two-phase field (PdTe + PdTe₂); the first temperature gives the beginning, the second the maximum of the effect in the heating curves.

TABLE 2

Phase boundaries from the isopiestic experiments [6]

Composition (at.% Te)	Temperature of the tie-line (K)	Composition (at.% Te)
$L/(L + PdTe)$		$(L+PdTe)/PdTe$
46.2	967	51.7 ₅
48.2 ₅	987	52.4
49.5	996	52.9
49.7 ₅	998	53.1
51.7	1009	53.8
53.7 ₅	1017	54.6
$PdTe/(PdTe+L)$		$(PdTe+L)/L$
55.2	1017	56.6
$L/(L+PdTe_2)$		$(L+PdTe_2)/(PdTe_2)$
59.6	1004	64.5
$PdTe/(PdTe+PdTe_2)$		$(PdTe+PdTe_2)/PdTe_2$
56.6	909	65.6
56.7	913	
56.8	941	65.0
56.7 ₅	969	64.5
56.5	989	64.3

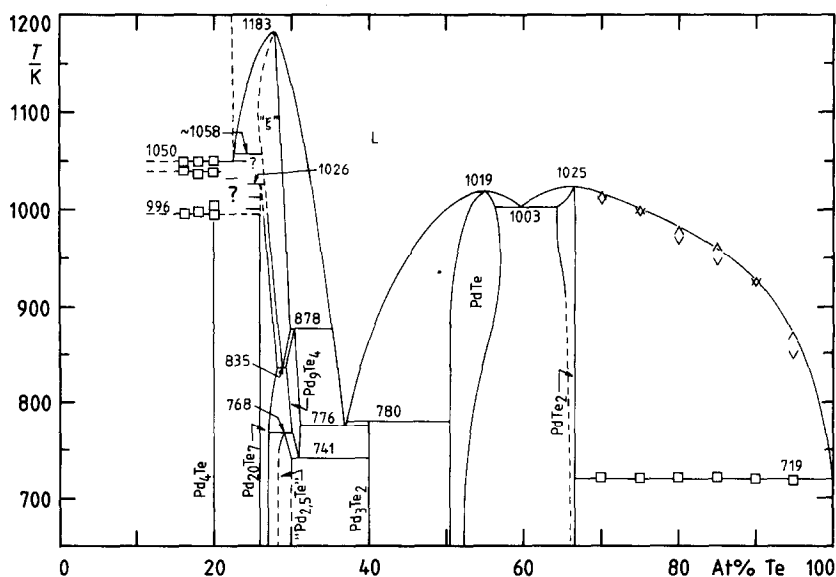


Fig. 1. Pd-Te phase diagram with data points from DTA: \square , invariant thermal arrest; Δ , ∇ , liquidus on heating and cooling respectively.

