phys. stat. sol. (a) 78, 137 (1983)

Subject classification: 1.2 and 14.2; 21; 21.1

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The Pd-Pt-H System: Phase Transformations at High Pressure and Superconductivity

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Studies on crystal structure and superconducting properties of hydrogen solid solutions in the Pd–Pt alloys with 2.8, 10, 15, 25, 40, and 60 at% Pt are presented. Palladium alloying with platinum is shown to decrease the maximum values of superconducting transition temperature attainable at hydrogenation. The phenomenon of dissolution to phases rich and poor in platinum is revealed for the solutions based on the alloys containing 15 to 60 at% Pt. Hydrogenation of the samples is performed at hydrogen pressures to 6.5 GPa and temperatures to 350 °C.

Изучена кристаллическая структура и сверхпроводящие свойства твердых растворов водорода в сплавах Pd-Pt с 2,8; 10; 15; 25; 40 и 60 at% Pt. Показано, что легирование палладия платиной приводит к понижению максимально достижимых при гидрировании значений температуры перехода в сверхпроводящее состояние. Обнаружено явление распада растворов на базе сплавов, содержащих от 15 до 60 at% Pt, на обогащенную и обедненную платиной фазы. Гидрирование образцов проводилось при давлениях водорода до 6,5 GPa и температурах до 350 °C.

1. Introduction

According to [1] the $Pd_{97.2}Pt_{2.8}$–H solution charged with hydrogen up to a hydrogen-to-metal atomic ratio $n = 0.93$ at high pressure and room temperature possessed a superconducting transition temperature $T_k = 8.9$ K that is approximately 4 K higher than the T_k-value for the Pd–H solution with the same concentration n. Hydrogen implantation into Pd–Pt alloys containing up to 30 at% Pt also resulted in Pd–Pt–H samples with high T_k-values exceeding the maximum value of $T_k \approx 8.8$ K reached in the case of Pd–H solutions [2]. Thus, from the viewpoint of superconducting properties the Pd–Pt–H is of indubitable interest and so it was worth studying in detail.

We considered researches of the Pd–Pt–H system the more urgent, as among the hydrogen solutions on the base of palladium alloys we had studied recently (Pd–Cu–H, Pd–Ag–H [3] and Pd–Ni–H [4]) no superconductors with T_k-values exceeding those in the Pd–H solutions were observed though, according to the data in literature, hydrogenation of Pd–Cu and Pd–Ag alloys by implantation [2] and Pd–Ni alloys at high hydrogen pressure and room temperature [5, 6] converted them into such superconductors. On the other hand, it has been found that just in these solutions at high hydrogen pressure and elevated ($\geqq 250$ °C) temperature there occur phase transformations which were never observed earlier at hydrogenating alloys constituting continuous substitution solutions, i.e. the formation of the tetragonal phase of the $Pd_{60}Ciu_{40}$–H solution being, most likely, associated with atomic ordering of its metallic

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sublattice [7] and dissolution of Pd–Ni–H solutions into the phases rich and poor in nickel [4]. Similar phenomena having been feasible in the Pd–Pt–H system, the structural studies were of interest. The alloys containing 2.8, 10, 15, 25, 40, and 60 at% Pt were studied in the present work.

2. Experimental

The ingots were melted from electrolytical palladium and platinum in an induction furnace in vacuum. After 10 h homogenization in vacuum at 1000 °C and water-quenching these ingots were rolled to strips ≈ 0.1 mm thick, then subjected to stress-relief annealing in vacuum at 1000 °C for 15 min, and again quenched in water. Chemical analysis of the strips has demonstrated their compositions to coincide with the calculated ones to an accuracy of 1% of the platinum content. The specimens were cut out of these polycrystalline strips.

Hydrogen compression was performed in "toroid"-type chambers by the method suggested in [8] (a detailed description of the method is given in [9]). The measuring error in the pressure was ± 0.1 GPa at $P_{H_2} \leqq 2$ GPa and increased to ± 0.3 GPa at $P_{H_2} = 6.7$ GPa. The temperature was measured accurately to $\pm$ 10 K with a chromel–alumel thermocouple insulated against exposure to hydrogen. The electrical resistance of the samples under high pressure was determined by a conventional four-probe technique, the sample dimensions being $5 \times 1 \times 0.1$ mm^3. During the process of measuring the temperature was kept constant to an accuracy of $\pm$ 1 K.

