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Superconducting properties of Be-Zr glassy alloys obtained by liquid quenching

R. Hasegawa and L. E. Tanner

Materials Research Center, Allied Chemical Corporation, Morristown, New Jersey 07960

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Based on x-ray diffraction, electrical resistivity, critical field, glass transition, and density measurements, several superconducting properties of glassy Be_xZr_{100-x} ($30 < x < 45$) alloys are studied. The transition temperature increases from about 1 K for $x = 45$ to 2.8 K for $x = 30$; this is attributed to the increase of the degree of disorder as Be concentration decreases. The glassy alloys are characterized as type-II medium-coupled superconductors with $\lambda = 1$ to 1.5 and with a high Ginzburg-Landau parameter of about 60.

I. INTRODUCTION

A wide variety of noncrystalline metallic films, obtained by vapor deposition on substrates at liquid-helium temperature, have been found to exhibit superconductivity.[1] These noncrystalline films are, in general, characterized as strong-coupled superconductors with the energy gap Δ given by $\sim 2.25k_BT_c$ and with the electron-phonon coupling parameter λ in the vicinity of 2. An additional characteristic of this class of superconductors is the softening of the phonon spectrum with an enhanced phonon density of states at small energies.[2,3] Although the critical temperatures of some amorphous vapor-quenched films are higher than liquid-helium temperature, these materials transform into crystalline phases(s) below at least 20 K. For example, amorphous Ga has $T_c = 8.6$ K and crystallizes at 15 K.[2]

Except for the systematic study of critical temperatures,[4] there has been little work reported on vapor-deposited amorphous transition metals.[5] The critical temperatures of these films as a function of the electron per atom ratio ($\mathfrak{z}$) follow a triangular shape, peaking at $\mathfrak{z} = 6.8$ for the 5*d* series. Collver and Hammond[4] have pointed out that this finding cannot be explained fully on the basis of the smearing of the density of states due to atomic disordering as proposed previously.[6]

Although the vapor-quenched amorphous films provide unique opportunities to study superconducting properties in noncrystalline solids, their thermal instability even at room temperature and the thickness limit (<1000 Å) make these materials less practical in technical applications. Moreover, voids and gaseous inclusions inherent to vapor-deposited films make quantitative property studies difficult. An attempt to synthesize thick glassy superconducting foils has been made for alloys in the Pd-Zr binary system.[7] A glassy $Pd_{35}Zr_{65}$ alloy has a value of $T_c = 3.5$ K.[7] More recently superconductivity has been found in glassy Au-La (Ref. 8) and Zr-Rh (Ref. 9) alloys. These liquid-quenched alloys are more densely packed than vapor-deposited films and are stable at room temperature, hence they are better suited for both fundamental and applied studies. We have recently found superconductitivy in binary Be-Zr glassy alloys obtained by rapid quenching from the melt; our findings are the subject of the present report.

II. EXPERIMENTAL DETAILS

Metallic Be-Zr glassy alloys are easily fabricated in the form of continuous ribbons (~30 μ thick and 1–2 mm wide) by means of liquid-quenching at rates exceeding 10^5 K/sec.[10] The glass formation range is from 30- to 50-at.% Be bracketing the eutectic (at 34.8-at.% Be; eutectic temperature 1238 K) and approaching the composition of the compound Be_2Zr.[11] The glassy structure was confirmed by x-ray diffraction using Cu $K\alpha$ radiation. A typical pattern showing broad intensity maxima is given in Fig. 1 and was obtained from the $Be_{30}Zr_{70}$ alloy. The thermal behavior of the glassy alloys was examined by means of differential scanning calorimetry using a continuous-heating rate

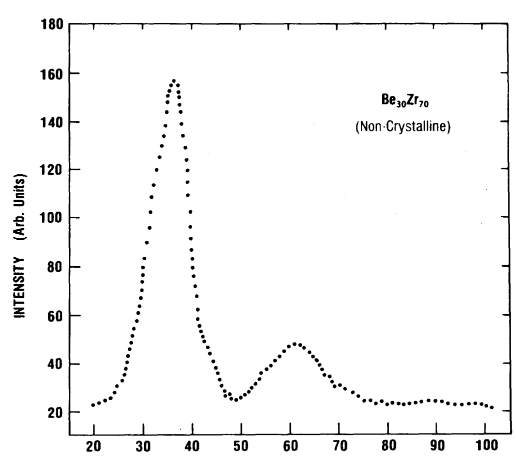

FIG. 1. X-ray-diffraction pattern for the $Be_{30}Zr_{70}$ glassy alloy.

of 20 K/min up to 1000 K. The thermograms show well-defined glass transition temperatures T_g which increase monotonically from 598 K at 30-at.% Be to 670 K at 50-at.% Be. Crystallization begins within 50 K of T_g in all alloys and produces the equilibrium phases α-Zr (hcp) and the phase Be_2Zr (hexagonal $C32$, B_2Al type).

