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Superconductivity of Pd-Au-H Solid Solutions

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It was revealed in /1/ that hydrogen implantation into alloys of palladium with noble metals (copper, silver, and gold) can convert them to superconductors whose superconducting transition temperature, T_k, reaches much higher values than that of Pd-H solutions. The discovery of this effect has stimulated to a considerable extent the extensive studies of the last few years on the superconducting properties of hydrogen solutions in the palladium alloys. A great number of works has been conducted in order to analyse what lies at the bottom of the effect (see review /2/).

Further experiments have shown, however, that at least in the case of the Pd-Cu-H and Pd-Ag-H solutions with f.c.c. metal sublattice the existence of superconductivity with anomalously high T_k values is not an equilibrium property of massive, homogeneous samples /3/. The technique for hydrogen compression to high pressures enabled us to saturate the $Pd_{60}Cu_{40}$ and $Pd_{80}Ag_{20}$ alloys (having nearly optimum compositions for achieving the highest T_k values on hydrogen implantation /1/) with hydrogen up to concentrations also approximating the optimum ones according to /1/. It turned out that at H-to-metal atomic ratio $n \lesssim 1$ the $T_k(n)$ dependence for the $Pd_{80}Ag_{20}$-H solutions is close to that for the Pd-H solutions, and in the $Pd_{60}Cu_{40}$-H solutions superconductivity is absent at $n \lesssim 0.6$ and $T \geq 2$ K.

The present note is devoted to the investigation of hydrogen solutions in the Pd-Au alloys containing 3, 9, 22.5, 50, and 75 at% Au. The ingots were melted from Pd (99.99%) and Au (99.999%) in an induction furnace in vacuum. After a 10 h homogenization in vacuum at 1000 °C and water-quenching these ingots were rolled into strips 0.15 mm thick, then subjected to stress-relief annealing in vacuum at 1000 °C for 5 min and again quenched in water. The

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specimens in the form of discs of 5 mm diameter were cut out of these strips.

Hydrogenation of Pd-Au samples was conducted by exposure under hydrogen pressures up to 8 GPa. Hydrogen compression was performed by the method suggested in /4/ (a detailed description of the method is given in /5/). The pressure and the temperature were measured accurate to ± 0.3 GPa and ± 10 °C, respectively. After the hydrogenation was completed, the high-pressure chamber was rapidly cooled down to ≈ -120 °C, then the pressure was lowered and the samples were taken out of the chamber and placed for storage into liquid nitrogen to prevent hydrogen losses. At atmospheric pressure a pronounced release of hydrogen from specimens began at $T \gtrapprox -50$ °C. The hydrogen concentration was measured to an accuracy of 5%; the technique is described in details in /6/. The T_k values were determined by the induction method at $T \geq 2$ K. An X-ray study was carried out by a phototechnique at $T = -190$ °C using a DRON-2.0 diffractometer with FeK_α radiation.

Under normal conditions Pd and Au form continuous disordered solid solutions with the f.c.c. lattice /7/. According to /8/, the gold alloying of palladium results in a rapid decrease in the critical temperature of the separation of the Pd-H solutions into the two isomorphous phases, γ_1 and γ_2, poor and rich in hydrogen, and at $T \gtrapprox 25$ °C hydrogen should form continuous interstitial solutions (based on the f.c.c. metal sublattice) with the Pd-Au alloys containing $\gtrapprox 17$ at% Au. Our recent experiments, however, have shown that at high pressure some new phase transitions followed by a diffusional redistribution of atoms of the metallic matrix may take place in the Pd-Me-H systems (dissolution into the poor and rich in palladium phases in the Pd-Ni-H /9/ and Pd-Pt-H /10/ systems; ordering in the $Pd_{60}Cu_{40}$-H system /6/), the temperature, T^*, above which these transitions occur with a detectable rate, being approximately equal for all the systems in hand running as high as ≈ 250 °C. Besides, gold was found to form a hydride with rather complicated (probably, orthorhombic) structure at $P_{H_2} \gtrapprox 2.8$ GPa and $T \gtrapprox 300$ °C /11/.

To examine whether analogous phenomena occur in the Pd-Au-H system, we have studied two series of samples. The samples of the first series were exposed at $P_{H_2} = 6.5$ GPa and $T = 200$ °C $< T^*$ for 24 h. The second ones were exposed initially at 350 °C for 24 h and then at 200 °C for another 24 h. The X-ray study has shown the samples of both series to be single-phase and to have near values of the parameters, a, of their f.c.c. metal sublattices, see