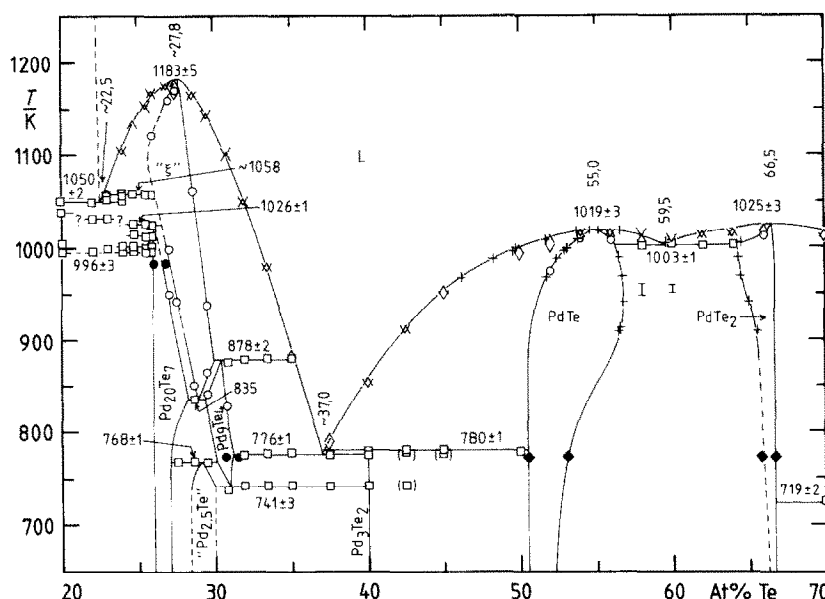


Fig. 2. Partial Pd-Te phase diagram with experimental data points: \square , invariant thermal arrest; \triangle , ∇ , liquidus on heating and cooling respectively; \circ , other effects; I, weak effects in the (PdTe + PdTe₂) two-phase field; +, phase boundaries from the isopiestic experiments [6]; \blacklozenge , Kjekshus and Pearson [3]; \bullet , Schubert and coworkers [18, 20]. (The uncertainties in the temperatures are estimated from the reproducibility of the thermal effects at different compositions.)

interpretation is given in the range between about 1000 and 1050 K for tellurium contents of up to 25 at.%.

The tellurium-rich part of the phase diagram is characterized by the eutectic between PdTe₂ and tellurium at 719 ± 2 K; the corresponding invariant arrest can be observed for all samples with tellurium contents of more than 66 at.%. As in many other transition-metal-tellurium systems [4, 21, 22] the shape of the liquidus curve indicates a degenerate eutectic, *i.e.* a eutectic point very close to pure tellurium.

The homogeneity ranges of the two phases PdTe and PdTe₂ exist between 50 and 66.7 at.% Te, which contrary to previous reports [2, 3] are separated by a two-phase field at all temperatures. This can be proved not only by the shape of the isopiestic "equilibrium curves" in ref. 6 but also by the appearance of an invariant thermal arrest at 1003 ± 1 K for samples with compositions between 58.0 and 64.0 at.% Te that is due to a eutectic reaction. The eutectic point itself is located around 59.5 at.% Te. The phase boundaries at higher temperatures were constructed according to the data of Table 2 which are in very good agreement with the thermoanalytical results; at lower temperatures the data by Kjekshus and Pearson [3] were used. One can see from Fig. 2 that the two-phase region between PdTe and PdTe₂ narrows considerably with increasing temperature without closing completely, however. For two samples in this two-phase field, with 58.0 and 60.0 at.% Te, an extremely weak, yet reproducible thermal effect was

observed around 950 K; the beginning and the maximum of the peak in the ΔT curve on heating are marked in Fig. 2. Although no unequivocal explanation can be given for this effect the possibility is considered that it is due to an ordering reaction in the phase PdTe as frequently observed in NiAs phases at lower temperatures.

For samples with tellurium contents between 40 and 50 at.% an invariant thermal arrest was observed at 780 ± 1 K which separated into two effects on repeated heating and cooling. However, it could be shown that for samples with more than 40 at.% Te, annealed at 743 K for 9 days, the splitting had disappeared in the first heating run, whereas on cooling and subsequent reheating two peaks could be distinguished again. This indicates that one of them is caused by a lack of thermodynamic equilibrium in the samples. An additional thermal effect at 742 K appeared in the ΔT curves of the sample with 42.5 at.% Te when heated a second time which again disappeared after annealing the sample. (The corresponding data points are shown in parentheses in Fig. 2) In contrast, three different invariant thermal arrests could be distinguished at 40 at.% Te independent of thermal treatment: those at 741 ± 3 K and 776 ± 1 K could also be observed at lower tellurium contents (down to 30.8 at.% Te and 31.9 at.% Te respectively). These effects together with the liquidus data obtained allow the following conclusion to be drawn. The thermal arrest at 780 K is caused by the peritectic decomposition of the phase Pd_3Te_2 ; that at 776 K is due to the eutectic between Pd_9Te_4 and Pd_3Te_2 (with the eutectic point itself around 37 at.% Te), whereas the thermal arrest at 741 K corresponds to the eutectoid decomposition of Pd_9Te_4 into Pd_3Te_2 and a phase designated here " $\text{Pd}_{2.5}\text{Te}$ ". Both Pd_3Te_2 and Pd_9Te_4 have been described previously by Matković and Schubert [19, 20]. The phase " $\text{Pd}_{2.5}\text{Te}$ " which is possibly identical with a phase of the same stoichiometry discovered by Grønvold and Røst [13] apparently forms by a peritectoid reaction at 768 ± 1 K from $\text{Pd}_{20}\text{Te}_7$ (identified by Wopersnow and Schubert [18]) and Pd_9Te_4 ; the corresponding thermal effect can be observed for samples with 27.5, 28.6 and 29.5 at.% Te. An additional invariant arrest at 878 ± 2 K appears in samples with compositions between 30.8 and 35.0 at.% Te; it is thought to be caused by the peritectic decomposition of Pd_9Te_4 . For all invariant thermal arrests discussed up to now the construction of the phase diagram is in excellent agreement with the change in their intensity with composition.

