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Phase Relationships of Palladium Selenides

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The palladium – selenium system has been studied by differential thermal analysis, calorimetry, metallographic and X-ray diffraction techniques. The presence of the well-known phases $PdSe_2$, PdSe, $Pd_{17}Se_{15}$ and Pd_4Se is verified, and the additional phases Pd_7Se_4, Pd_3Se, $Pd_{3.5}Se$ and $Pd_{4.5}Se$ are characterized. All these phases are subject to decomposition on heating, and their decomposition temperatures are determined. A phase diagram of the palladium – selenium system is presented.

1. INTRODUCTION

Palladium selenides with compositions Pd_4Se and PdSe were first prepared by Roessler.[1] Thomassen[2] described the existence of a selenium-rich compound $PdSe_{2-x}$ with two-fold symmetry, while Wöhler, Ewald and Krall[3] prepared $PdSe_2$ with hexagonal symmetry. The existence of PdSe was later confirmed by Moser and Atynski.[4] As a result of an X-ray investigation of palladium chalcogenides Grønvold and Røst[5] confirmed the existence of Pd_4Se and $PdSe_2$. The crystal symmetry of the former was found to be tetragonal with lattice constants $a=5.2324$, $c=5.6470$ Å. The detailed structure[6] and the low-temperature thermodynamic properties[7] of Pd_4Se were reported in later papers. The structure of orthorhombic $PdSe_2$ ($a=5.741$, $b=5.866$, $c=7.691$ Å) was found[8] to be of a deformed pyrite-like type and isostructural with PdS_2.

In addition to these phases, $Pd_{1.1}Se$ with cubic structure ($a=10.604$ Å) was found, and the existence of a phase with composition around $Pd_{2.8}Se$ was indicated. Further structural work on the $Pd_{1.1}Se$-phase was carried out by Geller[9] who showed that the composition of the phase was $Pd_{17}Se_{15}$ and determined the atomic positions. The thermal expansion of $Pd_{17}Se_{15}$ was investigated by Kjekshus[10] by X-ray diffraction in the temperature range 20 to 650 °C. The melting temperature was reported to be 665 ± 15 °C. For PdSe the X-ray diffraction study by Schubert *et al.*[11] showed a tetragonal structure ($a=6.73$, $c=6.91$ Å) of the same type as for PdS. Raub *et al.*[12] found a phase which is superconducting below 0.66 K with assumed composition Pd_6Se or Pd_7Se. The X-ray diffraction pattern was very diffuse and prevented further characterization of the phase.

The present investigation was undertaken in order to characterize the occurring phases in more detail. A further scope was to determine the temperature-composition phase diagram of the palladium selenium system. After completion of this paper the crystal structural determination of Pd_7Se_4 by Matković and Schubert[13] has become known to us. In their paper the existence of the phases $Pd_{3.5}Se$ and $\sim Pd_3Se$ is also reported.

2. EXPERIMENTAL

The palladium used for most of the preparations was a 99.99 mass per cent pure product from Balzer, Switzerland, and the selenium was a 99.998 mass per cent pure product from Boliden Gruvaktiebolag, Sweden. The alloys were prepared by heating the desired amounts of the two elements to fusion in evacuated and sealed silica glass tubes. They were then crushed, annealed at various temperatures and finally quenched in water. The earlier prepared Pd_4Se sample was used for calorimetric determinations without and with addition of selenium or palladium.*

* It was then discovered that the calorimetric Pd_4S and Pd_4Se samples unfortunately had been interchanged. The earlier reported[7] molar thermodynamic values are thus in error. They should be corrected by multiplication by the ratio of the molar masses, 1.1025 and 0.90707 for Pd_4S and Pd_4Se, respectively.

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The powdered samples were examined in focusing X-ray diffraction cameras of the Guinier type, using $CuK\alpha_1$-radiation ($\lambda = 1.5405$ Å) and silicon as a calibration standard ($a = 5.43054$ Å[14] at 20 °C). X-Ray high temperature investigations were carried out in a 19 cm camera. Single crystals were examined in Weissenberg-type cameras.

The samples were also investigated by metallographic methods. Polished surfaces were examined in polarized light. Hot aqua regia was used for etching the surfaces.

