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The Pd-Ni-H System at High Pressure

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Studies on crystal structure, superconducting and magnetic properties of hydrogen solid solutions in the Pd-Ni alloys with 5, 20, 40, 60, and 80 at% Ni are presented. For solutions on the base of alloys containing 20 to 80 at% Ni the phenomenon of dissolution in poor and rich nickel phases is revealed. Hydrogenation of the samples is performed at hydrogen pressures up to 7 GPa and temperatures up to 350 °C.

Изучены кристаллическая структура, сверхпроводящие и магнитные свойства твердых растворов водорода в сплавах Pd-Ni с 5, 20, 40, 60 и 80 at% Ni. Обнаружено явление распада растворов на базе сплавов, содержащих от 20 до 80 at% Ni, на обедненную в обогащенную никелем фазы. Гидрирование образцов проводилось при давлениях водорода до 7 ГПа и температурах до 350 °C.

1. Introduction

In recent years much attention has been focussed on the superconducting properties of hydrogen solid solutions in palladium alloys, and a number of new results are of interest (see, for instance, review [1]). When treating the data in question, hydrogen was implied to be an interstitial component of the alloys that occupies interstices in the f.c.c. metal lattice and only increases its parameter. It seemed somewhat disturbing, however, that the superconducting properties of these Pd-Me-H solutions charged with hydrogen by different techniques (implantation, electrolytically, under high pressure) were sometimes found to differ drastically. Research into one of the systems of solutions of this type [2], Pd-Cu-H, charged with hydrogen under high pressure, has shown [3] that at $0.5 \text{ GPa} \leq P_{\text{H}_2} \leq 2 \text{ GPa}$ and $T > 220 \text{ °C}$ there occurs an irreversible phase transformation accompanied by a tetragonal distortion of the f.c.c. metal sublattice and, most probably, caused by its atomic ordering.

A new phase transformation revealed in the Pd-Cu-H system suggests that for other Pd-Me-H systems as well a structural investigation, particularly, in conjunction with studies on other physical properties, may yield some interesting results. The Pd-Ni-H system seemed to be promising for such an investigation because of the cardinal difference among the concentration dependences of the temperature of transition into the superconducting state, T_{K} , obtained for this system in cases of sample hydrogenation by implantation [1] or electrolytically [4] and under high pressure [5, 6]. The alloys with 5, 20, 40, 60, and 80 at% Ni are under study in the present work.

2. Experimental

The ingots were melted in an induction furnace in vacuum from electrolytical palladium and nickel. After a 10 h homogenization at 1100 °C and water-quenching, these ingots were rolled to strips $\approx 0.1 \text{ mm}$ thick, then subjected to stress-relief annealing

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in vacuum at 1100 °C for 5 min and again quenched in water. The samples were cut from these polycrystalline strips.

Hydrogen compression to pressures of ≈ 2 GPa was performed in “piston-cylinder”-type chambers, to pressures of ≈ 7 GPa in “toroid”-type chambers by the method suggested in [7]. Petrol was used to create a hydraulic gate. The temperature in those chambers was measured with an accuracy to ± 2 and ± 10 K, respectively, and the pressure to ± 0.03 and ± 0.3 GPa. Measurements of the electrical resistance were conducted by a conventional four-probe technique, the Curie points were determined by a differential transformer method [8].

The Pd–Ni–H samples aimed at further investigation at atmospheric pressure were produced by exposing at fixed values of hydrogen pressure ($P_{H_2} \leq 7$ GPa) and temperature ($200^\circ\text{C} \leq T \leq 350^\circ\text{C}$). The high-pressure chamber was then rapidly cooled, the pressure lowered to atmospheric, the samples were removed from the chamber and later on kept in liquid nitrogen. In case of the “piston-cylinder”-type chamber the quenching was done down to $\approx -20^\circ\text{C}$, and in case of the “toroid”-type chamber down to $\approx -50^\circ\text{C}$ (such quenching has been shown to be sufficient to prevent hydrogen losses from the proper samples at atmospheric pressure). The hydrogen content in the samples was determined with an accuracy of 5% by decomposing them into metal and molecular hydrogen in a pre-evacuated container of known volume at $T \leq 500^\circ\text{C}$.

