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Low-temperature electrical resistivity of as-cast glassy, relaxed, and crystallized $Pd_{40}Cu_{30}Ni_{10}P_{20}$ alloys

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Abstract

Low-temperature (300–4.2 K) electrical resistivity behaviours of as-cast glassy, relaxed, and crystallized $Pd_{40}Ni_{10}Cu_{30}P_{20}$ alloys have been investigated. It is found that the resistivity of the as-cast glassy alloy is about 257 $\mu\Omega$ cm at ambient temperature and decreases with a temperature coefficient of resistivity (TCR) of 2.1×10^{-4} K^{-1} in the temperature range of 280–50 K and 89×10^{-4} K^{-1} in the temperature range of 12–4.2 K. The relaxation effect slightly increases the resistivity by a factor of about 10% while crystallization decreases the resistivity of the alloy. Surprisingly, we found that all samples, as-cast glassy, relaxed, crystallized, and well-crystallized alloys, exhibit similar temperature dependences of the electrical resistivity in the temperature range investigated. TCR changes at around 10–20 K for all samples are linked with rapid increase of the magnetization in the alloys.

Research into bulk metallic glass is currently one of the most dynamic areas of materials science, in which multicomponent alloys with a good glass-forming ability and wide supercooled liquid region have been fabricated [1, 2]. PdCuNiP is known to be one of the best glass-forming systems for forming glasses with a diameter of up to 72 mm [3]. A number of viscosity [4], diffusion [5], density [6], thermal expansion [7], structure [8], specific heat capacity [9], ultrasonic [10], crystallization at ambient pressure [11–16] and at high pressure [17], time-dependent nucleation [18], statistical variation of the nucleation process [19], multi-glass transition [20, 21], and thermal conductivity [22] measurements have been performed on the glassy system. High-temperature (above 300 K) electrical resistivity measurements as a probe for glass and crystallization transitions were reported for

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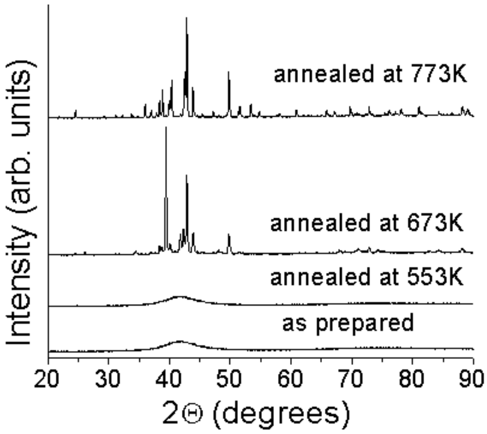

Figure 1. X-ray diffraction patterns recorded for the as-cast glassy, relaxed, and crystallized $Pd_{40}Cu_{30}Ni_{10}P_{20}$ alloy.

the $Pd_{40}Ni_{10}Cu_{30}P_{20}$ glassy alloy [23]. In this paper, we report low-temperature (below 300 K) electrical resistivity behaviours of as-cast glassy, relaxed, and crystallized $Pd_{40}Ni_{10}Cu_{30}P_{20}$ alloys, in which low-temperature electronic transport behaviours of the alloys will be obtained.

A master alloy ingot with the composition of $Pd_{40}Cu_{30}Ni_{10}P_{20}$ was prepared by arc melting a mixture of pre-alloyed $Pd_{60}P_{40}$, Pd, Ni, and Cu of purity ranging from 99.9 to 99.999 at.%, together with B_2O_3 flux in a purified argon atmosphere. B_2O_3 flux was used in order to enhance the glass-forming ability of the alloy by eliminating the heterogeneous nuclei. A glassy rod sample of 5 mm in diameter and 50 mm in length was prepared by a Cu-mould casting method. The rod has a shiny surface and no indication of interaction between rod and Cu mould was detected. The formation of a single glassy phase in the samples was confirmed by x-ray diffraction (XRD) and transmission electron microscopy measurements. The XRD patterns were recorded using a Philips PW 1820 diffractometer with Cu Kα radiation. Thermal analyses were performed in a Perkin-Elmer differential scanning calorimeter DSC 7 at a heating rate of 20 K min^{-1} under a flow of purified argon. It was found that the sample exhibits an endothermic event characteristic of the glass transition at $T_g = 575$ K, followed by one exothermic event indicating a eutectic crystallization process at $T_x^{onset} = 666$ K. These data agree well with the data reported in the literature for this alloy [10, 11, 20]. Heat treatments of the as-cast glassy alloy were performed in a quartz tube with a vacuum of 10^{-5} mbar at 553, 673, and 773 K for 2 h to fabricate relaxed, crystallized, and well-crystallized samples of the alloy, respectively. Electrical resistivity measurements were done with standard four-probe techniques using alternating currents of order 10 mA at frequencies below 100 Hz and lock-in detection of the voltage drops. Most measurements mapping out the temperature dependences were performed on 5 mm diameter disc-shaped samples with a thickness of about 0.5 mm. Measurements of relative changes after heat treatments were done using a precision sample mount with contact needles, while absolute values of resistivity were established using samples shaped as elongated bars. Measurements were repeated four times for all samples. Magnetization measurements were performed in a commercial SQUID magnetometer in the range $1.8 \text{ K} \leqslant T \leqslant 100$ K under applied fields up to 200 Oe. Small discs about 1.5 mm in diameter were cut and mounted with their surface parallel to the applied field.