Densities were measured by a vacuum pycnometric method using kerosene as a displacement liquid. Differential thermal analysis (DTA) was carried out in a "Mettler Recording Thermoanalyzer". About 50 mg of the samples were enclosed in evacuated silica ampoules. The most suitable heating speed was found to be 2 K per min. Palladium was used as a reference metal. A previously described adiabatic shield calorimeter[15] was used for heat capacity and transitional enthalpy determinations on $Pd_{3.5}Se$, $Pd_{3.7}Se$, $Pd_{4.0}Se$ and $Pd_{4.2}Se$. Approximate values for the transitional enthalpies are presented here, while heat capacity results and integrated thermodynamic properties will be reported in another paper.

3. RESULTS AND DISCUSSION

a. Phase analysis

A series of palladium selenide samples were annealed at different temperatures. After quenching of the alloys, X-ray powder photographs were taken. In some cases it was necessary to grind the samples and reanneal them in order to obtain better equilibration. Results of the X-ray investigation are presented in Table 1, from which it appears that eight binary solid phases were found in the Pd–Se system. They are: $PdSe_2$, PdSe, $Pd_{17}Se_{15}$-($Pd_{1.13}Se$), Pd_7Se_4($Pd_{1.75}Se$), Pd_3Se, Pd_7Se_2-($Pd_{3.5}Se$), Pd_4Se and $Pd_{4.5}Se$.

$PdSe_2$ was found to be the most selenium-rich phase. Further addition of selenium resulted in the formation of a selenium-rich liquid above 220 °C. As regards PdSe, X-ray powder patterns of this phase were obtained for samples annealed up to 590 °C. For samples annealed at 650 °C and quenched from this temperature, a mixture of $PdSe_2$ and $Pd_{17}Se_{15}$ was obtained. PdSe is formed rather slowly and annealing for several days was necessary to get a pure X-ray powder pattern.

Some single crystals of PdSe were obtained, and by means of Weissenberg photographs the tetragonal symmetry of the structure was confirmed. The lattice constants were determined to be $a = 6.733 \pm 0.001$ Å and $c = 6.918 \pm 0.001$ Å from powder data, in agreement with the results by Schubert *et al.*[11]

The phase $Pd_{17}Se_{15}$ with a cubic type structure has been described earlier. Its decomposition temperature was found to be 680 °C. On further increase in palladium content the X-ray reflections from $Pd_{17}Se_{15}$ decrease rapidly in intensity and in the photograph of a sample $Pd_{1.7}Se$ (63 atomic % Pd) they are almost extinct. The major phase now present appears to have composition between $Pd_{1.70}Se$ and $Pd_{1.80}Se$, as the X-ray photograph of the latter contains additional reflections from a

Table 1. Phases observed by X-ray powder diffraction of quenched samples.

Atomic % Pd	Pd_xSe x	Annealing temp. °C	Phases observed	Atomic % Pd	Pd_xSe x	Annealing temp. °C	Phases observed
28.6	0.40	440	$Se + PdSe_2$	74.4	2.90	350	$Pd_7Se_4 + Pd_3Se$
33.3	0.50	440	$PdSe_2$	75.0	3.00	350	Pd_3Se
35.7	0.56	570	$PdSe_2 + PdSe$	75.8	3.13	350	$Pd_3Se + Pd_{3.5}Se$
45.5	0.91	570	$PdSe_2 + PdSe$	77.4	3.42	350	$Pd_3Se + Pd_{3.5}Se$
50.0	1.00	590	PdSe	77.8	3.50	350	$Pd_{3.5}Se$
50.0	1.00	650	$PdSe_2 + Pd_{17}Se_{15}$	78.7	3.70	350	$Pd_{3.5}Se + Pd_4Se$
53.1	1.13	350	$Pd_{17}Se_{15}$	78.7	3.70	580	$Pd_{3.5}Se$
60.0	1.50	350	$Pd_{17}Se_{15} + Pd_7Se_4$	79.7	3.93	500	$Pd_{3.5}Se + Pd_4Se$
63.0	1.70	350	$Pd_{17}Se_{15} + Pd_7Se_4$	80.0	4.00	590	$Pd_{3.5}Se + Pd_{4.5}Se$
63.6	1.75	350	Pd_7Se_4	80.0	4.00	500	Pd_4Se
64.3	1.80	350	$Pd_7Se_4 + Pd_3Se$	81.6	4.43	500	$Pd_4Se + Pd_{4.5}Se$
66.7	2.0	420	$Pd_{17}Se_{15} + Pd_3Se$	82.14	4.60	300	$Pd_4Se + Pd$
66.7	2.0	400	$Pd_7Se_4 + Pd_3Se$	85.50	6.51	500	$Pd_{4.5}Se + Pd$

phase still richer in palladium. Combination of unit cell dimension and density determinations leads to the stoichiometry Pd_7Se_4($Pd_{1.75}Se$), which corresponds to 63.6 atomic % Pd.