The magnetization of the samples was measured with 5% error in a pulsed magnetic field up to 5 T by the induction method [9] in the temperature range 4.2 to 200 K, the pulse duration being ≈ 0.01 s. Samples for the magnetic measurements were couples of strips $6 \times 1 \times 0.2$ mm³ in size, the total weight being ≈ 20 mg. An X-ray study was carried out by a phototechnique at $T = 90$ K using a DRON-1 diffractometer with CuK α radiation, the samples being in the form of discs ≈ 5 mm in diameter. The temperature of transition to the superconducting state was determined by the induction method.

3. Results and Discussion

The phase diagrams of the Pd–H and Ni–H systems are similar. Both the systems reveal in the T – P_{H_2} diagrams a line of isomorphous phase transformation, $\gamma_1 \rightleftharpoons \gamma_2$, ending in a critical point, the $(P_{H_2})_{cr}$ value for the Ni–H system being higher than that for the Pd–H system by approximately three orders of magnitude [10 to 12]. Nickel and palladium form continuous disordered solid solutions with f.c.c. lattice [13]. It was shown in [6] that at room temperature the pressure of the $\gamma_1 \rightarrow \gamma_2$ transition increases monotonously with nickel content of the alloys from $P_{H_2} \approx 1.8$ kPa for the Pd–H solutions to ≈ 0.6 GPa for the Ni–H solutions. The data of the present work agree with these results of [6] and demonstrate that as palladium being doped with nickel, the line of the $\gamma_1 \rightleftharpoons \gamma_2$ transformation is found to be shifted rigidly towards higher pressures.

3.1 Electrical resistance of Pd–Ni alloys under high hydrogen pressure

The isotherms presented in Fig. 1 were taken during stepwise increase and decrease in pressure with an exposure in each point for a certain period of time, $\Delta\tau$, up to the termination of the temporal resistance drift, $R(\tau)$, caused by the diffusional nature of the formation of Pd–Ni–H solid solutions. There are final values of R given in Fig. 1. As one can see from the figure, all the $R(P_{H_2})$ isotherms plotted possessed distinct anomalies corresponding to the $\gamma_1 \rightarrow \gamma_2$ and $\gamma_2 \rightarrow \gamma_1$ transitions.

The shape of the $R(P_{H_2})$ dependences for the Pd–Ni alloys under study remained nearly unchanged with temperature varying within $100^\circ\text{C} \leq T \leq 350^\circ\text{C}$. At $T \gtrsim 250^\circ\text{C}$ typical values of $\Delta\tau$ were $\lesssim 30$ min in the ranges of the $\gamma_1 \rightarrow \gamma_2$ and

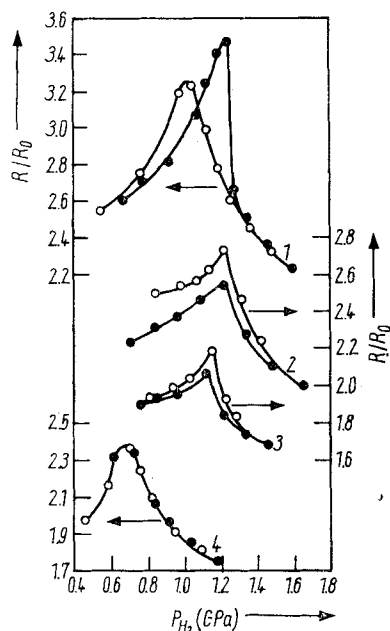


Fig. 1. Electrical resistance isotherms ($T = 250^\circ\text{C}$) of Pd-Ni alloys in hydrogen atmosphere. (1) 100, (2) 80, (3) 60, (4) 40 at% Ni. $\bullet$ increasing pressure, $\circ$ decreasing pressure. R_0 is the resistance of the samples under normal conditions

$\gamma_2 \rightarrow \gamma_1$ transitions and ≈ 5 min in the single-phase regions. At lower temperatures these values increased rapidly and at 100°C reached hours. A typical phase diagram where cations of maxima on the $R(P_{\text{H}_2})$ dependences are plotted, can be found in Fig. 2.

