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Electrical resistivity of palladium-silver alloys at high temperatures

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The electrical resistivity ρ has been measured as a function of temperature T between 300 and 900 K on Pd-Ag alloys containing 30.0-, 34.8-, 40.0-, 44.3-, and 49.9-at.% Ag. All the ρ-vs-T curves are monotonic with respect to T. We do not confirm the minimum at about 700 K in the ρ-vs-T curves observed by Ahmad and Greig. We suggest that the anomalous behavior of ρ results from strain effects and thus is not an intrinsic property of the Pd-Ag system.

INTRODUCTION

Recently, Ahmad and Greig[1] have described a minimum in the electrical resistivity-versus-temperature (ρ-vs-T) curve of $Pd_{60}Ag_{40}$ alloy at about 700 K. This minimum appears to be very similar to that observed in $Ni_{35}Cu_{65}$ alloy at approximately the same temperature. Previous to the work by Ahmad and Greig, the high-temperature minimum in Ni-Cu systems have been attributed to the electron scattering from giant magnetic moments.[2,3] Because of the observed ρ minimum in $Pd_{60}Ag_{40}$, its similarity to the minima in Ni-Cu alloys, and the general chemical similarity between the two alloy systems, Ahmad and Greig concluded that the giant moments are not the cause for the ρ minimum in Ni-Cu alloys. In fact, they suggest that a temperature-dependent decrease in the impurity electrical resistivity brought about by a decrease in the interband s-d scattering with increasing temperature is the mechanism for the ρ minimum in both the systems. Because of the uniqueness of the high-temperature ρ minimum in $Pd_{60}Ag_{40}$ alloy, we decided that it would be of considerable interest to explore this phenomenon further by determining the electrical resistivity of other Pd-Ag alloys. Our results and their implications are briefly described in this paper.

EXPERIMENTAL CONSIDERATIONS

The alloys of $Pd_{1-x}Ag_x$, where $x = 30.0$, 34.8 40.0, 44.3, and 49.9 at.% were prepared by arc melting using facilities and techniques described elsewhere.[4] The source of Pd was 99.99% pure sponge produced by Engelhard Industries, Inc.; 99.999% pure Ag from American Smelting and Refining Co. was used as the second component for making the above binary alloy system. The arc-melted ingots, each weighing about 10 g, were sealed into evacuated silica tubes and homogenized at about 1300 K for 60 h. After this treatment, wires of the cross section of 1 mm^2 were prepared using a wire-drawing facility. These wires were cleaned and resealed into evacuated silica capsules, annealed at 1200 K for 1 h and then rapidly cooled in air without breaking the capsules.

The electrical resistivity measurements were made using the conventional four-probe method. Temperatures above 300 K were produced by a platinum-wound vacuum furnace. The facilities for determining the electrical voltages were the same as used for low-temperature studies described before.[5]

RESULTS AND DISCUSSION

The ρ-vs-T curves between 300 and 900 K of the Pd-Ag alloys described above are shown in Fig. 1. From this plot it is obvious that the temperature dependence of the resistivity for these alloys is simply monotonic. None of the curves exhibit a resistivity minimum of the type observed by Ahmad and Greig[1] in their $Pd_{60}Ag_{40}$ sample. In particular, our sample of the same composition behaves perfectly normal, i.e., ρ gradually increases with increasing temperatures without showing any anomalous behavior.

Figure 2 presents the values of the electrical resistivity of our annealed alloys as a function of Ag

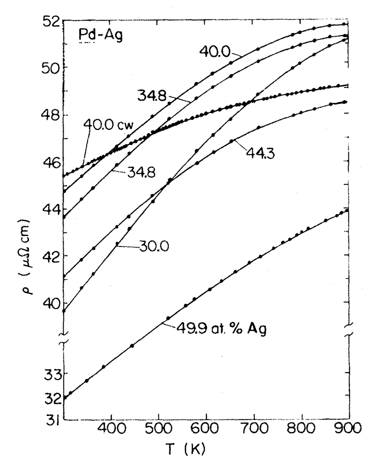

FIG. 1. Electrical resistivity of palladium-silver alloys between 300 and 900 K.

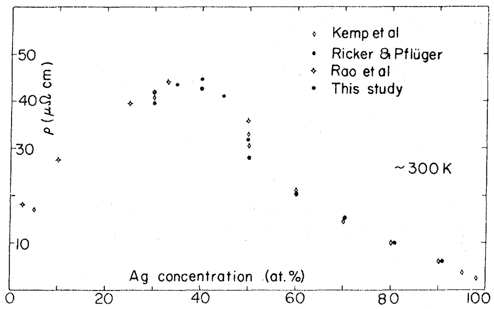

FIG. 2. Electrical resistivity of palladium-silver alloys as a function of silver concentration.

concentration at ~ 300 K. From this plot one sees a smooth curve with a maximum near 40-at.% Ag. Figure 2 also shows the resistivity data for the available concentrations as measured by Kemp *et al.*,[6] Ricker and Pflüger,[7] and Rao.[8] The data points associated with Ricker and Pflüger were estimated from Fig. 1 of Ref. 7. In general, our data are in good agreement with previous studies except with those by Simon[9] (not shown in Fig. 2) which appear to be in error. It should be remarked that an anomalous behavior in the ρ-vs-T curve of $Pd_{60}Ag_{40}$ has also been reported by Ricker and Pflüger[7] in 1966. They observe a maximum in ρ at about 300 K and a minimum in the neighborhood of 500 K. Clearly, the extremum values are at different temperatures than those observed by Ahmad and Greig. The measurements by Ricker and Pflüger[7] in the concentration range of 10–70-at.% Pd, were made on wires of diameter between 0.35 and 0.50 mm and of length between 50 to 100 cm. Their samples were annealed in argon atmosphere for 30 min and then quenched in water. Ricker and Pflüger do not provide any explanation for the anomalous behavior in the ρ-vs-T curve of their $Pd_{60}Ag_{40}$ specimen.

