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SUPERCONDUCTIVITY IN HYDROGEN-CHARGED
COPPER-IMPLANTED PALLADIUM

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INTRODUCTION

The palladium-hydrogen system has been studied extensively, but superconductivity in this system was not discovered until 1972 when Skoskiewicz¹ found a maximum transition temperature $T_{c,max} = 6.6$ K for an atom ratio $H/Pd = 0.94$. Since then superconductivity has also been reported² in the Pd-D and the Pd-M-H(D) system where M is one of the noble metals copper, silver, or gold. The highest transition temperature $T_{c,max} = 16.6$ K was observed by Strikzker³ for an alloy with the composition $H/Pd_{55}Cu_{45} \approx 0.7$.

EXPERIMENTAL METHODS

A number of methods have been used to achieve the high H-concentration required for superconductivity in Pd and its alloys.² For PdH_x , these include (a) electrolytic charging at room and dry ice temperature,⁴⁻⁶ (b) high pressure charging using several kbar,⁷ (c) precharging to $H/Pd \approx 0.7$ at 4 bar and 300°C with additional implantation of H at liquid helium temperature,⁸ (d) H implantation only at 4 K into thin evaporated Pd films,⁹ and (e) codeposition of H and Pd at 4 K.¹⁰ Of these, electrolysis at dry ice temperature appears to be most widely used for PdH_x because of its relative ease for reaching $H/Pd \approx 1.0$ with the attendant $T_{c,max} \approx 9$ K. The higher transition temperatures for the Pd alloys, on the other hand, have only been achieved with the precharging-implantation method.³ Of the other methods, only high pressure charging has been reported for the Pd alloys.¹¹ However, the high pressure experiments fail to reproduce the higher transition temperatures achieved with the implantation method.

*References are listed at the end of this report.

Hydrogen solubility in Pd¹² and Pd-Ag alloys¹³ has been studied in some detail. PdH_x forms an isotropically expanded fcc host lattice of Pd in which the H atoms occupy a fraction of the octahedral sites. Below the critical point at $T_{cr} = 565$ K, PdH_x exists in the form of a mixture of low H concentration α phase and high H concentration β phase separated by a miscibility gap. At room temperature the maximum concentration of the α phase and the minimum concentration of the β phase are $\alpha_{max} = 0.008$ and $\beta_{min} = 6.07$, respectively.¹² For Pd-Ag alloys, on the other hand, T_{cr} and β_{min} become progressively smaller with increasing Ag concentration, and the miscibility gap narrows.¹³ The decreased H solubility in Pd-Ag alloys,¹³ and probably other Pd alloys as well, may be a contributing factor for the lack of success in achieving high transition temperatures in uniform alloys using high pressure charging.¹¹

In this report we discuss a new method for producing superconducting Pd-Cu alloys which requires only electrolytic charging at dry ice temperature. Singly charged Cu ions were implanted at 100 keV into 38 μm thick Pd foil (nominal purity 99.99%, Fe content ≤ 10 ppm) to a dose of 8×10^{16} at./cm². The range and range straggling of 100 keV Cu ions in Pd are expected to be $\langle x \rangle = 0.023$ μm and $\sigma = 0.013$ μm , respectively.¹⁴ Because of sputtering¹⁵ the surface will recede during the implantation by several Cu ion ranges and the implant profile will be given approximately by a complementary error function $\text{erfc}[(x - \langle x \rangle)/\sqrt{2}\sigma]$, where x is the depth into the sample. The relative fraction of Cu atoms at the surface under such steady-state conditions is given by the inverse of the Cu self-sputtering yield S_{Cu} . For $S_{Cu} = 4.3 \pm 0.8$,¹⁶ a maximum Cu concentration (atom fraction) of 0.23 ± 0.04 is obtained

at the surface corresponding to a Cu atom density of $(1.6 \pm 0.3) \times 10^{22}$ at./cm³ since Cu can be assumed to be substitutional.¹⁷ The total remaining Cu implant dose calculated from S_{Cu} and the range parameters is $(3.7 \pm 0.7) \times 10^{16}$ at./cm². An independent determination of the implant dose using Rutherford backscattering (RBS) yielded $(2.5 \pm 0.5) \times 10^{16}$ at./cm², a reasonably close value in view of the uncertainties of the experiments, the sputtering yield, and the range parameters. The Cu-implanted foils were epoxied onto a hollow plexiglas tube which held the thermocouple and other needed connections with the implant facing out. Charging with H was performed in an electrolytic bath at dry ice temperature using the method of van Dongen and Mydosh.⁶ Samples charged in this way to $H/Pd \approx 1$ were immediately placed in liquid nitrogen upon removal from the electrolyte. During the subsequent transfer to liquid helium the temperature of the samples never exceeded 77 K.