The T - P_{H_2} phase diagram of the $\text{Pd}_{60}\text{Ni}_{40}$ -H system (Fig. 2) apart from the curve of the $\gamma_1 \rightleftharpoons \gamma_2$ transformation, has a line of Curie points, T_C for the γ_1 -phase (the γ_2 -phase is paramagnetic in the temperature and pressure range studied). In an inert medium the Curie point of $\text{Pd}_{60}\text{Ni}_{40}$ alloy increases approximately linearly with pressure, the slope being $(dT_C/dP)_{\text{in}} \approx 2.0 \text{ K GPa}^{-1}$ [14]. A considerable and monotonous decrease of the Curie point of the alloy in hydrogen atmosphere is, thus, caused by an increase of the hydrogen solubility in the γ_1 -phase of the $\text{Pd}_{60}\text{Ni}_{40}$ -H solution at increasing pressure (at $T = 100^\circ\text{C}$ and $P_{\text{H}_2} = 0.2 \text{ GPa}$ the concentration of the solution reaches the hydrogen-to-metal atomic ratio $n = 0.05 \pm 0.03$). The drift time for the Curie point of the $\text{Pd}_{60}\text{Ni}_{40}$ -H γ_1 -solution did not exceed 15 to 20 min after changing the hydrogen pressure.

As a whole, it can be said that the phase diagrams for the Pd-Ni-H solutions in question are completely analogous to those for Ni-H [12] and Pd-H [10] solutions. Further investigation has shown, however, that in Pd-Ni-H solutions there occur phenomena that are not observed in Ni-H and Pd-H solutions: in case of the alloys with 20, 40, 60, and 80 at% Ni exposed at $T \gtrsim 250^\circ\text{C}$ and $P_{\text{H}_2} > (P_{\text{H}_2})_{\gamma_1 \rightarrow \gamma_2}$ (this region is shaded in the T - P_{H_2} diagram of the $\text{Pd}_{60}\text{Ni}_{40}$ -H system, Fig. 2) over time periods exceeding considerably the period required for their saturation with hydrogen,

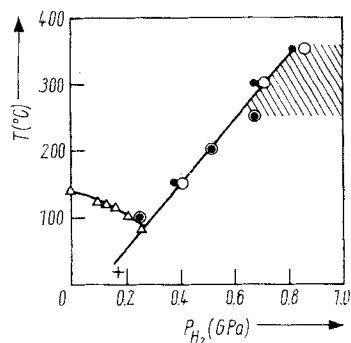


Fig. 2. T - P_{H_2} phase diagram of the $\text{Pd}_{60}\text{Ni}_{40}$ -H system. $\bullet$ pressures of the $\gamma_1 \rightarrow \gamma_2$ transition, $\circ$ $\gamma_2 \rightarrow \gamma_1$, + pressure of the $\gamma_1 \rightarrow \gamma_2$ transition according to [6], Δ Curie points

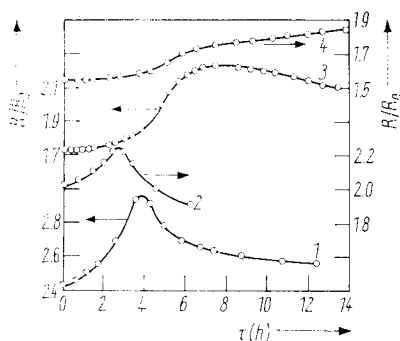


Fig. 3. Time dependences of electrical resistance of Pd-Ni alloys at $T = 350^\circ\text{C}$ and $P_{\text{H}_2} = 2\text{ GPa}$. (1) 80, (2) 60, (3) 40, (4) 20 at% Ni. R_0 is the resistance of the samples under normal conditions

there appears a relatively slow temporal drift of resistance. The drift rate increased and decreased with temperature. Typical $R(\tau)$ dependences at 350°C and $P_{\text{H}_2} = 2\text{ GPa}$ are given in Fig. 3. The curves were obtained as follows: the samples were preexposed at $P_{\text{H}_2} = 2\text{ GPa}$ and $T = 200^\circ\text{C}$ up to the termination of the temporal resistance drift ($\Delta\tau \lesssim 1\text{ h}$), and the temperature was then increased to 350°C in a jump-like manner.