On the basis of our electrical resistivity data on Pd-Ag alloys in the annealed state, we must conclude that the mechanism proposed by Ahmad and Greig may not be applicable to this system. Because we do not confirm their minimum in the annealed $Pd_{60}Ag_{40}$ sample, we feel that their implication about the resistivity minimum in Ni-Cu alloys and its relation to the giant moment clouds is questionable. Ahmad and Greig do not provide any information about the metallurgical history and state of their $Pd_{60}Ag_{40}$ sample. In the $Pd_{1-x}Ag_x$ system, holes first appear at the Fermi level when $x = 0.6$ and the number of these localized pockets of holes increase to have a maximum effect around $x = 0.4$. The Pd-Ag system is therefore rather unique from the viewpoint of the resistivity behavior with plastic deformation. Specifically, Aarts and Houston-Macmillan,[10] Rao,[11] Chen and Nicholson,[12] and Westerlund and Nicholson[13] have clearly demonstrated that between concentrations of 45–80-at.% silver the electrical resistivity initially decreases and then increases with further plastic deformation. Recently, this study has been extended to lower concentrations of silver, to show that this well-known K effect is observed for the Pd-Ag system in the range from about 25 to 80 at.% of silver.[14] Explanations for this observation, which has also been seen in a few other binary systems, have been of two types: First, it has been proposed[15-18] that the resistivity decrease results from the decrease in the short-range order in these alloys due to the cold work introduced. The subsequent increase in resistivity with further straining is expected with the dominance of electron scattering of dislocations. Second, it has been suggested[19] that the above effect on straining results from inhomogeneous dilations which produce a movement of conduction electrons from compressed to expanded regions, giving a shift in local Fermi level with respect to the density of electronic states curve. The experimental evidence,[13] however, seem to favor the former model. We suspect that the anomalous behavior first observed by Ricker and Pflüger and recently reported by Ahmad and Greig is not a unique feature of annealed Pd-Ag system. It appears to us that it is associated with the metallurgical procedures used to make the samples for ρ studies. Specifically, we would like to suggest that the strain effects mentioned above, which could also be induced by rapid quenching are responsible for the anomalous behavior observed. We would like to give some additional information which supports our point of view. A single run on a cold-worked $Pd_{60}Ag_{40}$ wire, prepared by the methods given above was made with increasing temperature. The results are shown in Fig. 1 (curve 40.0 cw). Although this curve does not show a resistivity minimum at elevated temperatures, the temperature dependence of the sample is obviously quite different from that of the annealed specimen. In fact, the magnitude of the resistivity for the cold-worked sample which is larger than that for the annealed one below 400 K is consistently lower than that of the annealed one above 400 K. This indicates that, indeed, cold work considerably influences the shape of ρ-vs-T curves of Pd-Ag alloys with Ag concentrations in the neighborhood of 40-at.% Ag. Further studies on the effects of cold work at different concentrations of Ag in the neighborhood of 40 at.% would be invaluable.

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[1]H. M. Ahmad and D. Greig, Phys. Rev. Lett. 32, 833 (1974).
[2]R. W. Houghton, M. P. Sarachik, and J. S. Kouvel, Phys. Rev. Lett. 25, 238 (1970).
[3]K. Levin and D. L. Mills, Phys. Rev. B 9, 2354 (1974).
[4]S. Arajs and G. P. Wray, J. Phys. E 2, 518 (1969).
[5]S. Arajs, Can. J. Phys. 47, 1005 (1969).
[6]W. R. G. Kemp, P. G. Klemens, A. K. Shreedhar, and G. K. White, Proc. R. Soc. Lond. A 233, 480 (1956).
[7]T. Ricker and E. Pflüger, Z. Metallkunde 57, 39 (1966).
[8]K. V. Rao, Ö. Rapp, Ch. Johannesson, and H. U. Åström, *International Conference on Magnetism* 1976 *Proceedings*, Physica B 406 (1977).
[9]P. R. F. Simon, in *Proceedings of the Ninth International Conference on Low Temperature Physics* (Plenum, New York, 1965), p. 1045.
[10]W. H. Aarts and A. S. Houston-MacMillan. Acta Met. 5, 525 (1957).
[11]K. K. Rao, Acta Met. 10, 900 (1962).
[12]W. K. Chen and M. E. Nicholson, Acta Met. 12, 687 (1964).
[13]R. W. Westerlund and M. E. Nicholson, Acta Met. 14, 569 (1966).
[14]K. Thygesen, K. V. Rao, S. Arajs, J. I. Budnick, and T. J. Burch, Bull. Am. Phys. Soc. 21, 803 (1976). Although this abstract refers only to measurements on $Pd_{50}Ag_{50}$ matrix and its alloys with different concentrations on Fe, similar studies for other binary PdAg hosts with Ag concentrations down to 25% were also reported at this conference. A detailed paper on these results will be published elsewhere.
[15]E. Klockholm and B. Hyatt, Trans. Am. Inst. Min. Metall. Engrs. 215, 792 (1959).
[16]W. Köster and T. Halpern, Z. Metallkd. 52, 821 (1961).
[17]U. Dehlinger, Z. Metallkd. 53, 577 (1962).
[18]J. B. Gibson, J. Phys. Chem. Solids 1, 27 (1956).
[19]H. J. Logie, J. Jackson, J. C. Anderson, and G. R. N. Nabarro, Acta. Met. 9, 707 (1961).