The Pd–Pt–H samples to be studied at normal pressure were produced by exposing the initial Pd–Pt alloys at fixed values of hydrogen pressure and temperature. The high-pressure chamber was then rapidly cooled down to ≈ -120 °C, the pressure was lowered, and the samples were taken out of the chamber and placed for storage in liquid nitrogen to prevent hydrogen losses (no noticeable losses of hydrogen from the samples thus prepared were detected at normal pressure and $T \leqq -120$ °C). The hydrogen concentration of the samples was measured to an accuracy of 5%; the technique is described in detail in [7]. An X-ray study was carried out by a phototechnique using a DRON-2,0 diffractometer with FeK$_\alpha$ radiation. The samples were in the form of discs 5 mm in diameter. The T_k-values were determined by the induction method at $T \geqq 2$ K.

3. Results and Discussion

Hydrogen forms with palladium wide ranges of interstitial solid solutions on the base of a f.c.c. metal sublattice. The T–c diagram of the Pd–H system reveals a cupola of separation into the two isomorphous phases, γ_1 and γ_2, the parameters of the critical point being $T_{cr} = 292$ °C, $(P_{H_2})_{cr} = 1.97$ MPa [10]. Platinum alloying of palladium decreases T_{cr} and increases $(P_{H_2})_{cr}$. The critical temperature drops below 25 °C at platinum content of ≈ 14 at%, and hydrogen solubility in the alloys with a higher platinum content is a continuous function of pressure at room temperature [11]. In [12] the hydrogen solubility in Pd–Pt alloys and the behaviour of their electroresistance have been studied in detail at room temperature and hydrogen pressures up to 2.4 GPa. It was found that at any given value of P_{H_2} the hydrogen solubility in the alloys decreases monotonously with increasing platinum content, but distinct supercritical anomalies on the $R(P_{H_2})$ curves are observed even for the alloy containing 50 at% Pt. To begin with, we decided to see whether the Pd–Pt–H system experiences any new phase transformations at elevated temperature.

3.1 Electroresistance of the Pd–Pt alloys under high hydrogen pressure

Fig. 1 exhibits the resistance isotherms for the $Pd_{75}Pt_{25}$ and $Pd_{40}Pt_{60}$ alloys in an inert medium (petrol) and in hydrogen at 200 °C. The curves are obtained in the process of a stepwise increase in pressure. After a pressure change in hydrogen atmosphere a temporal resistance drift caused by the diffusion nature of the formation of Pd–Pt–H solid solutions was observed. The samples were exposed at each fixed P_{H_2}-value up to the end of the drift going on for $\Delta\tau \approx 15$ min in the case of the $Pd_{75}Pt_{25}$ alloy and for $\Delta\tau \approx 40$ min in the case of the $Pd_{40}Pt_{60}$ alloy, the final value of R being plotted in the figure.

As seen from Fig. 1, the $R(P_{H_2})$ curves deviate from the similar curves obtained at measurements in an inert medium that points to a considerable hydrogen solubility in the alloys under experimental conditions. The curve $R(P_{H_2})$ for the $Pd_{75}Pt_{25}$ alloy demonstrates a distinct supercritical anomaly at $P_{H_2} \approx 0.5$ GPa. The shape of this curve and the location of the supercritical anomaly are in line with the data of [12].

At $T \geqq 250$ °C the behaviour of the sample resistance in hydrogen atmosphere is different: there occurs a prolonged drift of the resistance at fixed values of T and P_{H_2}. Typical curves $R(\tau)$ at 350 °C for the $Pd_{75}Pt_{25}$ and $Pd_{40}Pt_{60}$ alloys are presented in Fig. 2. The curves were obtained as follows. The samples were pre-exposed at $P_{H_2} = 6.7$ GPa and $T = 200$ °C up to the termination of the temporal resistance drift, and the temperature was then increased to 350 °C in a jump-like manner. As seen from Fig. 2, a pronounced drift of the resistance of the $Pd_{75}Pt_{25}$ sample went on for ≈ 1 h that exceeds considerably $\Delta\tau \approx 15$ min required for its termination even at 200 °C (though the kinetics of hydrogenation of this alloy should be accelerated by temperature since $P_{H_2} = 6.7$ GPa and $T \geqq 200$ °C are far from the critical values). The drift of the resistance of the $Pd_{40}Pt_{60}$ sample did not stop actually after 10 h. It is worth noting that the resistance changes shown in Fig. 2 are found to be irreversible. For instance, the resistance of the samples at 200 °C after pre-exposure at 350 °C for 10 h proved to be lower than that before this procedure, its decrease being approximately the same as that occurring at 350 °C (half-filled symbols in Fig. 1).

