Effect of oxygen on the electronic properties of Pd

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Low-field magnetization measurements on ion-implanted Pd-O foils predoped with Fe are presented. It is demonstrated that oxygen causes a significant reduction in the ferromagnetic Curie temperatures of the samples. Two separate effects are observed. First, an increase occurs in the critical concentration required for ferromagnetism, at a rate of about 70%/at. % O. This increase is associated with large defect clusters stabilized by the oxygen during implantation. Secondly, a decrease is found of dT_C/dx_{Fe}, the rate at which the Curie temperature increases with the Fe concentration, with an initial decrease of 25%/at. % O. This effect is attributed to a reduction by the same amount of the Pd density of states by oxygen.

INTRODUCTION

The basic question of the solubility of oxygen in Pd is still unanswered. Early studies by Raub and Plate[1] concluded that Pd has a large solubility for oxygen of approximately 0.4 at. % at 1200 °C. Recent surface-sensitive studies[2,3] pointed to a subsurface oxygen state; however, the predicted solubility is considerably less than that given by Raub and Plate. Finally, the recent work of Park and Alstetter[4] places the solubility limit of oxygen in Pd in the ppm range. Thus the two reported values of solubility differ by 5 orders of magnitude.

In an effort to quantify the effect of oxygen in solid solution on the electronic properties of Pd, we recently implanted a known amount of oxygen into Pd foils.[5] These foils were predoped with small amounts of Fe— just enough to make the implanted regions ferromagnetic. Using the ferromagnetic transition temperature T_c as a probe for the density of states at the Fermi energy of Pd, we concluded that oxygen reduces the Pd density of states at the significant rate of 25%/at. % O.[5]

In this Brief Report we describe an extension of our earlier work[5] to higher Fe concentrations for a more systematic study of this effect. We now find that in addition to reducing the Pd density of states, oxygen in solid solution in Fe-doped Pd also increases the critical concentration of Fe required for long-range ferromagnetic order in Pd-Fe alloys. We attribute this latter effect to extended defect clusters, stabilized by the oxygen during the implantation process, in agreement with earlier results.[6]

EXPERIMENTAL DETAILS

The samples were prepared in the Ion Implantation Facility at the Institut für Nukleare Festkörperphysik of the Kernforschungszentrum Karlsruhe (Karlsruhe, Germany). The implantation parameters were the same as previously used.[5] The starting material was high-purity Johnson-Matthey Pd foil of 0.35 mm thickness (impurity concentration was less than 25 ppm) cut into 4×12-mm^2 pieces. These pieces were then subjected to Fe$^+$ implantation at an ion energy of 175 keV, yielding a Gaussian Fe concentration profile of 50 nm range (distance of maximum of Fe profile below the surface of the foil).[5] The total Fe$^+$ fluence was chosen so as to yield Fe concentrations in the maximum of the profile in the range $0.75 \le x_m \le 2.64$ at. % Fe. This concentration range was considerably larger than that previously used[5] and allowed for a much more precise determination of the effect of oxygen on the electronic properties of Pd, as discussed below. The absolute accuracy of x_m, the maximum of the Fe-concentration profile, is only about 30% due to uncertainties in the model calculations.[6] However, the relative accuracy is much better, estimated at about 1%.[6] The absolute value for x_m was adjusted by requiring that the critical concentration for ferromagnetism agrees with that of bulk alloys[7] (see below).

After taking magnetization measurements to determine the ferromagnetic Curie temperature T_{Cm} associated with the maximum in the Fe-concentration profile, all samples were then subjected to oxygen implantation. The O$^+$ implantation energy was 65 keV, i.e., the energy required to yield an oxygen-concentration profile peaked at the same range as that for the Fe$^+$ implantations.[5] Thus the maximum of the oxygen-concentration profile coincides with that of the Fe profile at about 50 nm below the Pd foil surface.[5,6] Initially, all samples were subjected to an O$^+$ implantation as to yield a maximum in the oxygen-concentration profile of $x_m = 0.95$ at. % O. The calculated oxygen concentrations were scaled by the same factor as the Fe concentration (see above). After measuring the magnetization of all samples, they underwent a second identical oxygen implantation, now yielding a new maximum oxygen concentration of $x_m = 1.90$ at. %, twice the previous value.