Four probe dc resistance measurements were made with currents¹⁸ varying from 40 mA to 2 A. Temperature control to about 0.5 K was accomplished by means of a thermal link to the liquid helium bath. Stable temperatures were measured with a thermocouple calibrated at 4.2 K and at the superconducting transitions of Nb, Pb, and V. T_c was defined as the average of the temperatures at 10 and 90 percent of the normal state resistance.

RESULTS

After electrolysis and transfer to the liquid helium bath, the superconducting transition curve was measured. Following this initial measurement the sample was warmed up to increasingly higher temperatures and the transition curves were remeasured. The warming procedure involved withdrawing the sample from the liquid helium bath until it reached a given temperature, then quickly returning it. Figure 1 shows results obtained on a sample following this procedure. Starting with an initial value of 11.1 K, T_c increases to 12.4 K after the sample is warmed to 113 K. Subsequent warmup steps reduce T_c until, after warming to 193 K, T_c begins to increase again, from 10.9 K to 12.4 K. The remaining warmup steps above 203 K all produce a decrease in T_c . The normal state resistance of the sample above the critical temperature remains fairly constant for warmup steps up to 213 K indicating a small loss of H from bulk up to this point.^{1,11} Above 213 K, H is released from bulk as indicated by the increase in normal state resistance.¹⁹ After warmup to 273 K the onset of the superconducting transition is just visible at 4.2 K.

In pure PdH_x , the maximum observed transition temperature is about 9 K for $\text{H/Pd} \approx 1.0$.² Indeed, pure Pd samples studied by us under experimental conditions identical to those for the Cu implanted samples did not exceed $T_c \approx 9$ K. Thus, the elevated T_c values observed in our experiment must be due to the Cu-implanted region. The changes in T_c above 9 K induced by warming up the sample must then be caused changes in H concentration in the implant region since no other atomic species is sufficiently mobile below 273 K.