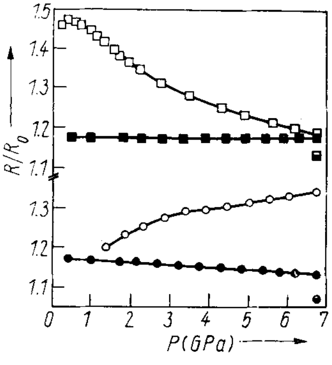

Fig. 1

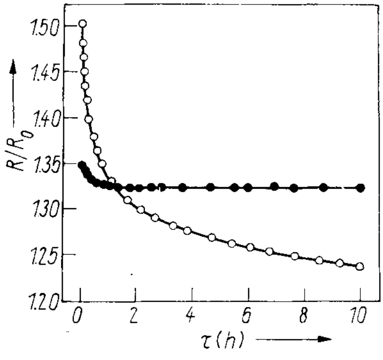

Fig. 2

Fig. 1. Electrical resistance isotherms at 200 °C for the $Pd_{75}Pt_{25}$ (squares) and $Pd_{40}Pt_{60}$ (circles) alloys in an inert medium (■, ●) and in hydrogen (□, ○) as well as in hydrogen after 10 h pre-exposure at $P_{H_2} = 6.7$ GPa and 350 °C (half-filled symbols). R_0 is the resistance of the samples at atmospheric pressure and room temperature

Fig. 2. Time dependences of electroresistance of the $Pd_{75}Pt_{25}$ (●) and $Pd_{40}Pt_{60}$ (○) alloys at 350 °C and $P_{H_2} = 6.7$ GPa. R_0 as in Fig. 1

Thus, the electroresistance behaviour demonstrates that at high hydrogen pressure and $T \geqq 250$ °C irreversible phase transformations occur in the $Pd_{75}Pt_{25}$–H and $Pd_{40}Pt_{60}$–H solutions. Note that $T^* \approx 250$ °C, above which these transformations were observed to start, is close to the temperatures of the onset of irreversible phase transformations in the Pd–Cu–H [7] and Pd–Ni–H [4] systems. Just as in those systems, the T^*-magnitude is likely to be determined by kinetic reasons.

3.2 *X-ray data*

Two series of measurements were carried out on the samples obtained by exposing to $P_{H_2} = 2$ and 6.5 GPa. In its turn, at each of these pressures the samples were obtained by the two different methods: by exposing for 24 h at 200 °C (i.e. below $T^* \approx 250$ °C) and for 24 h at 350 °C and then for another 24 h at 200 °C (a comparison of the data for these samples made it possible to find out whether any irreversible changes took place in the samples under study in the process of their exposing to 350 °C).

All the Pd–Pt–H samples hydrogenated at 200 °C constituted single-phase solid solutions with a f.c.c. metal sublattice. The parameters of f.c.c. sublattices of such solutions (further on being denoted as a^{200}) synthesized at $P_{H_2} = 2$ GPa are shown in Fig. 3 by open circles. To demonstrate a possible spread in the experimental data, for some of the alloys there are given two a^{200}-values obtained on the samples hydrogenated under the same conditions but in different experiments. The a^{200}-values exhibited in