The resistivities of the glassy alloys were measured by a conventional four-probe method with a current of about 100 μA in the temperature range 1.9–200 K. The absolute accuracy of the resistivity was about ±10% and its relative value was accurate to within 10 ppm. The accuracy of the temperature was better than ±0.01 K in the vicinity of 2 K. The densities of the ribbons were determined by comparing the specimen weight in air and in Bromoform (CBr_4; density: 2.865 g/cm^3) at room temperature.

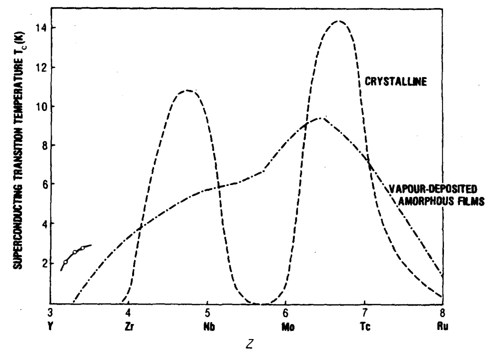

FIG. 3. Critical temperature vs electrons per atom ratio for the $4d$ transition-metal series. The data for the amorphous vapor-quenched films were taken from Ref. 4. The T_c values of the glassy Be-Zr alloys are shown by circles connected by a solid line.

III. RESULTS AND DISCUSSION

Examples of the resistivity ratio ρ_S/ρ_N (where subscripts S and N denote superconducting and normal, respectively) for the glassy Be-Zr alloys are shown in Fig. 2. The transition is sharp with a temperature width of less than 0.1 K, which is indicative of a single-phase glass. The normal resistivity, ρ_N, slightly above T_c ranges between 200 and 300 $\mu\Omega$cm. In Fig. 3 the values of T_c of the liquid-quenched glassy alloys are compared with those of the vapor-deposited amorphous films[4] and crystalline metals of the $4d$ transition-metal series. The T_c values for alloys having Be contents between 45 and 50 at.% were not determined because they fall below the lower limit of our apparatus (~1.9 K). The trend shown in Fig. 3, however, suggests that T_c for the $Be_{45}Zr_{55}$ alloy is approximately 1 K. The results of the measurements of the upper critical field H_{c2} in the vicinity of T_c are shown in Fig. 4.

The residual resitivities at 4.2 K (Table I) may give the values of the electron mean free path l. For $Be_{30}Zr_{70}$ the value of l is estimated to be about 2.0 Å by assuming two free electrons per atom. This assumption may be valid for Be, but not for Zr which has two $4d$ electrons. However, a recent systematic study[12] of the superconducting properties for various metals indicates a reasonable agreement between the theory and experiment for elemental Zr when the Fermi energy E_F and the density of states at $E_F, N(E_F)$, are taken as 8.2 eV and 0.63/(eV spin), respectively. In addition, an earlier specific-heat study on Zr gives $N(E_F) = 0.42/(\text{eV atom})$.[13] These values are close to $E_F = 8.0$ eV and $N(E_F) = 0.35/(\text{eV atom})$ obtained in the free electron model when two free electrons per atom is assumed for the present glassy system. The superconducting transition temperatures in noncrystalline metal alloys exhibit a smooth variation with composition,[4] which may be interpreted as a result of the short electron mean free path in glassy metals. Thus, a drastic change of $N(E_F)$ by alloying is not expected, which may justify the use of two electrons per atom for the noncrystalline Be-Zr alloys.

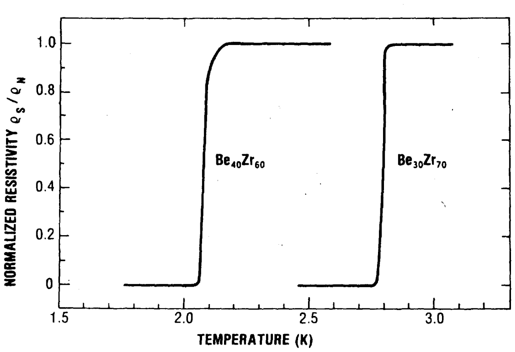

FIG. 2. Resistivity ratio ρ_S/ρ_N as a function of temperature for $Be_{30}Z_{70}$ and $Be_{40}Zr_{60}$ glassy alloys.

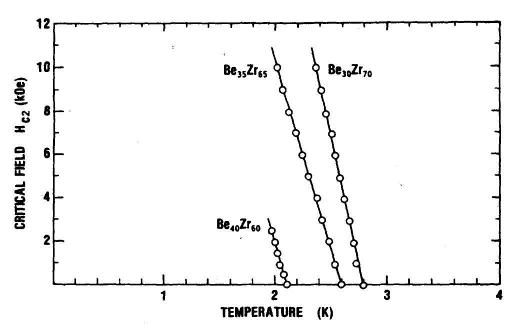

FIG. 4. Upper critical field as a function of temperature. The circles correspond to the midpoint of the normal-to-superconducting transition.

TABLE I. Superconducting properties of Be-Zr alloys.