The magnetization was measured in a low-field magne-

tometer employing a commercial superconducting quantum-interference device (SQUID) probe.[8] The magnetization of the samples was measured upon warming in a field of 1 G, after initially cooling the samples in the same field to 4.2 K. The samples were oriented with the foil surface parallel to the field. The sensitivity of the magnetometer was about 5×10^{-8} emu. The Earth's magnetic field was shielded to less than 0.05 G by a μ-metal shield.[8]

RESULTS AND DISCUSSION

Figure 1 displays a typical set of magnetization measurements as a function of temperature in a magnetic field of 1 G. The samples are ion-implanted binary Pd-Fe foils. The concentrations given refer to the maximum value of the concentration profile x_m (see above). As has been observed previously,[5,6] the magnetization curves for the various concentrations are essentially shifted horizontally on the temperature scale. The shape of these curves is determined by the Fe-concentration profile and also by the magnetic anisotropy. The exact shape is difficult to interpret and we have no explanation for the fact that the magnetization-versus-temperature curves in this experiment are curved more than in two previous ones.[5,6] The main purpose, however, is only to obtain an accurate, relative value for the highest Curie temperature, corresponding to the maximum Fe concentration at the center of the profile. This can be easily achieved by parallel shifting the M-versus-T curves so that they all coincide. This fixes their relative T_{Cm} to an accuracy of better than ± 2 K. The absolute value for T_{Cm} is then fixed by arbitrarily setting its value for the highest Fe concentration to 60 K, the temperature of the onset of magnetization for this sample (Fig. 1).

The effect of oxygen on the ferromagnetic transition is demonstrated in Fig. 2 for one Fe concentration. As has been previously observed, the decrease of the ferromagnetic transition due to oxygen doping is pronounced. Again, using the parallel-shifting procedure, we find a decrease of T_{Cm} from 60 K to 45.2 K and 35.2 K for the two oxygen-doping levels of 0.95 and 1.90 at. %, respectively.

All our present results are summarized in Fig. 3, where we display T_{Cm} for the binary Pd-Fe foils and those doped with the two different oxygen levels, versus the Fe concentration (concentration in the maximum of the implanted profile). For comparison we also show the Curie temperatures of bulk Pd-Fe samples.[5,8,9] As mentioned above, the absolute values for the Fe concentrations of the implanted foils were fixed by requiring that the linear extrapolation of the bulk data and those of the implanted binary foils to the concentration axis yield the same concentration (the so-called critical concentration for ferromagnetism), in agreement with earlier results.[5,6,10]

The difference in the slope dT_C/dx_{Fe} between the bulk alloys and implanted binary foils (42.4 versus 24.6 K/at. % Fe) is partly due to radiation defects, which decrease the Pd density of states, as has been shown earlier,[5,6] and partly due to the uncertainty in determining T_{Cm}, the maximum Curie temperature of the center of the profile. The concentration of radiation-induced defects is known to saturate in metals at fairly low fluences and does not change any more in the range of fluences used here,[5,6] i.e., all Fe-doped foils have approximately the same amount of radiation defects.

