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2003 J. Phys.: Condens. Matter 15 4809

(http://iopscience.iop.org/0953-8984/15/27/312)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **15** (2003) 4809–4815 PII: S0953-8984(03)59752-1

Superconductivity of bulk $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ metallic glass

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Received 19 February 2003, in final form 5 June 2003
Published 27 June 2003
Online at stacks.iop.org/JPhysCM/15/4809

Abstract

Results of superconducting transition temperature measurements are presented for the bulk metallic glass $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ before and after annealing. The superconducting critical temperature T_c is 1.84 K for the as-prepared metallic glassy sample and 3.76 K for the annealed sample at zero magnetic field, respectively. The temperature gradient $(-\mathrm{d}H_{c2}/\mathrm{d}T)_{T_c}$ of the upper critical field H_{c2} near the critical temperature T_c of the bulk metallic glass $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ is about 2.5 T K^{-1}. Annealing of the metallic glass leads to a decrease of $(-\mathrm{d}H_{c2}/\mathrm{d}T)_{T_c}$ to 1.2 T K^{-1}. The origin of the reduction of the critical temperature T_c in the amorphous $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ is ascribed to a smearing of the density of states by the disordered atomic structure.

Metallic glasses have long represented an intriguing class of materials. However, studies of the low-temperature properties of metallic glasses have been impeded by the inability to prepare bulk specimens of the conventional metallic glasses. Recently, a new class of 'bulk' metallic glass (BMG) has been developed that forms alloys through the conventional casting process at a low cooling rate [1–5]. Although these BMGs, which have a large three-dimensional supercooled liquid region, offer new opportunities for investigating the physical properties of BMGs through various physical methods, few investigations of superconductivity in BMGs have been reported so far. The differences between the superconductivities of glassy and crystalline states are significant for understanding the unique microstructural characteristics and nature of the BMGs. In this work, we present the results of low-temperature electric transport and superconductivity in the representative BMG $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ and its corresponding crystallized state.

Ingots of the glass with nominal composition $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ were synthesized from a mixture of pure elements in an arc-melting furnace under a Ti-gettered

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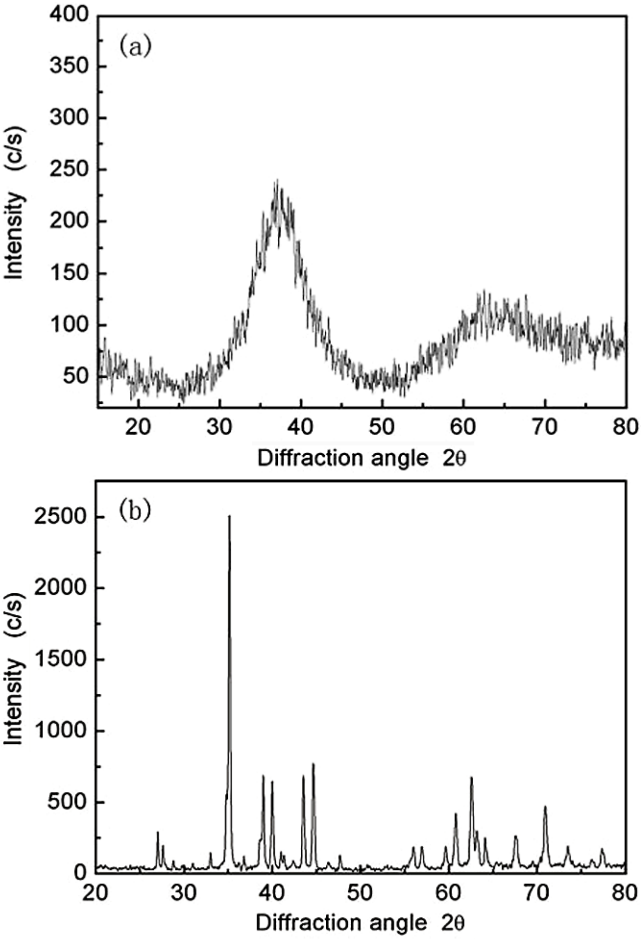

Figure 1. XRD patterns of the same $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ sample (a) before and (b) after annealing at 820 K for 20 min.

Ar atmosphere. The bulk amorphous alloy with dimensions of $2 \times 12 \times 50$ mm^3 was prepared by sucking the re-melted alloy into the copper mould. The details of the preparation procedure can be referred to in [6–8]. The amorphous nature of the sample that was cast was verified using x-ray diffraction (XRD) with Cu Kα radiation and differential scanning calorimeter (DSC). Specimens with the dimensions $1 \times 2 \times 10$ mm^3, for use in the superconductivity study, were cut from the cast rod. The fully crystallized alloy was prepared by annealing the as-prepared BMG at a temperature of 820 K with a vacuum of 1.5×10^{-3} Pa for 20 min. The annealing temperature is far higher than the glass transition temperature T_g ($T_g = 623$ K) and the crystallization temperature T_x ($T_x = 698$ K). Electrical resistivity was measured as a function of temperature by PPMS (a Physical Property Measurement System, made by Quantum Design, USA) using a standard four-probe technique.