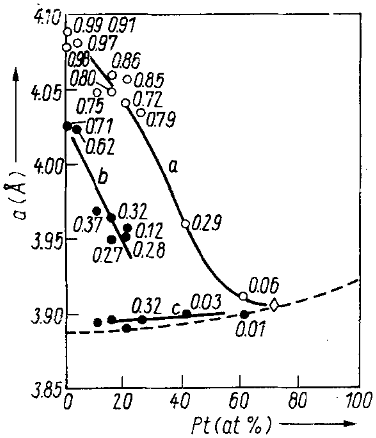

Fig. 3

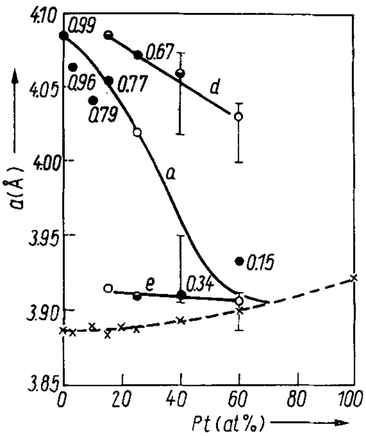

Fig. 4

Fig. 3. Parameters of the f.c.c. metal lattice for the Pd–Pt–H solutions at $T = -190$ °C and atmospheric pressure. Dashed line is for the initial Pd–Pt samples (curve from Fig. 4), ○ the samples after 24 h exposure at 200 °C and $P_{H_2} = 2$ GPa (curve a), ● the same samples after partial release of hydrogen under normal conditions (curves b and c), ◇ see text. Figures indicate the hydrogen content of the samples

Fig. 4. Parameters of the f.c.c. metal lattices for the Pd–Pt–H samples produced by 24 h exposure at 200 °C and $P_{H_2} = 2$ GPa after 24 h pre-exposure at 350 °C and $P_{H_2} = 2$ GPa. Parameters for the phases of the multi-phase samples are denoted by symbols ●, ◒, and ○ in the sequence of their decreasing content in the samples; × parameters for the initial Pd–Pt samples. Curves d and e–see text. Curve a is taken from Fig. 3. In the case of multi-phase samples the average hydrogen concentration is indicated

Fig. 3 agree satisfactorily with the dependences $a(n)$ derived in [12] for the Pd–Pt–H solid solutions and, as a function of the platinum content of the Pd–Pt alloys, lie on a fairly smooth curve a. The curve should close up with the similar curve for the Pd–Pt alloys with no hydrogen (dashed line in Fig. 3) and approximately for the $Pd_{30}Pt_{70}$ alloy (◇ in Fig. 3), since according to [12] the hydrogen solubility in this alloy is negligibly small even at $P_{H_2} = 2.4$ GPa and room temperature.

The data for the Pd–Pt–H samples hydrogenated at $P_{H_2} = 2$ GPa and $T = 200$ °C after preliminary exposure to 350 °C are listed in Fig. 4. As is seen from the comparison with the data presented in Fig. 3, in the case of Pd and $Pd_{97.2}Pt_{2.8}$ and $Pd_{90}Pt_{10}$ alloys an exposure to 350 °C resulted in no appreciable changes neither in the a^{200}-values nor in the hydrogen solubility. The samples with $\geqq 15$ at% Pt proved to consist of a mixture of phases with f.c.c. metal sublattices. The most probable transformation occurring in these solutions at 350 °C is believed to be, just as in the case of Pd–Ni–H solutions [4], their dissolution in phases rich and poor in palladium.

The character of the dissolution varies with the platinum content of the alloys. The $Pd_{85}Pt_{15}$–H and $Pd_{75}Pt_{25}$–H solutions experience a two-phase dissolution. Their X-ray photographs display sharply defined lines of three phases. One of them represent a residue of a solid solution, $Pd_{85}Pt_{15}$–H or $Pd_{75}Pt_{25}$–H, respectively, which had not enough time to transform to a new phase state during the exposure at $P_{H_2} = 2$ GPa and $T = 350$ °C (the a-values for these phases fall on curve a in Fig. 4). Parameters a of the other two phases correspond to a^{200}-parameters for the hydrogen solutions in nearly pure palladium (corresponding points are connected with curve d in Fig. 4) and in Pd–Pt alloy containing ≈ 70 to 80 at% Pt (the points are linked with curve e). At dissolution of the alloys with 40 and 60 at% Pt a significant role seems to be played by processes of a continuous precipitation, which is, in particular, evidenced by the great width of the lines of palladium-rich and palladium-poor phases in the diffraction patterns for the dissoluted samples (Fig. 4 demonstrates uncertainties in the a-values for the phases occurring due to the smearing of the diffraction lines). It is of interest that the a-parameter of the basic phase contained in the partly dissoluted $Pd_{40}Pt_{60}$–H solution (● in Fig. 4) is noticeably greater than the a^{200}-parameter of the $Pd_{40}Pt_{60}$ solution and conforms to the a^{200}-parameter for the solution on the base of the alloy with ≈ 45 at% Pt. This can be explained by the fact that in the process of precipitation of particles of a new phase out of the $Pd_{40}Pt_{60}$–H solution matrix its rather homogeneous (the diffraction lines remain relatively sharp) depletion in platinum occurs (in our case down to ≈ 45 at% Pt).