We observe large changes in T_C versus x_{Fe} as oxygen is implanted into the Pd foils predoped with Fe (Fig. 3). Unlike our earlier study, where x_{Fe} was less than 1.1 at %,[5] it is now clear that the critical concentration, i.e., the linear extrapolation to the concentration axis, has increased significantly for the oxygen-doped samples. The change in the critical concentration is from 0.17 at. % Fe for the binary foil to 0.28 and 0.41 at. % Fe, for the oxy-
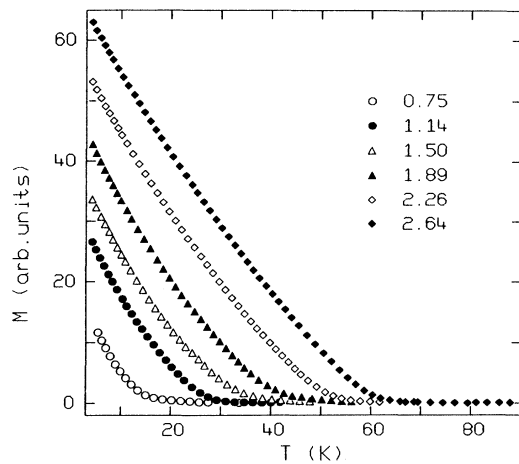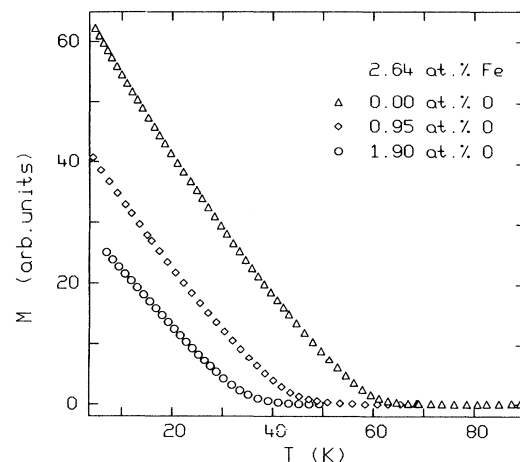

FIG. 1. Magnetization in 1 G measured upon warming after initially cooling in the same field to 4.2 K, for various Fe-doped foils. The numbers refer to x_{Fe}, the Fe concentration (at. % Fe) in the maximum of the implanted Fe-concentration profile.

FIG. 2. Same as Fig. 1 for a Pd foil with $x_{Fe} = 2.64$ at. % Fe without oxygen and also implanted with 0.95 and 1.90 at. % oxygen.

60

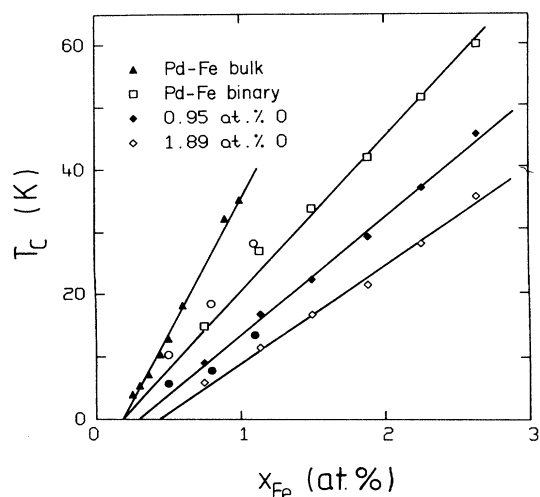▲ Pd-Fe bulk
□ Pd-Fe binary
◆ 0.95 at.% O
◇ 1.89 at.% O

T_C (K)

40

20

0

0   1   2   3

x_{Fe} (at.%)

FIG. 3. T_C vs Fe concentration for bulk alloys (▲), implanted binary foils (□), and the same foils after oxygen implantation of 0.95 at.% (◆) and 1.90 at.% (◇). Also shown are previous results from Ref. 5 for implanted binary foils (○), and the same foils implanted with 2 at.% oxygen (●).

gen concentrations of 0.95 and 1.90 at.%, respectively. Thus the change in the critical concentration is essentially linear in the oxygen concentration at 73%/at.% O. Also shown in Fig. 3 are the T_C values for our previous work for x_{Fe}=0.5, 0.8, and 1.1 at.% Fe, both for the binary foils and those doped with 2 at.% oxygen. The T_C values from our previous work are somewhat higher than our present data. This may be due to somewhat different target temperatures leading to a different defect concentration being stabilized during the implantation process. However, the relative changes induced by the oxygen implantation are compatible with our present results, with the exception of the 0.5-at.% Fe sample. We do not have any explanation for the previously measured anomalously high-T_C value for the 0.5 at.% Fe sample doped with 2 at.% oxygen[5] (Fig. 3). This high-T_C value led to our erroneous conclusion that the critical concentration is not affected by the oxygen implantation.[5]