Starting from the eutectic point at about 37 at.% Te and 776 K the liquidus curve rises rather steeply to a maximum at about 27.8 at.% Te and 1183 ± 5 K. With increasing palladium content it drops again and around 22.5 at.% Te it meets an invariant thermal arrest at 1050 ± 2 K which is possibly due to another eutectic reaction. At higher palladium contents no liquidus effects could be detected in the temperature range investigated (up to 1450 K) suggesting a drastic increase in liquidus temperatures as would be expected because of the comparatively high melting point of palladium (1825 K). The observed maximum in the liquidus curve is interpreted as congruent melting point of a high temperature phase which has not been

described explicitly in the literature up to now and which is designated ξ in the present study. On both sides of the maximum the solidus temperatures could be evaluated from the heating curves, and between 27 and 29.5 at.% Te those thermal effects could be observed which correspond to the crossing of the two-phase regions of the ξ phase with $\text{Pd}_{20}\text{Te}_7$ and Pd_9Te_4 respectively.

In the composition range below 26 at.% Te we investigated by DTA nine samples with tellurium contents between 16.1 and 25.9 at.%. A number of apparently invariant thermal arrests were observed between 995 and 1060 K. The data points listed in Table 1 and shown in Figs. 1 and 2 were obtained after annealing the samples at 953 K for 10 days. Although in most cases the variation in the intensity of the thermal effects with composition can be clearly followed, it is still impossible at the moment to offer a reasonable interpretation in this composition range. As mentioned above, it can be assumed that the effect at 1050 K is caused by a eutectic reaction with pure palladium. The invariant arrest at 1026 ± 1 K is attributed to the peritectoid decomposition of $\text{Pd}_{20}\text{Te}_7$ because its intensity increases noticeably with increasing tellurium content.

The Pd_4Te phase has been described repeatedly in the literature [13, 16, 17]; it is shown in Fig. 1 according to its stoichiometry at 20 at.% Te as a line compound. As far as the results of Kharkin *et al.* [17] which were obtained with thin films are also valid for bulk samples it is possible that this phase exists — according to the stoichiometry $\text{Pd}_{3.5}\text{Te}$ obtained in ref. 17 — at somewhat higher tellurium contents, *i.e.* around 22 at.% Te.

To clarify the obviously complicated phase relationships in this part of the system a series of quenching experiments was performed. Powdered samples with compositions between 16 and 27 at.% Te were annealed and quenched from 973, 1018 and 1043 K, and then investigated in Debye-Scherrer cameras. However, with this simple method an unambiguous identification of the phases present in the samples was impossible because of their extremely complicated powder patterns. Nevertheless, it should be noted that the strongest lines of the Pd_4Te phase could be clearly identified in all samples up to 24.0 at.% Te, and even up to 25.5 at.% Te at 973 K. Since its lattice parameter is virtually unchanged over this whole composition range, it has to be concluded that the phase has a very narrow homogeneity range. The average value $a = 12.675(8)$ Å is in excellent agreement with the one reported by Grønvdal and Røst [13] ($a = 12.674$ Å). The weak invariant thermal arrest at 996 ± 3 K in this composition range could possibly be caused by an ordering transition in Pd_4Te which would not be observed in the Debye-Scherrer powder patterns (where only the strongest lines could be distinguished anyway).