Reflections from Pd_7Se_4 can still be observed in a sample with 74.4 atomic % Pd, whereas one with 75.0 atomic % Pd seems to be a pure phase. A sample with 75.8 atomic % Pd shows additional X-ray reflections from a phase still richer in palladium. Metallographic examinations confirm that the phase composition is near to Pd_3Se.

The X-ray and metallographic investigations show that the composition of the next phase is near $Pd_{3.5}Se$ (77.8 atomic % Pd). This phase forms twinned crystals of monoclinic symmetry.

X-Ray powder patterns of Pd_4Se were obtained for samples annealed at 500 °C and lower temperatures. Rather long annealing time is necessary in order to obtain the Pd_4Se phase in pure state. Further increase of the palladium content causes the X-ray reflections from Pd_4Se to decrease rapidly in intensity and they are missing in a sample with 81.8 % atomic % Pd ($Pd_{4.5}Se$), which appears to be the most palladium-rich intermediate phase. For samples still richer in metal, reflections from palladium appear in the X-ray photographs.

The photographs of quenched $Pd_{4.5}Se$ contain only a few very broad and diffuse lines. Metallographic examinations of several metal-rich samples confirm the existence of a phase having a composition around $Pd_{4.5}Se$. In alloys annealed above about 400 °C the crystals show a characteristic lamellar structure when examined in polarized light. X-Ray high temperature photographs show sharp reflections from the phase $Pd_{4.5}Se$ when taken above 400 °C (see below). The positions of the broad lines obtained after quenching correspond fairly well to the strongest reflections in the high temperature exposures. After prolonged annealing of $Pd_{4.5}Se$ at 200 and 300 °C reflections from Pd_4Se and Pd are found in X-ray powder photographs. It therefore seems likely that $Pd_{4.5}Se$ is a high temperature phase. According to the high temperature X-ray investigation, the $Pd_{4.5}Se$-phase exists at least to a temperature of 600 °C. The powder pattern of the high temperature phase is also presented below.

b. DTA, calorimetric results and phase diagram

The results of the differential thermal investigations are given in Fig. 1. As mentioned above, some

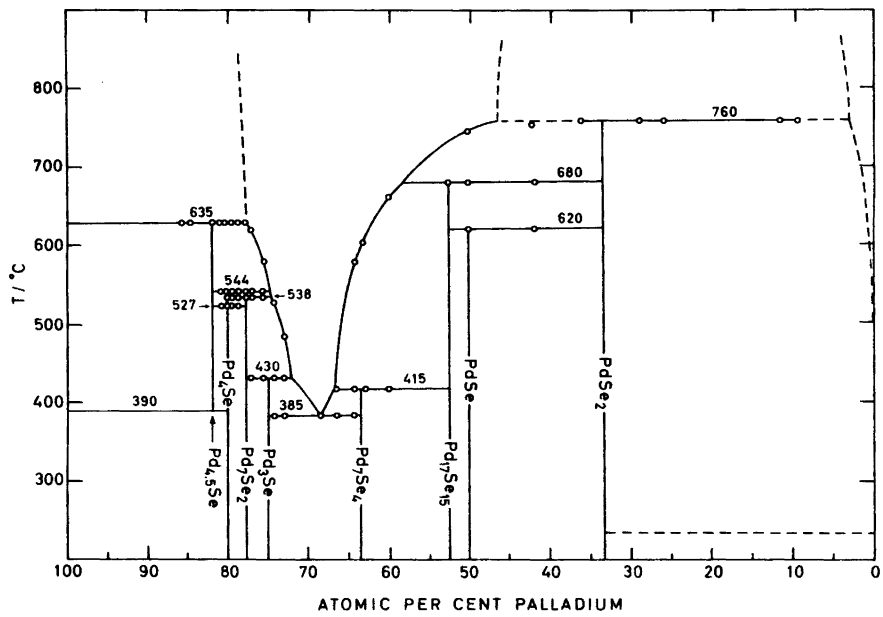

Fig. 1. Temperature-composition phase diagram of the palladium selenium system.

of the phases need prolonged annealing time in order to be formed. Accordingly, the results of the DTA analysis depend to some extent on the heat treatment of the samples. The data given in Fig. 1 refer, however, to transitions approaching equilibrium conditions.