The anomalous behaviour of electrical resistance seemed most probable to be due to new irreversible phase transformations taking place in the solutions under study. As to the temperature $\approx 250^\circ\text{C}$ at which the transformations start and which depended weakly on both pressure and composition of the Pd-Ni alloys, its magnitude is likely to be determined by kinetic reasons.

3.2 X-ray data

At first we studied the constitution of the Pd-Ni-H samples which underwent no irreversible phase transition at high temperatures and were to be ordinary γ -solutions.

All the Pd-Ni-H samples subjected to an X-ray study in the present work were exposed to $T \approx -20^\circ\text{C}$ for some minutes in the course of manipulations at atmospheric pressure. This temperature was low enough to brake the hydrogen exchange between the samples and the environment but, at the same time, it was high enough for redistribution of hydrogen within the samples to occur and their phase composition to come to an agreement with the metastable (i.e. at a fixed total content of hydrogen in the solution) T - c diagram during these some minutes (see [10, 15]). According to such diagrams, at atmospheric pressure and $T \lesssim -20^\circ\text{C}$ the Pd-H and Ni-H samples with $n_{\gamma_1}^{\max} < n < n_{\gamma_2}^{\min}$ consist of a mixture of the γ_1 - and γ_2 -phases of concentrations $n_{\gamma_1}^{\max}$ and $n_{\gamma_2}^{\min}$, and those with $n \geq n_{\gamma_2}^{\min}$ constitute single-phase solutions (for Pd-H solutions $n_{\gamma_1}^{\max} \lesssim 0.008$, $n_{\gamma_2}^{\min} \approx 0.6$ (see [10]), and for Ni-H solutions $n_{\gamma_1}^{\max} \lesssim 0.02$, $n_{\gamma_2}^{\min} \approx 0.7$ [16]). Thus, to treat the data obtained at atmospheric pressure correctly we needed investigating such a separation for the Pd-Ni-H solutions under study.

The Pd-Ni-H samples aimed at the given series of measurements were produced by exposing at fixed P_{H_2} and $T \leq 350^\circ\text{C}$ during 1 h, that was sufficient for hydrogenation of the Pd-Ni alloys to be completed, but was much less than the period of time required for the phase transformation to occur, observed in the γ_2 -solutions on the base of alloys with 20 to 80 at% Ni (see, for instance, Fig. 3). The X-ray study has shown that the $\text{Pd}_{80}\text{Ni}_{40}$ -H, $\text{Pd}_{20}\text{Ni}_{80}$ -H, and Ni-H solutions with $0.2 \lesssim n \lesssim 0.6$ consist of a mixture of the two phases with a f.c.c. metal lattice, their parameters, a , denoted with closed circles in Fig. 4, being independent of the hydrogen content in the sample. In case of the samples with $n \gtrsim 0.6$ no lines of phases with smaller a -value were observed on X-ray patterns.

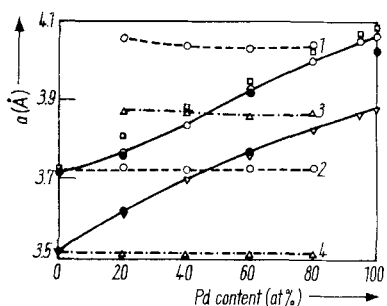


Fig. 4. Parameters a of the f.c.c. metal sublattice for different phases of Pd-Ni-H solutions at $T = 90$ K and atmospheric pressure. ∇ initial Pd-Ni samples, $\square$ after exposure at $T = 200$ °C and $P_{H_2} = 2$ GPa for 5 h, $\circ$ after exposure at $T = 350$ °C and $P_{H_2} = 2$ GPa for 10 h ((1) phases poor in nickel, (2) rich in nickel), $\triangle$ the same samples after annealing in vacuum at $T = 300$ °C for 2 ((3) phases poor in nickel, (4) rich in nickel), $\bullet$ phases of concentrations $n_{\gamma_1}^{max}$ and $n_{\gamma_2}^{min}$ h (see text)

As is seen from Fig. 4, the smaller values of a -parameters for the two-phase samples are close to those for corresponding alloys with no hydrogen. It is reasonable to assume them to be parameters of γ_1 -phases of composition $n_{\gamma_1}^{max}$, whereas greater parameters to relate to γ_2 -phases of composition $n_{\gamma_2}^{min}$. The $a(n_{\gamma_1}^{max})$ and $a(n_{\gamma_2}^{min})$ values obtained for the Ni-H solutions are in line with the data of [12, 16].