Figure 1 shows the XRD pattern from the transverse cross section of our samples (the surface of 2×50 mm^2) before and after annealing. The pattern of figure 1(a) consists only of a broad peak, with no diffraction peaks corresponding to crystalline phases. It can be seen that, in figure 1(b), the sample is fully crystallized after annealing at temperature 820 K for 20 min.

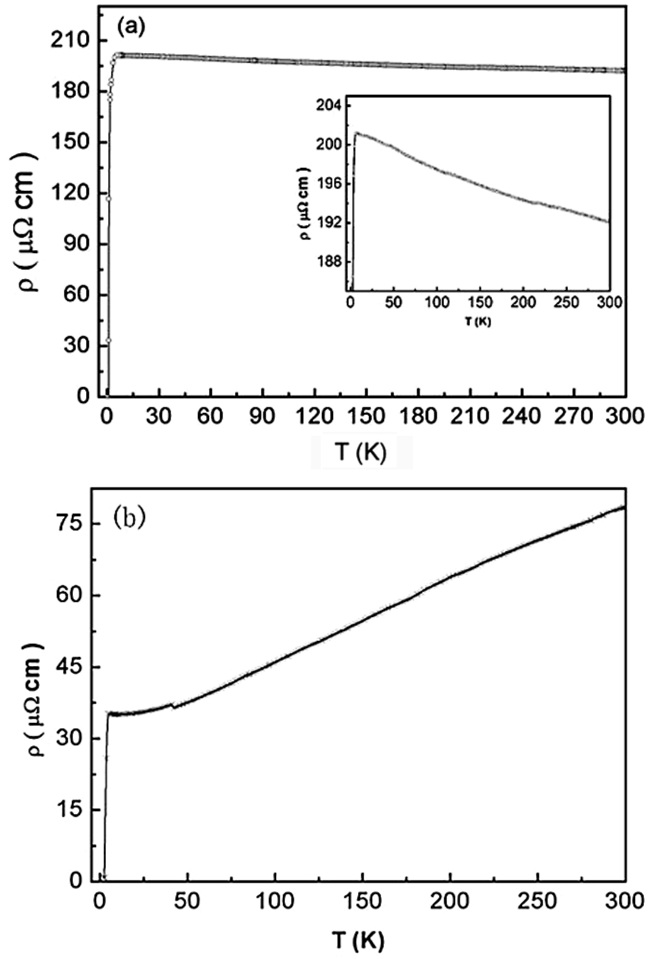

Figure 2. Resistivity as a function of temperature of the (a) amorphous and (b) annealed samples of $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$.

The resistivity of the amorphous (A) and annealed (B) samples was measured from room temperature down to 1.5 K. Figure 2 shows the temperature dependence of the electrical resistivity ρ of the amorphous and annealed samples. Annealing results in a drop of the room temperature resistivity from 190 $\mu\Omega$ cm for the amorphous sample A to 78 $\mu\Omega$ cm for the annealed sample B. The temperature dependence of resistivity is semiconductor-like with $\mathrm{d}\rho/\mathrm{d}T < 0$ for the sample A, and it changes to the metallic-like ($\mathrm{d}\rho/\mathrm{d}T > 0$) for the annealed sample B. Between 4.2 and 300 K, the total variations $|\rho(4.2\ \mathrm{K})/\rho(300\ \mathrm{K})|$ are 1.06 for sample A and 0.45 for sample B, respectively.

According to the Mooij correlation [9], the slope $\mathrm{d}\rho/\mathrm{d}T$ becomes negative above a critical resistivity $\rho_c = 150\ \mu\Omega$ cm. In the light of more available data, this critical resistivity was not universally accepted [10], but there is still agreement on a system-dependent ρ_c. The negative slope in $\rho(T)$ is related to disordered atomic structure in the glassy state. The amorphous sample A with room-temperature resistivity of 190 $\mu\Omega$ cm demonstrates a negative slope of $\mathrm{d}\rho/\mathrm{d}T$.