The assumption that the dissolution of the alloys containing $\geqq 15$ at% Pt into phases rich and poor in platinum takes place at $P_{H_2} = 2$ GPa and $T = 350$ °C is also confirmed by the results of the investigation of such solutions having lost a certain amount of hydrogen during a several days exposure in silicon under normal conditions (a noticeable release of hydrogen ceased after several hours). The phase compositions of the samples were, of course, far from equilibrium for normal conditions, but their diffraction patterns possessed a good reproducibility. The X-ray data for the samples hydrogenated at $P_{H_2} = 2$ GPa and $T = 200$ °C are presented in Fig. 3 (closed circles). The samples based on palladium and the $Pd_{97.2}Pt_{2.8}$ alloy are single-phase ones. Samples with platinum content from 10 to ≈ 25 at% consist of a mixture of two phases, rich and poor in hydrogen. A very small amount of hydrogen being left in the samples based on the $Pd_{60}Pt_{40}$ and $Pd_{40}Pt_{60}$ alloys, their parameters differ weakly from those of the initial alloys (with no hydrogen).

Data for the samples hydrogenated at $P_{H_2} = 2$ GPa and $T = 200$ °C after being pre-exposed to 350 °C are given in Fig. 5. As is seen from the figure, the constitution of the samples after a partial hydrogen release under normal conditions agrees with

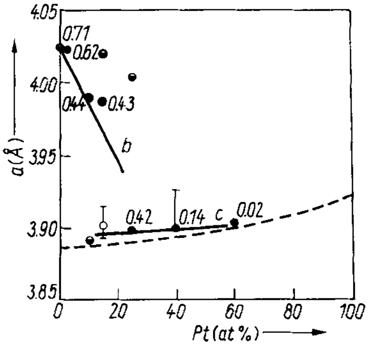

Fig. 5. Parameters of the f.c.c. metal lattices for the same samples as in Fig. 4 but after a partial hydrogen release under normal conditions. Curves b and c are taken from Fig. 3. Symbols as in Fig. 4

the conclusion drawn when discussing Fig. 4 that the samples based on the alloys with ≥ 15 at% Pt contain phases rich and poor in platinum. Most clearly Fig. 5 demonstrates the presence of platinum-poor phases in the case of the $Pd_{85}Pt_{15}$ and $Pd_{75}Pt_{25}$ alloys (compare the a-values indicated by half-filled circles with curve b). Thus, one may ascertain that in the Pd–Pt–H solid solutions the values of parameters of the crystal lattices of precipitations of the platinum-rich and platinum-poor phases change after a partial hydrogen release from the sample in just the same manner as the values of the parameters of bulk samples with the corresponding platinum contents.

Almost all the facts said about the processes occurring in the Pd–Pt–H solutions at $P_{H_2} = 2$ GPa are also valid if a similar sample treatment is performed at $P_{H_2} = 6.5$ GPa. The X-ray data for such samples are presented in Fig. 6 to 8 which

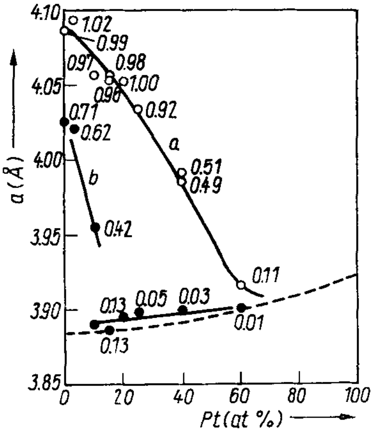

Fig. 6

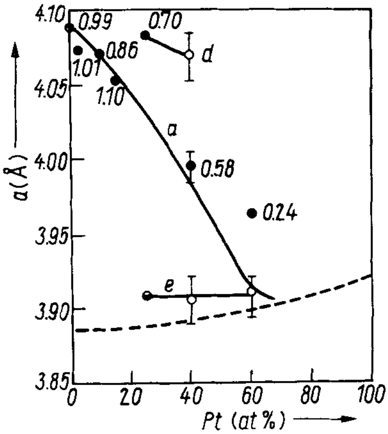

Fig. 7

Fig. 6. The analogue of Fig. 3, but for the samples obtained by 24 h exposure at 200 °C and $P_{H_2} = 6.5$ GPa. (Curve c is the lower solid line)