The selenium-rich samples show a thermal arrest at 760 °C. The effect seems to have a maximum near the composition $PdSe_2$, and obviously corresponds to the decomposition of this phase. A rough extrapolation of the thermal effect indicates an extension from about 5 to 45 atomic % palladium. When $PdSe_2$ is heated in evacuated ampoules to temperatures above 760 °C, the samples are clearly melted. It seems therefore likely that two liquid phases (containing approximately 5 and 45 atomic % Pd, respectively) exist in equilibrium just above 760 °C, see Fig. 1.

The thermal arrest at 620 °C refers to the decomposition of PdSe. Unless the samples were annealed below 620 °C, this thermal effect was missing. This is in agreement with the results of the X-ray examination – showing that PdSe is formed very slowly. The decomposition of PdSe is of the peritectoid type, and results in the formation of two solid phases, $PdSe_2$ and $Pd_{17}Se_{15}$. The phases $Pd_{17}Se_{15}$ transforms peritectically at 680 °C into $PdSe_2$ and a melt richer in palladium. The Pd_7Se_4-phase decomposes peritectically at 415 °C, whereby $Pd_{17}Se_{15}$ and a melt are formed. The formation of Pd_7Se_4 during cooling is considerably delayed, and a metastable eutectic consisting of Pd_3Se and $Pd_{17}Se_{15}$ is observed for incompletely equilibrated samples. The metastable eutectic melts at 375 °C. Both X-ray and DTA experiments show that this unstable eutectic vanishes in annealed samples. The corresponding thermal effects are not indicated in Fig. 1. There only the stable eutectic, consisting of Pd_7Se_4 and Pd_3Se with estimated gross composition 69 atomic % Pd and melting temperature 385 °C is shown. The Pd_3Se-phase decomposes peritectically at 430 °C, whereas the $Pd_{3.5}Se$-phase seems to be stable to 538 °C. Two additional thermal transitions were observed near the latter temperature, one at 527 °C, and the other at 544 °C.

In order to clarify the phase relationships in this region, heat capacity measurements were carried out. The transformation temperatures were determined to be 527, 538 and 544 °C, and the integrated enthalpies of transformation are summarized in Table 2. The effect at 538 °C obviously corresponds to the decomposition of the $Pd_{3.5}Se$-phase on heating. The steep drop in transformational enthalpy with increasing palladium content makes us suggest that it ought to be absent in the truly equilibrated Pd_4Se-phase. Similarly, the comparatively small value for the 527 °C transition in Pd_4Se [600 J mol^{-1} of (1/5) Pd_4Se] is presumably also due to incomplete equilibration. Thus, the 527 °C transition should probably be related to a structural change in the Pd_4Se-phase. This view is further supported by the DTA results of well annealed samples of $Pd_{4.5}Se$, which show complete absence of all three transitions in the range 527 to 544 °C. The transition at 544 °C is also characteristic of the Pd_4Se-phase, which thus appears to undergo a polymorphic change at 527 °C and decomposes peritectically at 544 °C into the $Pd_{4.5}Se$-phase and a liquid of approximate composition Pd_3Se.

Table 2. Transformation enthalpies of palladium selenides (J/mol).

Sample composition	Transformation temperature			
	527 °C	538 °C	544 °C	635 °C
(1/4.5)$Pd_{3.5}Se$	10	3350	1100	250
(1/4.7)$Pd_{3.7}Se$	370	2200	1350	1800
(1/5)Pd_4Se	600	600	1350	–
(1/5.2)$Pd_{4.2}Se$	700	50	1100	5400

According to the heat-capacity measurements on $Pd_{4.2}Se$ the eutectoid formation of $Pd_{4.5}Se$ takes place near 390 °C whereas the phase decomposes peritectically at 635 °C. The latter transition temperature was also clearly observed by the DTA method. The maximum of this effect seems to be near the composition $Pd_{4.5}Se$. The transition of $Pd_{4.5}Se$ into palladium and a melt has also been confirmed by metallographic examination of quenched samples.

c. Structural characterization of some phases

Structural data of the phases Pd_3Se, $Pd_{3.5}Se$ and $Pd_{4.5}Se$ have been only sparingly presented in the literature. The front reflections in the X-ray powder photographs of these phases and the newly described Pd_7Se_4-phase[13] are given in Table 3.