The superconductivity phenomenon was observed in the $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ alloy. The low-temperature resistivity and the superconducting transition temperatures, T_c, of the

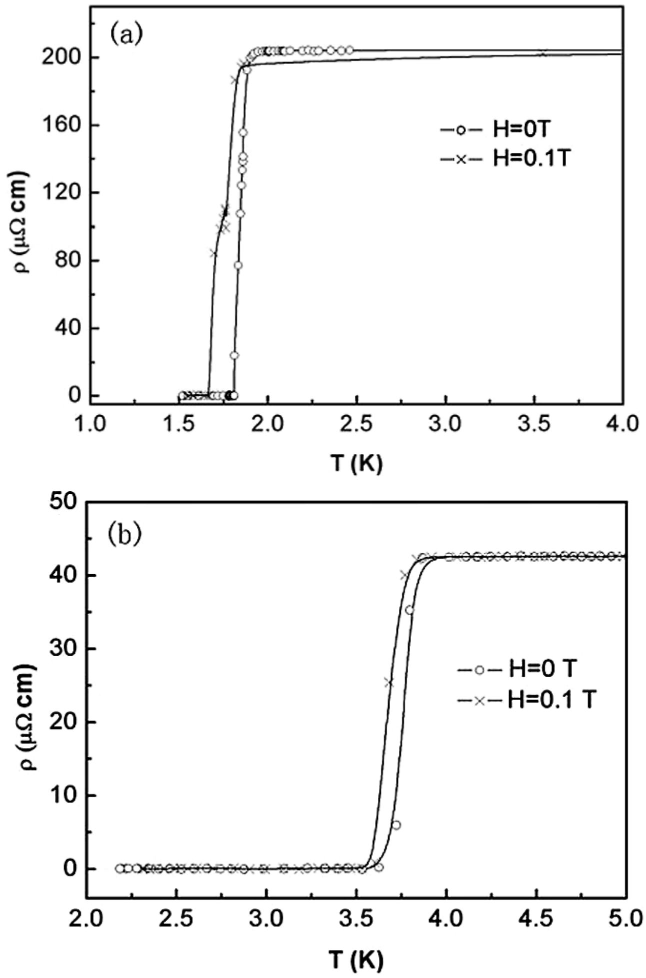

Figure 3. The superconducting transition of the (a) amorphous and (b) annealed samples of $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ at zero and 0.1 T applied magnetic field.

amorphous (A) and annealed (B) samples are plotted in figure 3. As shown in figures 2 and 3, both the amorphous (A) and annealed (B) samples pass the superconducting transition at low temperature. The critical temperature, T_c, is defined at the point at which the resistivity reaches half of its normal-state value. A sharp resistive transition with $T_c = 1.84$ K is observed for the amorphous sample A. For the annealed sample B, a much broader transition with the critical temperature $T_c = 3.76$ K is observed. The transition width in zero field, ΔT_c—taken as the temperature interval where the resistivity changes from 10 to 90% of the normal-state value—was 70 mK for the amorphous sample A and 0.17 K for the annealed sample B, respectively. The sharp resistive transition (transition width $\Delta T_c = 70$ mK), indicative of a single phase, hints at rather good homogeneity of the BMG.

The measurement of the field-dependent resistivity was carried out in two ways. In the first, applying a constant magnetic field (0.1 T), the resistivity of the BMG $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ as a function of temperature was measured. In the second, the temperature is fixed and the field is varied from $H = 0$ to 40 kOe. The results of the first set of

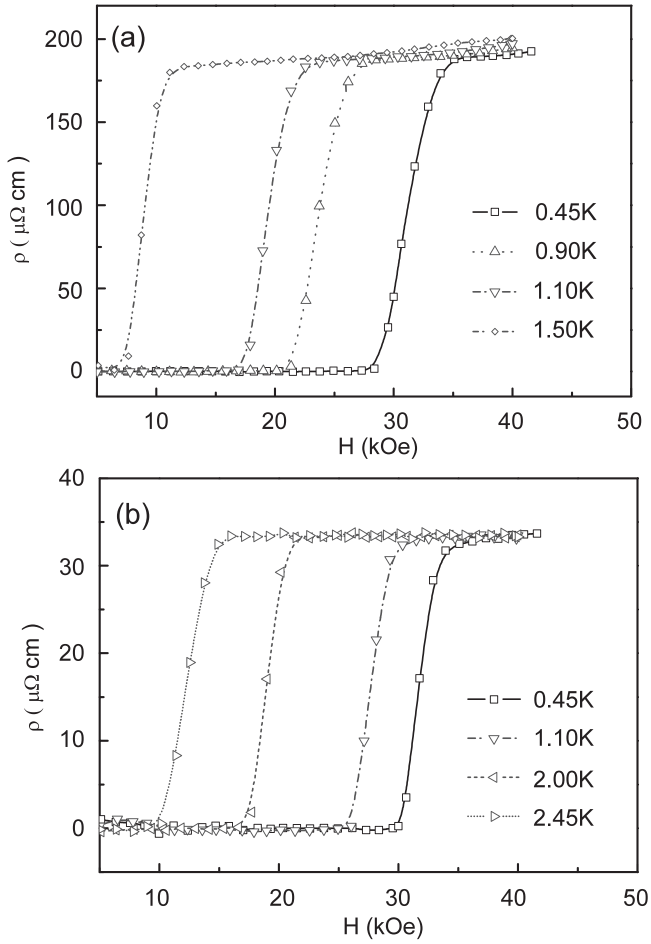

Figure 4. The resistivity of the (a) amorphous and (b) annealed samples as a function of magnetic field at different temperatures.