To evaluate the changes in a -parameters of Pd-Ni-H γ_2 -solutions with hydrogen concentration, a series of samples was prepared by exposure at $P_{H_2} = 2$ GPa and $T = 200$ °C for 2 h. Their parameters, a^{200} , are shown with squares in Fig. 4. The hydrogen concentration in the alloys with 0.5, 20, 40, 60, 80, and 100 at% Ni was $n = 0.99, 1.03, 1.12, 1.20, 1.16, 1.21$, and 1.09, respectively. The a^{200} -values obtained for the Pd-H and Ni-H γ_2 -solutions of the concentrations mentioned are in line with the data of [17] and [12].

The above results enabled us to go on to elucidating the question what happens to the Pd-Ni-H γ_2 -solutions in the process of a prolonged exposure in hydrogen atmosphere at $T \approx 250$ °C. For this purpose a number of samples were produced by exposing at $T = 350$ °C and $P_{H_2} = 2$ GPa for 10 h. The data of X-ray investigation of such samples are denoted in Fig. 4 with open circles. According to these data, the samples based on nickel, palladium, and Pd₉₅Ni₅ alloy were ordinary γ_2 -solutions, for which $a^{200} > a^{350} > a(n_{\gamma_2}^{min})$ (the a^{350} -value for the Ni-H solution is not shown in order to simplify the figure). A decrease in a^{350} -value compared to a^{200} is due to the fact that at $P_{H_2} = 2$ GPa the hydrogen solubility in all the metals under study is smaller at 350 than at 200 °C.

In case of samples based on alloys with 20, 40, 60, and 80 at% Ni the situation was quite different. They proved to consist of three phases with f.c.c. metal lattices. The value of the parameter a for one of the phases lay between the values $a(n_{\gamma_2}^{min})$ and a^{200} for a corresponding alloy (these points are connected with the solid line in Fig. 4) and coincided with the a^{350} -value for the same alloy charged with hydrogen at $P_{H_2} = 2$ GPa and $T = 350$ °C for 1 h. Thus, one of the three phases observed in the investigated samples was a residue of the Pd-Ni-H γ_2 -solution which had not enough time to transform into a new phase state during the exposure at $P_{H_2} = 2$ GPa and $T = 350$ °C. The parameters a of the other two phases depended weakly on the concentration of the starting Pd-Ni alloys and corresponded to the a^{350} -parameter for palladium containing a few atomic percent of nickel (these points are linked with dashed curve 1 in Fig. 4) and that for nickel (curve 2).

In the light of these data, the most probable process occurring at a prolonged exposure of the alloys with 20 to 80 at% Ni at $T \approx 250$ °C and $P_{H_2} > (P_{H_2})_{\gamma_1 \rightarrow \gamma_2}$, is believed to be a dissolution of hydrides of these alloys to a hydride of nearly pure nickel and a hydride of palladium with some atomic percent of nickel. The kinetics of the dissolution, however, remains relatively sluggish even at 350 °C, as is seen already from the curves of electrical resistance presented in Fig. 3. The kinetics inertia

is confirmed by a X-ray examination as well. For instance, a detectable amount of the γ_2 -phase of the $\text{Pd}_{60}\text{Ni}_{40}\text{-H}$ solution was retained in the samples even after exposing them at $P_{\text{H}_2} = 2$ GPa and $T = 350^\circ\text{C}$ for 48 h.