Pd_7Se_4 ($Pd_{1.75}Se$). After two weeks annealing at 405 °C some crystals could be picked out of a

Table 3. X-Ray powder data (spacings in Å) of Pd_7Se_4, Pd_3Se and Pd_7Se_2 after quenching from about 400 °C, and high temperature data of $Pd_{4.5}Se$ at 500 °C. The intensities are given as very weak (vw), weak (w), medium (m), strong (s) and very strong (vs).

Pd_7Se_4			Pd_3Se		Pd_7Se_2			$Pd_{4.5}Se$	
d	*hkl*	I_0	*d*	I_0	*d*	*hkl*	I_0	*d*	I_0
3.915	111	w	3.085	vw	2.744	002	vw	2.297	s
3.696	102	w	2.578	w	2.575	$\bar{1}20$	w	2.232	s
3.433	020	vw	2.491	m	2.438	202	m	1.606	w
3.256	112	vw	2.459	s	2.397	112	s	1.302	m
3.041	013	vw	2.426	s	2.383	$\bar{3}11$	vs	1.290	w
2.895	120	m	2.393	s	2.365	400	v	1.204	m
2.869	103	vw	2.363	s	2.346	121	v	1.117	w
2.847	022	w	2.305	w	2.335	$\bar{1}12$	w	1.004	w
2.785	121	vs	2.260	s	2.329	220	w		
2.646	113	v	2.236	s	2.316	$\bar{1}21$	w		
2.385	014	w	2.229	s	2.219	401	s		
2.379	202	w	2.203	s	2.169	221	s		
2.299	104	m	2.163	vw	2.160	410	m		
2.247	212	w	2.149	w	2.124	$\bar{2}21$	s		
2.236	031	m	2.136	vw	2.049	411	vw		
2.202	123	m	2.103	w	2.039	320	m		
2.180	114	w	2.091	s	1.972	$\bar{4}11$	w		
2.119	220	w	2.083	w	1.862	$\bar{1}22$	vw		
2.107	203	vw	2.056	m	1.847	402	w		
2.089	032	w			1.707	421	vw		
2.074	221	vs			1.697	931	m		
2.064	131	s			1.686	$\bar{1}13$	m		
2.045	024	s			1.665	$\bar{1}31$	m		
2.016	213	vs			1.657	213	w		

crushed sample. Weissenberg photographs showed that the crystal lattice is of an orthorhombic, primitive type. The following lattice constants were determined by use of Guinier powder data which were refined by a least squares method:

$a = 5.381$ Å, $b = 6.873$ Å, $c = 10.172$ Å.

The estimated errors are about 0.02 %. These values are slightly higher than those found by Matković and Schubert[13] ($a = 6.863$, $b = 5.375$, $c = 10.162$ Å) who determined the atomic arrangement. The density of $Pd_{1.75}Se$ was determined to be 9.39 ± 0.05 g cm^{-3}. Within experimental errors the density corresponds to a unit cell content of 14 Pd and 8 Se atoms. The stoichiometric composition may be given as Pd_7Se_4.

Pd_3Se. We have not yet succeeded in indexing the powder pattern of Pd_3Se. The observed front reflections are presented in Table 3.

Pd_7Se_2 ($Pd_{3.5}Se$). In a sample which had been annealed for several days some twinned crystals were found. The crystals were examined in Weissenberg cameras, and the symmetry was found to be of a monoclinic type. The indexing refers to the following lattice constants: $a = 9.462$ Å, $b = 5.354$ Å, $c = 5.501$ Å and the angle $\beta = 86.50°$. The lattice constant values have been refined by least squares treatment of the X-ray powder data and the estimated errors are about 0.02 %. The density of $Pd_{3.5}Se$ was found to be (10.78 ± 0.06 g cm^{-3}). This is in accordance with a unit cell content of 14 Pd and 4 Se atoms. Thus, the stoichiometric composition equals Pd_7Se_2.

$Pd_{4.5}Se$. As mentioned above, sharp X-ray reflections of the high temperature phase can be obtained when exposed above 400 °C. We have, however, not yet succeeded in indexing the powder pattern. The front reflections of a high temperature X-ray exposure are given in Table 3.

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