Figure 1 shows x-ray diffraction patterns recorded for as-cast glassy, relaxed, crystallized, and well-crystallized $Pd_{40}Ni_{10}Cu_{30}P_{20}$ alloys. It is clear that during heat treatment at 553 K, the

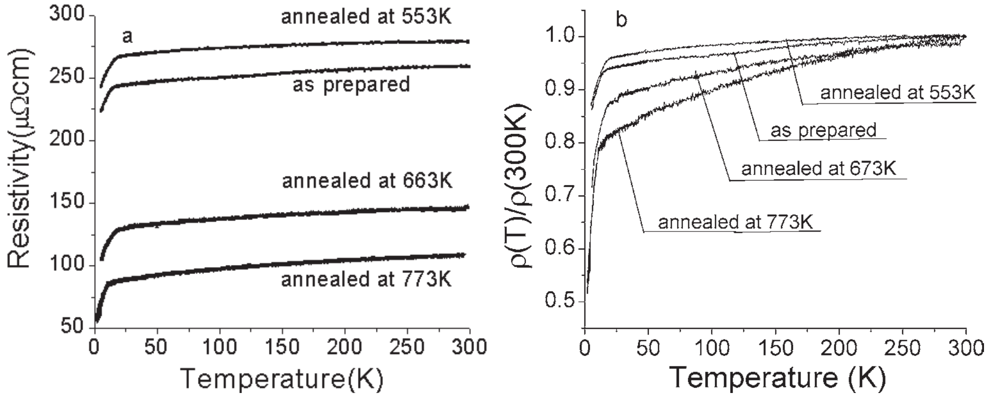

Figure 2. (a) Low-temperature (300–4.2 K) electrical resistivity for the as-cast glassy, relaxed, and crystallized $Pd_{40}Cu_{30}Ni_{10}P_{20}$ alloy. (b) Reduced electrical resistivity for the as-cast glassy, relaxed, and crystallized $Pd_{40}Cu_{30}Ni_{10}P_{20}$ alloy.

Table 1. Electrical resistivity, ρ, at 300 K, temperature coefficients of resistivity (TCR), and the kink temperature, T_{kink}, of as-cast glassy, relaxed, and crystallized $Pd_{40}Ni_{10}Cu_{30}P_{20}$ alloy.

			TCR (10^{-4} K^{-1})	
Sample	ρ ($\mu\Omega$ cm)	T_{kink} (K)	280–50 K	12–4.2 K
As cast	257	15	2.1	89
553 K	284	16	1.2	77
673 K	147	18	3.5	142
773 K	108	12	6.0	199

sample still retains the amorphous structure, while for annealing at 663 and 773 K, the samples are in crystalline states. The well-crystallized sample consists of at least five intermetallic compounds reported in [20] while the sample annealed at 663 K contains metastable crystalline phases, which transform into more stable intermetallic compounds obtained in the sample annealed at 773 K. Figure 2 shows low-temperature electrical resistivity data for the four samples in the temperature range of 300–4.2 K. The resistivity of the as-cast sample is found to be about 257 $\mu\Omega$ cm at ambient temperature, which is similar to the values reported for the same alloy [23]. The temperature coefficients of resistivity (TCR) and the kink temperatures (T_{kink}), below and above which the value of the TCR dramatically changes, are listed in table 1. It is found that resistivity decreases with decreasing temperature with a positive TCR of $(1.2\text{–}6.0) \times 10^{-4}$ K^{-1} in the temperature range of 280–50 K. In the range of 280–250 K, the TCR becomes smaller and approaches zero. By combining high-temperature resistivity data reported for the same alloy (small negative TCR $= -0.81 \times 10^{-4}$ K^{-1} at 300 K) [23] with our low-temperature data, it seems that at around 300 K, the TCR of the $Pd_{40}Ni_{10}Cu_{30}P_{20}$ bulk glass changes from positive to negative. At temperatures below about 20 K (the kink temperature), the resistivity decreases much faster having a TCR of $(77\text{–}199) \times 10^{-4}$ K^{-1} in the temperature range of 12–4.2 K for all samples regardless of the structure state. The resistivity was measured down to 1.7 K. Neither an increase in slope nor a turn to a rise were detected. We also found that structural relaxation enhances the resistivity of the amorphous alloy while crystallization decreases the resistivity. How can one explain the existence of the kink temperature? No structural transition and no dramatic change in specific heat capacity were detected in the alloy [24]. To answer this question, we further performed magnetization measurements on