Fig. 7. The analogue of Fig. 4, but for the samples obtained by 24 h exposure at 200 °C and $P_{H_2} = 6.5$ GPa after 24 h pre-exposure at 350 °C and $P_{H_2} = 6.5$ GPa. Curve a is taken from Fig. 6

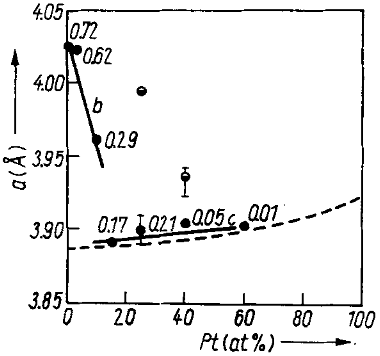

Fig. 8. The analogue of Fig. 5, except that the samples were the same as in Fig. 7 but after a partial hydrogen release under normal conditions. Curves b and c are taken from Fig. 6

are the analogues of Fig. 3, to 5, respectively. In fact, there is only one principle difference between these two groups of figures, i.e. at $P_{H_2} = 6.5$ GPa a 24 h exposure at 350 °C results in no detectable dissolution of the $Pd_{85}Pt_{15}$–H solution into the phases rich and poor in platinum. It is interesting to note that under the same conditions the $Pd_{75}Pt_{25}$–H solutions manage, according to the X-ray data, to dissolute completely (see Fig. 7), the dissolution resulting in a decreasing hydrogen solubility in the sample at $P_{H_2} = 6.5$ GPa and $T = 200$ °C from $n \approx 0.92$ (see Fig. 6) down to $n \approx 0.70$ (see Fig. 7). As one can easily demonstrate, it is the change in the average hydrogen concentration, n_{av}, of the solution containing $A = 25$ at% Pt that should be expected at its complete dissolution into the solutions with $B \approx 5$ at% Pt, $n_B \approx 1$ and $C \approx 75$ at% Pt, $n_C \approx 0$ (see Fig. 6, 7). Indeed, in this case

$$n_{av} = \frac{C - A}{C - B} n_B + \frac{A - B}{C - B} n_C \approx \frac{C - A}{C - B} n_B \approx 0.71 \, .$$

Besides the measurements described above, an X-ray study of the samples annealed in vacuum was also carried out in the present work. The annealing temperature was elevated in steps of 50 K each, at any fixed temperature the samples being kept for 1 h. The experiments have disclosed that a complete removal of the hydrogen from the samples requires an annealing at 300 °C. Having been subjected to such an annealing, all the samples except for the $Pd_{75}Pt_{25}$–H ones dissolved to the platinum-rich and platinum-poor phases, regained a single-phase homogeneous state with the initial values of parameters of their f.c.c. lattices. So, one can assert that the state of the dissolution to the phases rich and poor in platinum is not a thermodynamically equilibrium one for the Pd–Pt alloys studied (except for the $Pd_{75}Pt_{25}$ alloy) at atmospheric pressure and $T \geqq 300$ °C in the absence of hydrogen. As for the $Pd_{75}Pt_{25}$ alloy, the samples on its basis which experienced dissolution at a high hydrogen pressure and then were annealed in vacuum at 300 °C, retain their multi-phase constitution. X-ray photographs of these samples include two sets of lines of f.c.c. phases, their lattice parameters being 3.887 and 3.908 Å corresponding to the parameters for the Pd–Pt alloys containing $\leqq 25$ and ≈ 75 at% Pt. A further annealing in vacuum causes a decrease in the relative content of the phase with $a = 3.908$ Å of the samples, but traces of its diffraction lines are to be found in the X-ray photographs even after sample annealing at 700 °C. It seems appropriate to remind that at present one cannot preclude the existence of a miscibility gap in the Pd–Pt alloys [13]. The notable thermal stability of the two-phase state of the $Pd_{75}Pt_{25}$ samples examined in this work is in favour of the fact that such a phenomenon may occur.