The lattice parameters of the two phases PdTe and PdTe_2 were determined from the powder patterns between 45 and 70 at.% Te, in most cases for samples quenched from 850 K. The results were basically in good agreement with the data obtained by Kjekshus and Pearson [3] for 773 K. Only on the tellurium-rich side of PdTe as well as in the two-phase field

(PdTe + PdTe₂) deviations were observed which would indicate a considerably narrower homogeneity range. This is certainly due to an insufficient quenching rate, as already observed in ref. 3 where the authors stated that for tellurium contents of more than 52 at.% the lattice parameters are strongly dependent on the quenching rate.

4. Discussion

As already mentioned above, the Pd–Te phase diagram presented in Figs. 1 and 2 is somewhat in contradiction with earlier results by Medvedeva *et al.* [2] and by Kjekshus and Pearson [3]. There are no indications of the existence of a continuous solid solution at elevated temperatures between PdTe and PdTe₂ as reported by these authors; the corresponding evidence against it has been discussed in detail in the previous paragraph. The data points between 50 and 66.7 at.% Te shown in ref. 2, Fig. 1, which had been obtained by “thermal methods” are difficult to explain in the light of the present results. No corresponding effect, on either heating or cooling, could be detected below 1000 K in the course of our DTA measurements (with the exception of the very weak effect in the two samples with 58.0 and 60.0 at.% Te). As a possible explanation one could speculate that these experimental points are due to impurities in the samples. This assumption might be supported by the fact that the temperatures of the invariant equilibria given in ref. 2 — including the congruent melting points of PdTe and PdTe₂ — are up to 20 K lower than the values determined here.

Kjekshus and Pearson [3] concluded the existence of this continuous homogeneity range between PdTe and PdTe₂ at higher temperatures from the results of their high-temperature X-ray study; according to ref. 3, Fig. 2, the lattice parameters determined at 933 K decrease continuously between 50 and 66.7 at.% Te. However, a comparison with our Fig. 2 shows that, according to our data, only two of the seven data points in all are in the (PdTe + PdTe₂) two-phase field, of which one is very close to the phase boundary of PdTe₂. This leaves just one point at 60 at.% Te well within the heterogeneous region. Allowing some uncertainty in the composition of the samples and in the lattice parameter values themselves, the individual data points could be described equally well by alternative curves, which would result in constant values of the lattice parameters within the two-phase region. Yet the question remains, why the X-ray pattern of the sample with 60 at.% Te, which should contain the lines of both phases, was interpreted as single phase. In this connection it has to be pointed out that Kjekshus and Pearson [3] show the data point at 50 at.% Te within the phase PdTe, whereas it is clear from Fig. 2 that at 933 K the palladium-rich phase boundary is around 51 at.% Te. For the same reason an extension of the phase PdTe to tellurium contents as low as 48 at.% (as suggested in ref. 15) is ruled out. The peritectic reaction at 780 K can clearly be detected in the sample with 50.0 at.% Te. Furthermore, experience shows that the NiAs phases in

transition-metal-chalcogen systems are stable only at chalcogen compositions of more than 50 at.%, *i.e.* only with a certain amount of vacancies on the transition metal sublattice.