A considerably lower diffusion mobility of the metal atoms in the Pd-Ni-H solutions compared to that of hydrogen atoms proved, on the other hand, to be useful to confirm, in addition, the dissolution of these solutions at high pressure and increased temperature. An annealing in vacuum for 2 h of the samples on the base of the alloys with 20, 40, 60, and 80 at% Ni, produced by exposure at $P_{\text{H}_2} = 2$ GPa and $T = 350^\circ\text{C}$ for 10 h, resulted in a complete extraction of hydrogen from them, but the samples retained their three-phase nature. The phases which in the presence of hydrogen had $a^{200} > a^{350} > a(n_{\gamma_2}^{\min})$ were found to have now parameters a coinciding with those for corresponding Pd-Ni alloys with no hydrogen (∇ in Fig. 4). The values of the parameters which we used earlier to ascribe to phases poor in nickel (curve 1 in Fig. 4) decreased to those for such alloys with no hydrogen (curve 3). The same happened in the case of the phases considered to be hydrogen solutions on nickel base (curves 2 and 4, respectively).

After a further annealing of these samples in vacuum at $T > 400^\circ\text{C}$ the alloys, as revealed by the X-ray examination, recovered the single-phase homogeneous state with starting values of parameters of their f.c.c. lattices. The recovery of this initial state occurred also after plastic deformation of the dissolved samples with no hydrogen at room temperature. Such a behaviour of the samples demonstrates the fact that under normal conditions the dissolution to phases rich and poor in nickel is not an equilibrium property of Pd-Ni alloys themselves. It is the triple Pd-Ni-H solutions with a high hydrogen content which are found to dissolve.

3.3 Superconductivity

The available data concerning the behaviour of superconducting properties of hydrogen solid solutions in Pd-Ni alloys containing up to ≈ 10 at% Ni are in line with each other [1, 4 to 6]: over this concentration range the replacement of palladium by nickel causes a monotonous decrease in the maximum attainable temperature, T_k^m , of transition of Pd-Ni-H solutions to the superconducting state from ≈ 8.8 K for palladium to ≈ 1 to 2 K for the alloys with nickel atomic fraction $x_{\text{Ni}} \approx 0.1$. For the alloys with a higher nickel concentration no such an agreement is observed. The studies on the $\text{Pd}_{80}\text{Ni}_{20}$ alloy charged with hydrogen by implantation at helium temperature [1] and on the $\text{Pd}_{75}\text{Ni}_{25}$ alloy hydrogenated electrolytically at $T \approx 200$ K [4] have shown them to possess no superconductivity at $T \gtrsim 1.1$ K. The results obtained in the case of hydrogenation of Pd-Ni alloys under a high hydrogen pressure and room temperature [5, 6] were quite different: on the dependence $T_k^m(x_{\text{Ni}})$ a deep minimum at $x_{\text{Ni}} \approx 0.1$ was followed by a maximum ($T_k^m \approx 10$ K) at $x_{\text{Ni}} \approx 0.2$, and then the T^m values decreased sharply. It should be noted that the $T_k(n)$ dependences for the alloys with $x_{\text{Ni}} \approx 0.2$ exhibited a chaotic behaviour [6]. In the light of the arguments of the previous section, a divergence in the data of [1, 4] and [5, 6] can be straightforwardly explained if one assumes that in the Pd-Ni-H γ_2 -solutions with $x_{\text{Ni}} \gtrsim 0.2$ investigated in [5, 6] there occurred a dissolution to phases rich and poor in nickel, and that the jumps on the temperature dependences of electrical resistance, registered in those works, corresponded to the transition of the nickel-poor phases to the superconducting state.

The dependences $T_k(n)$ for the Pd-Ni alloys with 5, 20, and 40 at% Ni derived in the present paper are given in Fig. 5. The Pd-Ni-H samples were produced by exposing for 10 h at $P_{\text{H}_2} \leq 7$ GPa and $T \leq 350^\circ\text{C}$ (with the exception of solutions on the base of $\text{Pd}_{80}\text{Ni}_{20}$ and $\text{Pd}_{60}\text{Ni}_{40}$ alloys with maximum n -values, see below). Typical dependences $A(T)$ of the signal of disbalance of an ac bridge in the range of transition