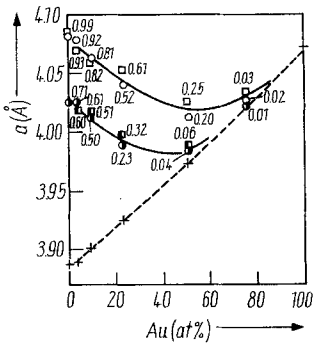

Fig. 1. Parameters a of the f.c.c. metal lattice at -190 °C and atmospheric pressure for the initial Pd-Au alloys (+) and for the Pd-Au-H samples exposed at P_{H_2} = 6.5 GPa: (o) 200 °C for 24 h; (□) 350 °C for 24 h and then 200 °C for 24 h; (◑, ◧) the same samples after partial hydrogen release at normal conditions

Fig. 1. The hydrogen concentrations of these samples proved to be also the same within the experimental error (the n-values are listed in Fig. 1). As is seen from Fig. 1, the samples of both series exhibited close values of a and n as well after partial losses of hydrogen through several days exposure at normal conditions (a noticeable release of hydrogen from the samples ceased in several hours; the diffraction pattern showed relatively narrow lines that evidenced a homogeneous hydrogen distribution over the samples volume, though its concentration of the samples was not thermodynamically equilibrium for normal conditions, compare with /8/). These results allowed one to conclude that no irreversible phase transitions (analogous to those observed in some other Pd-Me-H system /6, 9, 10/ and Au-H system /11/) took place at P_{H_2} = 6.5 GPa and T $\leq$ 350 °C in the Pd-Au-H system under study.

One more fact corroborating this conclusion is worth presenting. It has been shown in /12/ that at n $\lesssim$ 0.7 the dependences $\Delta V_o(n)$ of the increment of the unit-cell volume are very close for all the investigated hydrogen solutions in the f.c.c. disordered palladium-based alloys. The dependence $\Delta V_o(n)$ obtained in /12/ is plotted in Fig. 2 by a broken line. To extend the dependence

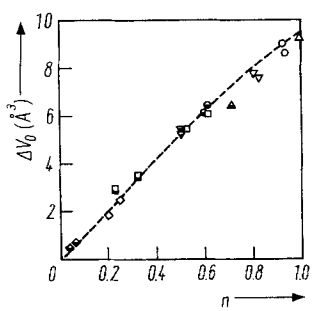

Fig. 2. Increase in the volume of the unit cells, ΔV_o, versus hydrogen concentration, n, of the Pd-Au alloys containing △ 0, o 3, ▽ 9, □ 22.5, ◇ 50 at% Au. Half-blackened symbols stand for the same samples but after partial release of hydrogen under normal conditions. The broken line - see the text

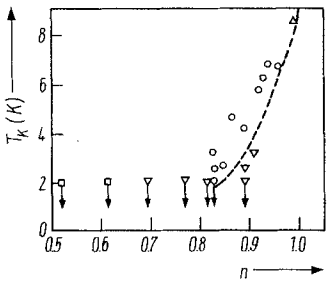

Fig. 3. Superconducting transition temperature, T_k, as a function of hydrogen concentration, n, of the Pd-Au alloys with △ 0, ○ 3, ▽ 9, □ 22.5 at% Au. Symbols with arrows stand for the samples possessing no superconductivity at $T \geqq 2$ K. The broken line shows the $T_k(n)$ dependence for the Pd-H solutions /2/

for $n \gtrsim 0.6$ we used the data of /13/ for the Pd-H γ_2 solutions. As is seen from Fig. 2, the values $\Delta V_o(n)$ for the samples of both series synthesized in the present work agree well with this dependence. Thus, one can ascertain that only ordinary γ-solutions on the base of the starting disordered Pd-Au alloys are formed in the Pd-Au-H system at high pressure and $T \leqq 350$ °C.

The samples of hydrogen solutions in alloys containing $\geqq 22.5$ at% Au obtained in the present work were revealed to possess no superconductivity at $T \geqq 2$ K. To get a more comprehensive information on the $T_k(n)$ dependences for the $Pd_{97}Au_3$-H and $Pd_{91}Au_9$-H solutions we have prepared additional samples by exposure to $P_{H_2} \leqq 8$ GPa and $200 \leqq T \leqq 350$ °C for 24 h. The width of the steps observed on the temperature dependences of the signal of disbalance of an ac bridge in the ranges of sample transition to the superconducting state did not exceed 0.15 K which was indicative of a homogeneous hydrogen distribution over the samples volume. The T_k values were estimated from the step midpoint locations. The results of measurements are depicted in Fig. 3. As is seen from the figure, the $T_k(n)$ dependences for the $Pd_{97}Au_3$-H and $Pd_{91}Au_9$-H solutions are close to that for the Pd-H solutions.

Thus, the gold alloying of palladium, as well as copper and silver alloying /3/, does not result in a distinct increase in T_k of the Pd-H solutions in the case of the sample hydrogenation under conditions close to thermodynamical equilibrium ones. As to the anomalously high T_k values observed in /1/, their appearance seems to be attributable to the specific properties of the metastable state of the thin (≈ 1500 Å) hydrogen-bearing layer obtained during hydrogen implantation at a low temperature.

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