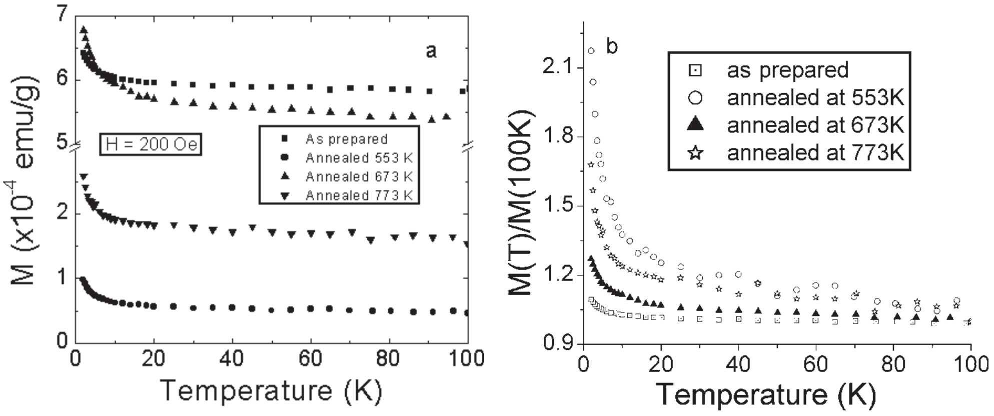

Figure 3. (a) Low-temperature (100–4.2 K) magnetization for the as-cast glassy, relaxed, and crystallized $Pd_{40}Cu_{30}Ni_{10}P_{20}$ alloy. (b) Reduced magnetization for the as-cast glassy, relaxed, and crystallized $Pd_{40}Cu_{30}Ni_{10}P_{20}$ alloy.

the same samples, as shown in figure 3. It can be observed that magnetization increases monotonically with decreasing temperature for all samples studied. However, below about 20 K (the kink temperature) it increases rapidly. This is more clearly seen from the departure from linearity in the reduced magnetization versus temperature plot in figure 3(b). We further performed zero-field-cooled (ZFC) and field-cooled (FC) dc magnetization measurements from 300 to 1.8 K at an applied field of 200 Oe for the as-prepared sample. It was found that there was no difference between the ZFC and FC magnetization curves in the temperature range of 1.8–300 K, indicating neither spin-glass nor ferromagnetic behaviour in the alloy at temperatures above 1.8 K. The ZFC and FC data could be fitted by a modified Curie–Weiss law [25], from which we deduced the effective moment per Ni atom to be 0.0596 μ_B. This value is in good agreement with 0.054 μ_B reported for a melt-spun amorphous $Ni_{80.2}P_{19.8}$ alloy [26]. The results observed here suggest that the rapid enhancement of the magnetization below about 20 K could reduce the scattering of electrons, resulting in a rapid decrease in resistivity of the alloys, as observed in figure 2. More magnetization measurements below 1.8 K would be useful to clarify the nature of spin–spin interactions in the alloys if they exist.

Following the Ziman theory [27–29], the resistivity of liquid metals or solid amorphous metals is proportional to the structure factor $S(k)$ at $2k_F$, the wavevector spanning the Fermi surface. For $Pd_{40}Ni_{10}Cu_{30}P_{20}$ bulk glass, it was found that the first peak of $S(k)$ becomes lower at the peak position, k_p, and broader as temperature increases in the temperature range above 300 K [21]. Structural relaxation in the glass could sharpen the first peak of $S(k)$ [30]. The differences between as-cast and relaxed samples mentioned above might be qualitatively explained as follows. When $2k_F$ for the $Pd_{40}Ni_{10}Cu_{30}P_{20}$ alloy is located between k_1 and k_2 in figure 4, $S(2k_F)$ increases after structural relaxation and it also increases from T_1 to T_2. Consequently, an enhancement of resistivity in the relaxed sample and a positive TCR are expected according to the Ziman theory, as observed in figure 2. When the sample crystallizes, atomic ordering arrangement substantially reduces the electronic scattering, resulting in a reduction of resistivity. In the sample annealed at 773 K, fewer defects, e.g., grain boundaries and chemical non-stoichiometry for the intermetallic compounds, are expected as compared to the sample annealed at 663 K. Thus, the resistivity becomes even lower, as observed in figure 2. Similar results were also reported for the PdNiP system [31].

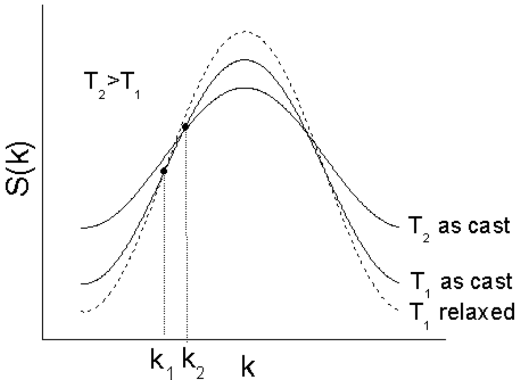

Figure 4. An illustration of possible interrelations of thermal and structural relaxation effects of the structure factor for the $Pd_{40}Cu_{30}Ni_{10}P_{20}$ bulk glass; $T_2 > T_1$.

Acknowledgments

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