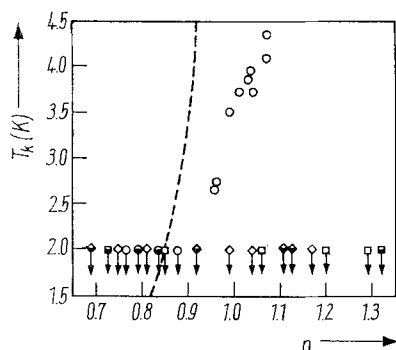


Fig. 5. Superconducting temperature T_k vs. hydrogen content n for hydrogen solutions in Pd-Ni alloys with $\circ$ 5, $\diamond$ 20, and $\square$ 40 at% Ni. The symbols with arrows stand for samples possessing no superconductivity at $T \geq 2$ K. The half-blackened symbols concern samples where dissolution to phases poor and rich in nickel was observed. Dashed line represents the $T_k(n)$ dependence for the Pd-H solutions [1]

to the superconducting state for the $\text{Pd}_{95}\text{Ni}_5\text{-H}$ solutions are demonstrated in Fig. 6. Relatively narrow steps on the $\Delta(T)$ dependences corresponding to such a transition are indicative of a homogeneous hydrogen distribution over the volume of the samples. The T_k -values were estimated by locations of the midpoint of these steps.

As is seen from Fig. 5, the $T_k(n)$ dependence for the $\text{Pd}_{95}\text{Ni}_5\text{-H}$ γ_2 -solutions is markedly shifted in respect to a similar dependence for Pd-H solutions (dashed line) towards higher n -values. At $T \geq 2$ K no transition to the superconducting state has been observed for the $\text{Pd}_{80}\text{Ni}_{20}\text{-H}$ and $\text{Pd}_{60}\text{Ni}_{40}\text{-H}$ γ_2 -solutions (empty symbols in Fig. 5). Thus, our data for the Pd-Ni-H γ_2 -solutions having undergone no separation to nickel-poor and nickel-rich phases agree with the data of [1, 4 to 6] and contradict the data of [5, 6].

A surprising result was the absence of superconductivity at $T \geq 2$ K in case of $\text{Pd}_{80}\text{Ni}_{20}\text{-H}$ and $\text{Pd}_{60}\text{Ni}_{40}\text{-H}$ samples dissolved to phases rich and poor in nickel (half-blackened symbols in Fig. 5), for even by the most understated estimates among the samples under study there were to be found such ones for which the hydrogen concentration in the nickel-poor phase was sufficient to make it a superconductor with $T_k \gg 2$ K. This effect might be due to suppression of superconductivity in particles of the nickel-poor phase by the surrounding paramagnetic medium owing to their small sizes.

Nevertheless, from our point of view, the most probable cause responsible for the appearance of superconductivity in the Pd-Ni-H samples with $x_{\text{Ni}} \approx 0.2$ studied in [5, 6] seems to be the dissolution with precipitation of particles of the phases poor in nickel. Indeed, the γ_2 -solutions of hydrogen in alloys with $x_{\text{Ni}} \geq 0.2$ do not possess superconductivity at $T \geq 2$ K even at the n -values exceeding considerably those reached in [5, 6] (see Fig. 5). But it is difficult to expect, at the same time, that one more new transformation may occur in those solutions at high hydrogen pressure and

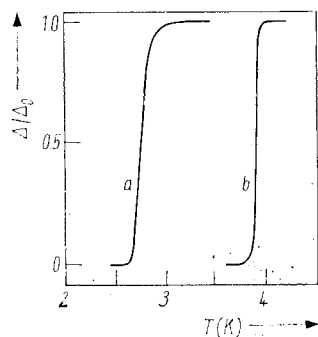


Fig. 6. Temperature dependences of the signal of disbalance Δ of an ac bridge in the range of transition to the superconducting state for $\text{Pd}_{95}\text{Ni}_5\text{-H}$ solutions with (a) $n = 0.96$ and (b) 1.04. Δ_0 is the magnitude of the signal for samples in the normal state

room temperature. In any case, our experiments have shown that the exposure of the $\text{Pd}_{80}\text{Ni}_{20}$ and $\text{Pd}_{60}\text{Ni}_{40}$ alloys, pre-charged with hydrogen at an increased temperature, at $P_{\text{H}_2} = 7$ GPa and room temperature for 48 h resulted neither in a change of the phase composition of the solutions formed at an increased temperature nor in the appearance of superconductivity (it is just the manner used to produce samples with a maximum hydrogen content, the data on superconductivity of which are presented in Fig. 5).