3.3 Superconductivity

Fig. 9 lists the values of superconducting transition temperature, T_k, for the Pd–Pt–H samples which have been X-rayed before, the data having been presented in the previous section (to find out which of the samples possesses a given T_k-value, one can base on its n-value). Besides, to study the dependence $T_k(n)$ for the $Pd_{97.2}Pt_{2.8}$–H solutions more thoroughly, some additional samples were prepared by exposing for 24 h to $P_{H_2} \leqq 6.5$ GPa at 200 °C $\leqq T \leqq$ 350 °C. Typical dependences $\Delta(T)$ of the disbalance signal of an ac bridge in the range of the transition to the superconducting state for some of the Pd–Pt–H samples are exhibited in Fig. 10.

Consider first the dependences $T_k(n)$ for the samples being, according to the X-ray data, ordinary homogeneous hydrogen solutions on the base of the initially disordered Pd–Pt alloys and palladium. As is seen from Fig. 9, the dependence $T_k(n)$ for the $Pd_{97.2}Pt_{2.8}$–H solutions obtained in the present work is more gently sloping than that for the Pd–H solutions (dashed line), and though at low n-values the $Pd_{97.2}Pt_{2.8}$–H solutions possess higher T_k-values than those of the Pd–H solutions, the maximum T_k-value reached for these solutions proves to be lower than that for Pd–H. At $T \geqq 2$ K no superconductivity was observed in the $Pd_{90}Pt_{10}$ samples with $n \leqq 0.97$. Superconductivity reappeared in the $Pd_{85}Pt_{15}$–H solutions, then vanished again, and the $Pd_{75}Pt_{25}$–H, $Pd_{60}Pt_{40}$–H, and $Pd_{40}Pt_{60}$–H solutions turned out to be nonsuperconducting at hydrogen contents up to $n = 0.92$, 0.51, and 0.11, respectively.

So, the dependence of T_k on the platinum content of the Pd–Pt–H γ-solutions is found to be nonmonotonous. To make sure of this fact once more, we studied in addition the $Pd_{80}Pt_{20}$–H γ-solutions (the $Pd_{80}Pt_{20}$ samples were prepared in the same way as the other Pd–Pt samples; the X-ray data for the $Pd_{80}Pt_{20}$–H solutions under study are presented in Fig. 3, 6). As seen from Fig. 9, the solution with $n = 1.00$ proved to be a superconductor, its T_k-value being close to that for the $Pd_{75}Pt_{15}$–H solution with the same n-value.

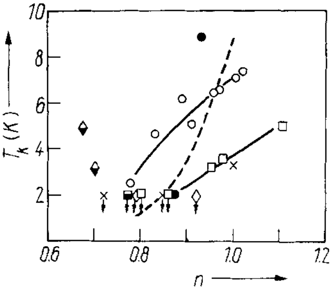

Fig. 9

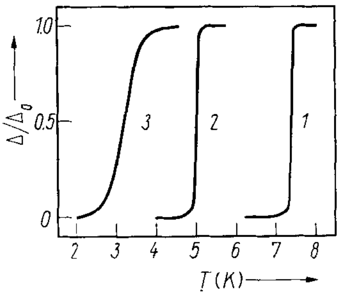

Fig. 10

Fig. 9. Superconducting temperature T_k vs. hydrogen concentration n for hydrogen solutions in the Pd–Pt alloys with ○ 2.8, □ 15, × 20, ◇ 25 at% Pt (data of the present work), ● 2.8 at% Pt (the data of [1]). Symbols with arrows stand for the samples possessing no superconductivity at $T \geqq 2$ K. The half-filled symbols concern the samples in which dissolution to the palladium-rich and palladium-poor phases was observed. Dashed line represents the $T_k(n)$ dependence for the Pd–H solutions [2]

Fig. 10. Temperature dependences of the signal Δ of disbalance of an ac bridge in the range of the transition to the superconducting state for the samples (1) $Pd_{97.2}Pt_{2.8}$–H, $n = 1.02$; (2) $Pd_{85}Pt_{15}$–H, $n = 1.10$; (3) $Pd_{75}Pt_{25}$–H, $n = 0.70$, the sample constituting a mixture of phases rich and poor in palladium. Δ_0 is the magnitude of the signal for the samples in the normal state