The critical concentration for ferromagnetism is determined by the percolation threshold of the polarization clouds which are formed when the Fe moments polarize the surrounding Pd matrix. The spatial extent of these clouds is responsible for the value of the critical concentration, and as long as this spatial extent of the polarization clouds does not change with alloying, the critical concentration should remain unchanged. To a first approximation, this spatial extent is determined by the Fermi momentum,[12] and small changes in the electron concentration from alloying dilute amounts as for the present alloys should have little effect on this parameter. Indeed, we have shown that the addition of 2 at.% B (Ref. 5), 2 at.% S (Ref. 11), or 2 at.% F (Ref. 11) does not change

the critical concentration of Fe-predoped Pd foils. Also, bulk Pd-Mn alloys have a similar critical concentration as Pd-Fe despite the fact that the moment associated with a Mn atom is considerably smaller than that of a Fe atom.[12] Thus the change in the critical concentration due to the oxygen seems to be an exception.

In previous studies of ion implantation it has been shown that oxygen present in small amounts in solid solution in the target material has the tendency to stabilize extended defect clusters.[6] If we assume for simplicity that the Pd susceptibility in these clusters has been significantly reduced, then any Fe atom located by chance inside these clusters will not be able to produce a polarization cloud and therefore will no longer participate in the long-range ferromagnetic order. Thus, in the presence of these large defect clusters, more Fe is needed to reach the percolation threshold and the critical concentration is increased. This mechanism, which would qualitatively explain our present results, was also invoked to explain earlier low-temperature implantation results on oxygen-contaminated Pd films implanted with Fe.[6] However, no direct observation of this "swiss-cheese-like" structure of the exchange-enhanced Pd susceptibility is available at present. Other experiments, such as Mössbauer-effect measurements, need to be performed. The observation of a strong paramagnetic line in Fe Mössbauer studies in ferromagnetic, highly disordered, oxygen-contaminated Pd-Fe films may be related to our findings.[13]

Whereas the critical concentration for ferromagnetism depends solely on the diameter of the polarization clouds, the variation of the ferromagnetic transition temperature T_C with the Fe concentration sensitively depends on the magnitude of the magnetic moment associated with a given cloud.[12] This magnetic moment, in turn, depends sensitively on the density of states at the Fermi energy, which is greatly reduced upon alloying. For example, it is known that boron, when added to Pd, reduces its density of states at the Fermi energy at a rate of 12%/at.% B.[14] From our previous experiments on Fe-doped Pd-B foils,[5] we have shown that this decrease causes a decrease in dT_C/dx_{Fe} by exactly the same amount. We thus concluded[5] that dT_C/dx_{Fe} is a good measure of the density of states at the Fermi energy. For our present study we find values for dT_C/dx_{Fe} of 24.6, 19.0 and 15.6 K/at.% Fe for the binary foil, the 0.95-at.%, and the 1.90 at.% oxygen-doped foils, respectively. This then corresponds to a decrease of the density of states at the Fermi energy of 25%/at.% O and 20%/at.% O for 0.95 and 1.90 at.% O respectively, i.e., almost linear in the oxygen concentration. These results are in good agreement with our earlier result of 25%.[5]

In summary, we have shown that oxygen implanted into Fe-predoped Pd foils has two separate effects. First, it uniformly decreases the density of states at the Fermi energy of Pd by an initial rate of about 25%/at.% oxygen, a very significant reduction. Second, by stabilizing large defect clusters during the implantation process, oxygen increases the critical concentration of Fe required for ferromagnetism, at a rate of about 70%/at.% oxygen.

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