measurements are also shown in figure 3. It is clear that the superconducting transition width, ΔT_c, is broadened by the applied magnetic field. The resistive transition as a function of applied field, as measured at constant temperature with the applied field perpendicular to the direction of current flow, is shown in figure 4. The upper critical field H_{c2}, defined as a mid-point of the transition, is plotted in figure 5 as a function of temperature. All $H_{c2}(T)$ curves are of approximately parabolic form. In the vicinity of T_c the upper critical field, H_{c2}, varies linearly with temperature. The temperature gradient $(-\mathrm{d}H_{c2}/\mathrm{d}T)_{T_c}$ near T_c of amorphous (A) and annealed (B) $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ is about 2.5 and 1.2 T K^{-1}, respectively. The upper critical field H_{c2} at zero temperature, H_{c2} (0), was estimated to be 3.6 T for the amorphous sample (A) and 3.2 T for the annealed sample (B), respectively. Preliminary measurements indicate that annealing effects have an influence on the parabolic behaviour of $H_{c2}(T)$ and on the slope near T_c. At present the PPMS system cannot complete the measurement of the magnetization and Meissner effect. This will be done as soon as possible in our work in the near future.

The origin of the reduction of the critical temperature, T_c, in the amorphous $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ is not fully understood at present. An explanation for the T_c

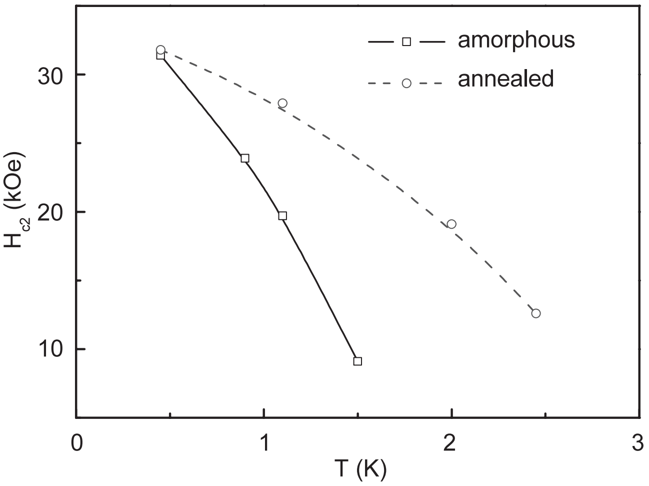

Figure 5. The upper critical field H_{c2} of the (a) amorphous and (b) annealed samples as a function of temperature.

of the amorphous sample (A) reported here is based on a smearing of the density of states by the disordered atomic structure, as has been proposed in [11–13]. This argument states that, because of a short mean free path in the disordered alloys, the electron energy states are broadened and the sharp structure in the density of states perhaps averaged over energy, which results in those alloys with a lower T_c in the amorphous state. The filamentary superconductivity, which still needs to be addressed, cannot be ruled out because of the very limited measurements on the topic that we present here. A further study of experiments and the superconducting mechanism for the BMG will be carried out in our future work.

A study of the electronic properties and superconductivity of the BMG $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ has been presented. The $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ metallic glass exhibits negative temperature coefficients of the resistivity between about 4.2 and 300 K, whereas the crystallized sample shows positive temperature coefficients of the resistivity down to the superconducting transition temperature. At zero magnetic field, the superconducting transition is sharp (transition width $\Delta T_c = 70$ mK) with critical temperature $T_c = 1.84$ K for the amorphous sample. After annealing, the transition width of the crystallized sample is broadened to be $\Delta T_c = 0.17$ K, with $T_c = 3.76$ K. The measured slope $(-\mathrm{d}H_{c2}/\mathrm{d}T)_{T_c}$ is about 2.5 and 1.2 T K^{-1} for the amorphous and annealed samples, respectively. It is hoped that these results will stimulate the theoretical interest to account for the experimental results.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (grant numbers 50171075, 50225101 and 50031010). Stimulating discussions with Prof W H Wang, Dr M X Pan, Dr X N Jing and Dr J L Luo are greatly appreciated.

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