As for the samples which experienced a dissolution to the platinum-rich and platinum-poor phases at high hydrogen pressure, the samples based on the $Pd_{40}Pt_{60}$ and $Pd_{60}Pt_{40}$ alloys possessed no superconductivity at $T \geqq 2$ K. The $\Delta(T)$ curves for the samples based on the $Pd_{75}Pt_{25}$ alloy revealed the steps typical for the superconducting transition, the width of these steps, however, was considerably greater than that in the case of homogeneous γ-samples of the $Pd_{97.2}Pt_{2.8}$–H and $Pd_{85}Pt_{15}$–H solutions (see Fig. 10). The steps were likely to be associated with the transition to the superconducting state of the palladium-rich phase contained in such samples (corresponding values of T_k are shown in Fig. 9 as functions of the average hydrogen concentrations in the samples). A somewhat surprising result was the absence of superconductivity in the palladium-rich phase of the $Pd_{85}Pt_{15}$–H sample (⬓ in Fig. 9) produced at $P_{H_2} = 2$ GPa, while such a phase of the $Pd_{75}Pt_{25}$–H sample obtained under the same conditions possessed $T_k \approx 5$ K, the more so as in the case of the $Pd_{85}Pt_{15}$–H sample the lattice parameter of this phase, and hence the hydrogen concentration, was higher. It seems probable that in the Pd–Pt–H system, as well as in the Pd–Ni–H system [4], a decrease in the T_k-values of the palladium-rich phase precipitations compared to the T_k-values of the bulk samples of the same composition is due to a strong effect of the surrounding nonsuperconducting matrix on the properties of those precipitations owing to their small sizes.

Comparing the present data on the superconductivity of the Pd–Pt–H solid solutions with those available in the literature one can note the following. The maximum T_k-values attainable through hydrogen implantation have been shown to reach 9 to 9.5 K for the alloys containing up to ≈ 30 at% Pt and to decrease rapidly at higher platinum contents of the alloys [2]. Such a behaviour of T_k does not, at least, contradict our data, especially taking into account that the implantation might produce solutions considerably oversaturated with hydrogen and that radiation defects having arisen in the process of implantation might encourage increasing T_k (for instance, the radiation defects have been discovered to result in the occurrence of superconductivity with $T_k \approx 3.2$ K in pure palladium [14]). The more unexpected result was that the T_k-values for the $Pd_{97.2}Pt_{2.8}$–H solutions reported in [1] differ greatly from the dependence derived in our work (see Fig. 9), the more so as in both cases hydrogenation of the samples was carried out by one and the same technique — under high hydrogen pressure. Reasons for such a discrepancy remain obscure. Unfortunately, no structural researches on the $Pd_{97.2}Pt_{2.8}$–H samples have been made in [1], nor does it offer a description of the technique used in preparing the starting $Pd_{97.2}Pt_{2.8}$ samples (in particular, of their heat treatment which may affect significantly the physical properties of the alloys), that complicates a direct comparison of the data of [1] and of the present work.

4. Conclusion

The studies performed on the Pd–Pt–H homogeneous solutions with the f.c.c. metal sublattice as well as those formerly conducted on the Pd–Cu–H, Pd–Ag–H [3], and Pd–Ni–H [4] solid solutions have revealed that the maximum T_k-values attainable at hydrogenation do not rise with decreasing palladium content. An interesting feature of the Pd–Pt–H solutions lies in a nonmonotonous change of the $T_k(n)$ dependences with increasing platinum content of the alloys, in particular, the absence of superconductivity at $T \geqq 2$ K in the $Pd_{90}Pt_{10}$–H solutions and its occurrence in the $Pd_{85}Pt_{15}$–H and $Pd_{80}Pt_{20}$–H solutions.

The authors would like to draw the readers' attention once more to the phenomenon of dissolution of the Pd–Pt–H solid solutions to phases rich and poor in palladium discovered in the present work. The Pd–Pt alloys proved to be the third group of palladium alloys (after Pd–Cu [7] and Pd–Ni [4]) which, being hydrogenated at lowered temperature, exhibit anomalous, in one or another respect, superconducting properties (see [2]), and whose hydrides are unstable relative to the phase transformations accompanied by diffusional redistribution of the metal atoms at elevated temperature and high pressure. Such a relation bears a resemblance to a regularity.

Acknowledgements

The authors wish to thank I. M. Romanenko (Institute of Experimental Mineralogy, Academy of Sciences of the USSR) for chemical analyses of the Pd–Pt alloys, A. I. Amelin for his assistance in the experiments, and V. G. Glebovskii in whose group the palladium–platinum alloys were melted.

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(Received February 18, 1983)