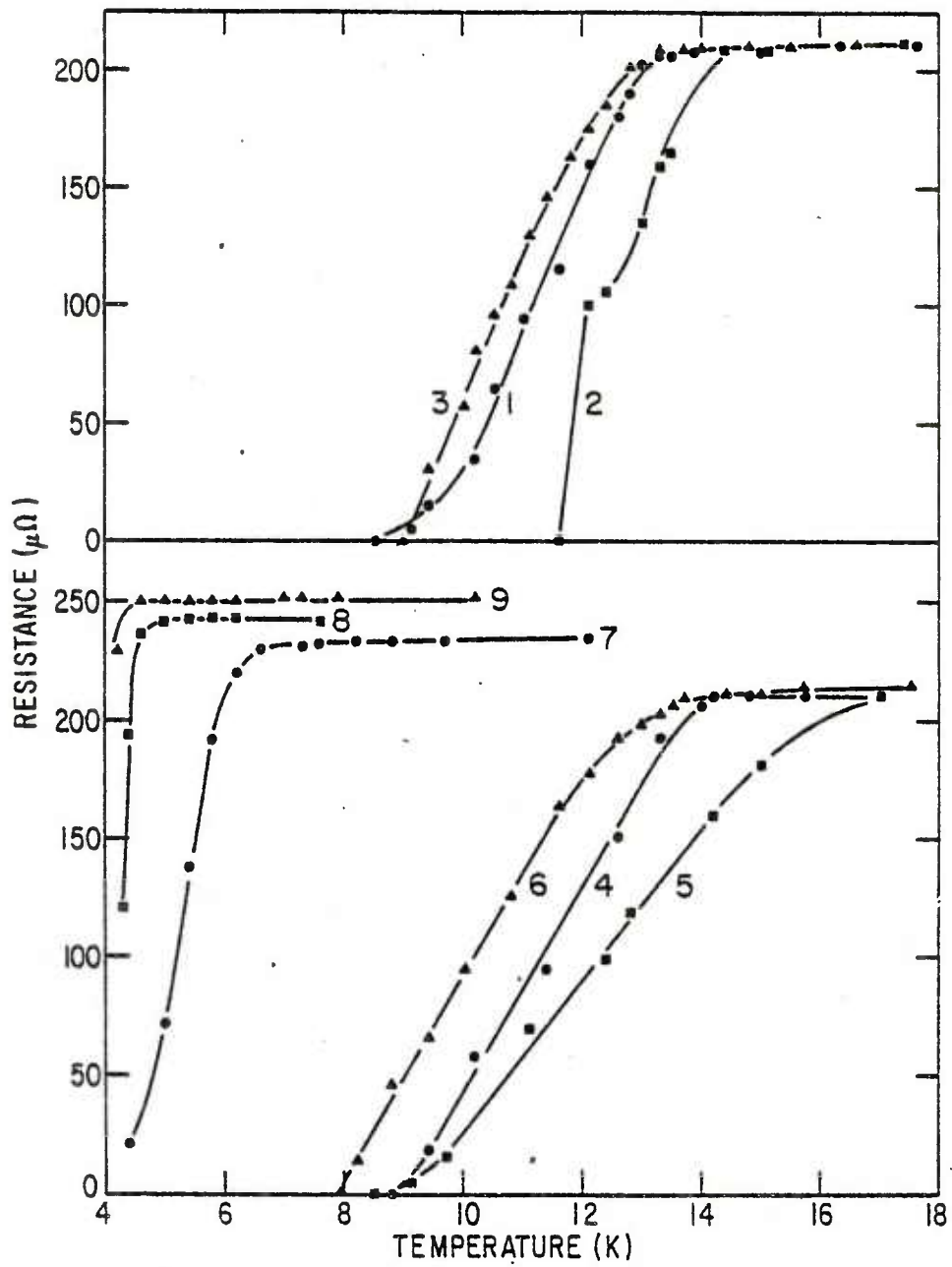


Figure 1. Superconducting transitions measured on a Cu implanted Pd sample immediately after electrolysis at dry ice temperature and transfer to the liquid helium bath (1). Transition curves measured after letting the sample warm up to 113 and 143 K and quickly cooling it again are labeled (2) and (3), respectively. Transition curves measured after warmup to 193, 203, 213, 253, 263, and 273 K are labeled (4) through (9), respectively.

Measurements of the H concentration and depth distribution by nuclear reaction analysis²⁰ in similar samples following the same warmup procedure reveal a strong correlation between H concentration in the implant region and T_c . The fact that both the H and Cu distributions are depth dependent may account for the broadness in some of the higher T_c transition curves.

Our theoretical analysis of the Cu concentration in the implant region suggests an alloy with a maximum concentration of ~ 23 at. percent Cu in Pd occurring at the surface. For a bulk alloy of similar composition, Stritzker³ reports $T_{c,max} \approx 13$ K, in good agreement with our value. However, our transition curves are broader than his, having onset temperatures as high as ~ 16 K. This is a value which in bulk alloys is reached only for concentrations of ~ 40 at. percent Cu. It is unlikely that our concentration is higher than ~ 23 at. percent Cu since the sputtering yield chosen in our analysis¹⁶ is already at the low range of reported values.¹⁵ Furthermore, our RBS data also indicate lower concentrations. A more complete characterization of the samples from both our and Stritzker's³ experiment is clearly desirable.

It has been reported that Pd films condensed onto a cool substrate can be made superconducting by irradiation with He^+ ions at low temperature without H implantation.²¹ Other authors have not succeeded in confirming these results²² but rather have found that the defects produced during irradiation tend to increase the H concentration required for a given value of T_c .⁹ In order to investigate whether damage resulting from the Cu implantation had an effect on T_c , an implanted sample was annealed at 773 K in Ar gas flow for one hour. Using Pd-Cu interdiffusion coefficients extrapolated from the temperature range 1104 - 1334 K,²³ the diffusion length is estimated to be

$\sim 10 \text{ \AA}$, sufficient to anneal defects but not so large as to modify substantially the implanted Cu profile. $T_{C,\text{max}} \approx 11.6 \text{ K}$ was observed for this sample with an onset of the transition curve at $\sim 15 \text{ K}$. Subsequent warmup steps eventually decreased T_C to below 4.2 K . Thus, it would seem that defects produced during Cu implantation have no significant effect on the observed T_C .

As an additional check, another Cu implanted sample was annealed at 973 K for one hour. Since Cu and Pd will interdiffuse by $\sim 0.1 \text{ \mu}$ under these conditions, the maximum Cu concentration in the implant profile will be reduced to less than five percent. Indeed, the maximum transition temperature observed on this sample was 8.8 K , reflecting superconductivity in essentially pure PdH_x .³

CONCLUSIONS

The results reported here indicate that the high transition temperatures in the Pd-noble metal system can be achieved with considerably simpler means than used previously.³ It appears that the pure Pd backing behind the Cu-implanted surface can act as a high concentration H reservoir for the low H solubility Pd-Cu alloy region. This opens up exciting new possibilities for the study and modification of this important system. It will be of interest to extend these measurements to higher Cu concentrations as well as to other implant species. Samples prepared as described in this report are particularly suited for H profiling using nuclear reaction analysis.²⁰ Measurements of the H concentration and distribution in superconducting Pd-noble metal-H systems should be extremely helpful in advancing our understanding of these systems.

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 18. A current of 2 A was passed through the samples while they remained in the superconducting state above 9 K. This result suggests critical currents on the order of 10^6 A/cm² in the implant region of our samples.
 19. Because of the way the sample is mounted, there are two narrow strips along the sample edge which are not exposed to the electrolyte. Thus, as distinct from References 1 and 11, normal-state resistance is only useful as a qualitative measure for H concentration.

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