3.4 Magnetic measurements

The last that we are going to consider in our work is the effect of hydrogen on the magnetization of Pd-Ni alloys. The Pd-Ni-H samples were produced by exposure for 2 h at $T \leq 300$ °C and $P_{\text{H}_2} \leq 2$ GPa. The X-ray examinations of the samples thus obtained have revealed no dissolution of the γ_2 -phases to the nickel-rich and nickel-poor phases. Thus, only ordinary γ -solutions were under investigation. In [18] it has been shown that the behaviour of the magnetic properties of Pd-Ni alloys is well described by equations of the theory of weak itinerant ferromagnetism [19, 20]. In the present work we have used these equations to treat the experimental data for the Pd-Ni-H samples.

Ferromagnetic ordering in the Pd-Ni alloys arises at a nickel concentration of 2.5 at%, further the Curie points, T_C , and the spontaneous magnetization, σ_0 , at $T = 0$ K increase monotonously up to $T_C^{\text{Ni}} = 631$ K and $\sigma_0^{\text{Ni}} = 0.616\mu_B/\text{atom}$ [21, 18], where μ_B is the Bohr magneton. The $\text{Pd}_{60}\text{Ni}_{20}$ and $\text{Pd}_{60}\text{Ni}_{40}$ alloys have been chosen for investigation. The $\sigma_0(n)$ dependences for these alloys are exhibited in Fig. 7. In full analogy with that done for the Ni-H solutions in [16], in the present work for the $\text{Pd}_{80}\text{Ni}_{20}$ -H and $\text{Pd}_{60}\text{Ni}_{40}$ -H solutions it has been shown that at atmospheric pressure their γ_2 -phases with hydrogen concentrations down to $n_{\gamma_2}^{\min}$ are found to be paramagnetic at $T \geq 4.2$ K, and the samples with $\sigma_0 \neq 0$ consist of a ferromagnetic γ_1 -phase of concentration $n_{\gamma_1}^{\max}$ and a paramagnetic γ_2 -phase of concentration $n_{\gamma_2}^{\min}$. Thus, the hydrogen concentration at which the $\sigma_0(n)$ dependences, being approximately linear in the $(\gamma_1 + \gamma_2)$ two-phase regions, intersect the $\sigma_0 = 0$ axis is $n_{\gamma_2}^{\min}$. As is seen from Fig. 7, the $n_{\gamma_2}^{\min}$ values estimated in this way for the $\text{Pd}_{80}\text{Ni}_{20}$ -H and $\text{Pd}_{60}\text{Ni}_{40}$ -H solutions are close to those for the Pd-H ($n_{\gamma_2}^{\min} \approx 0.6$ [1]) and Ni-H ($n_{\gamma_2}^{\min} \approx 0.7$ [16]) solutions.

Concluding we note that the suppression of ferromagnetic ordering on introducing hydrogen to Pd-Ni alloys is in agreement with the prediction of the rigid d-band model that earlier proved to be a good one to describe the magnetic properties of hydrogen solid solutions on the base of f.c.c. and h.c.p. alloys of 3d metals (see [15]).

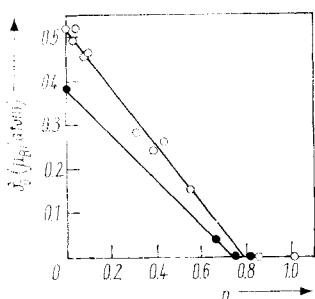


Fig. 7. Spontaneous magnetization σ_0 at $T = 0$ K in dependence on hydrogen content n in $\text{Pd}_{80}\text{Ni}_{20}$ (●) and $\text{Pd}_{40}\text{Ni}_{60}$ (○) alloys. The magnetization is given in μ_B/atom of the Pd-Ni alloy

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