From the thermal arrests observed in the present investigation the existence of a compound Pd_3Te_2 was concluded, which had also been found and identified by Matković and Schubert and whose crystal structure had been reported as orthorhombic [19]. We found that the powder pattern of a sample with 40.0 at.% Te quenched from 750 K was in good agreement with that given in ref. 19, with the exception of a few additional very weak lines. These additional lines are not surprising, since in the heating curves of the same sample thermal effects at 741 and 776 K were observed, which indicate the presence of small amounts of Pd_9Te_4 and/or " $\text{Pd}_{2.5}\text{Te}$ ". Whether this is due to a small error in the composition of our sample or to some deviation of the phase from the stoichiometric composition cannot be decided here. The assumption by Matković and Schubert [19] that Pd_3Te_2 is formed by a peritectoid reaction at 733 K is not confirmed by the present results; Fig. 2 shows the peritectic formation of this phase at 780 K. Furthermore, one can see that the phase " Pd_2Te " which had been suggested by Grønvold and Røst [13] and which had been shown by Medvedeva *et al.* [2] to form peritectically at 863 K does not really exist at this stoichiometry.

In a separate publication Matković and Schubert [20] described the phase Pd_9Te_4 ; the reported homogeneity range (about 30.7 - 31.5 at.% Te at 773 K) is in reasonable agreement with the phase boundaries in Fig. 2 (about 30.2 to 31.0 at.% Te at the same temperature). However, these authors reported the observation of single-phase Pd_9Te_4 at 703 K and 31.0 at.% Te and of $(\text{Pd}_9\text{Te}_4 + \text{Pd}_3\text{Te}_2)$ at 32.0 at.% Te and 723 K. This is not compatible with the phase diagram in Fig. 2 which, however, in the region under discussion is based only on the DTA results. As an explanation one could assume deviations from the annealing temperatures given in ref. 20 (which would have to be of the order of 50 K). However it is conceivable that the powder pattern of " $\text{Pd}_{2.5}\text{Te}$ " is very similar to the extremely complicated one of Pd_9Te_4 . In addition, Matković and Schubert [20] reported that at 27 at.% Te and 683 K they found a phase "similar to $\text{Pd}_{20}\text{Te}_7$ but apparently of simpler structure". Whether this was possibly $\text{Pd}_{20}\text{Te}_7$ itself, a heterogeneous mixture with " $\text{Pd}_{2.5}\text{Te}$ " or single-phase " $\text{Pd}_{2.5}\text{Te}$ ", remains unclear.

The high-temperature ξ phase shown in Figs. 1 and 2 has not been mentioned explicitly by Schubert and coworkers [18 - 20]. However, in ref. 20 a phase " Pd_5Te_2 " is mentioned (which is apparently not identical with our " $\text{Pd}_{2.5}\text{Te}$ ") with a powder pattern similar to that of Pd_9Te_4 .

The crystal structure of $\text{Pd}_{20}\text{Te}_7$ was determined to be rhombohedral (isotypic to $\text{Pd}_{20}\text{Sb}_7$) by Wopersnow and Schubert [18]. The phase width determined by these authors at 973 K (26.0 - 26.9 at.% Te) agrees quite well with our DTA results. However, it is surprising that at the same temperature they found the lines of $\text{Pd}_{20}\text{Te}_7$ up to 28.0 at.% Te (*cf.* ref. 18, Table 2); according to our phase diagram this composition is well within the homogeneity range of the phase ξ .

As already mentioned earlier, the phase relationships between 26 and 31 at.% Te shown in Figs. 1 and 2 are based on the thermal effects observed in the DTA measurements and are in accord with the change in their intensity with composition. A systematic X-ray examination of this region, which would certainly be necessary, was not possible with our experimental equipment because of the very complicated powder patterns. However, the agreement of the present phase diagram with the results of Schubert and coworkers [18 - 20] is quite good. The question of the accurate position of Pd₄Te which is shown here as a line compound at 20 at.% Te has also been discussed above. It can be assumed that this phase decomposes in a peritectoid reaction between 1000 and 1050 K.

In conclusion, it is thought that the phase relationships in the Pd-Te system have been clarified with some reliability between 30 and 100 at.% Te. The portion between 25 and 30 at.% Te certainly needs additional experimental confirmation, especially by very careful X-ray investigations, whereas the composition range below 25 at.% Te remains more or less unclear. However, it is hoped that the experimental results reported here could be of help for future studies to present a reliable phase diagram for this part of the system also.

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