Alloy	$T_c(K)$	$\Delta T_c(K)$	ρ(4.2K) ($\mu\Omega$ cm)	dH_{c2}/dT (kOe/K)	D^* (cm^2/sec)	λ	$N^*(E_F)$ (eV^{-1}atom^{-1})	d (Å)	Density (g/cm^3)	T_g (K)
$Be_{30}Zr_{70}$	2.80	0.01	294.0	−23.8	0.46	1.5	0.89	3.6	5.72	598
$Be_{35}Zr_{65}$	2.60	0.08	231.9	−17.0	0.65	1.2	0.77	4.9	5.65	613
$Be_{40}Zr_{60}$	2.10	0.01	282.1	−20.0	0.55	1.2	0.76	4.1	5.55	623
$Be_{45}Zr_{55}$	$\lesssim 1$	···	281.2	···	···	···	···	···	5.35	648

An extended Ginzburg-Landau-Abrikosov-Gorkov (GLAG) theory[14,15] gives

$$dH_{c2}/dT\,|_{T\to T_c} = -\eta(4k_B e/\pi)\rho N^*(E_F)\,, \qquad (1)$$

where $N^*(E_F)$ is the dressed density of states at the Fermi surface, ρ is the resistivity. The quantity η is an enhancement factor, taking the value of 1 for weak-coupled superconductors. Although many noncrystalline metal superconductors are classified as strong-coupled superconductors, the factor η for these materials is in the vicinity of 1.[1,16] We thus take $\eta = 1$ and obtain the values of $N^*(E_F)$ for the Be-Zr alloys by using Eq. (1) and Fig. 4. The results are listed in Table I. The quantity $N^*(E_F)$ is related to the electron-phonon coupling parameter λ through $N^*(E_F) = (1+\lambda)N(E_F)$, where $N(E_F)$ is the bare density of states at Fermi level E_F. The parameter λ, thus determined from the ratio $N^*(E_F)/N(E_F)$ and listed in Table I, ranges between 1 and 1.5. Accordingly, the glassy Be-Zr alloys may be classified as medium-coupled superconductors. For the transition temperature of disordered or amorphous superconductors, Garland obtained[17]

$$T_c = \frac{\langle\omega^2\rangle^{1/2}}{k_B} \times \exp\left(-\frac{1+\lambda}{0.52[1+\langle\omega^2\rangle^{1/2}/\omega_0][1-(\langle\omega\rangle/\omega_0)\mu^*]-\mu^*}\right), \qquad (2)$$

where μ^* is the Coulomb pseudopotential, and $\langle\omega\rangle$ and $\langle\omega^2\rangle$ are the average and the squared phonon energy, respectively. The energy ω_0 is the upper end point of the phonon spectrum and may be compared to the Debye temperature Θ_D. Equation (2) may be comparable to the McMillan formula[18] for T_c when $\langle\omega^2\rangle^{1/2} \lesssim \omega_0 \sim k_B\Theta_D$ and $\langle\omega\rangle/\omega_0 = 0.62$. The value of Θ_D for the $Be_{30}Zr_{70}$ alloy is estimated to be about 33 K if the McMillan formula is used by taking $\mu^* = 0.13$ as is usually the case.[19] The unusually small value of Θ_D is due to the large value of $\langle\omega\rangle/\omega_0$ assumed in the McMillan formula. This suggests that the average phonon energy must be shifted, relative to the crystalline case considered by McMillan, toward lower energies in the present case as in other noncrystalline superconductors.[20] The subtle difference of the shift among the glassy Be-Zr alloys may be reflected in the values of λ (Table I). According to McMillan,[18] the quantity $M\lambda\langle\omega^2\rangle$ should be constant for a given class of materials, where M is the atomic mass. Since both the density and the value of λ are larger for the $Be_{30}Zr_{70}$ alloys than those for the $Be_{40}Zr_{60}$ alloy (Table I), a larger shift of the center of gravity of the phonon spectrum toward a lower phonon energy for the former than the latter alloy may be expected. If such a trend toward a softer phonon spectrum is related to the degree of disorder as has been argued,[21] the degree of disorder increases as Be content decreases in the Be-Zr glassy system. This seems to be the case because the glass transition temperature T_g decreases with the lowering of the Be content[22] (see Table I). We may thus conclude that the increase of T_c or λ with decreasing Be in the Be-Zr glassy system is due to the increase of the degree of structural disorder.

The coherence length ξ_0 is about 8.3×10^{-5} cm for the $Be_{30}Zr_{70}$ alloy ($T_c = 2.8$ K). Thus, some insight into the superconducting properties of the present glassy alloys may be obtained by analyzing our data in the framework of "dirty limit" ($l \ll \xi_0$) superconductors. The temperature dependence of the coherence length $\xi(t)$ and the penetration depth $\lambda(t)$ are given by [23,24]

$$\xi(t) = 0.85(\xi_0 l)^{1/2}(1-t)^{-1/2}\,, \qquad (3)$$

$$\lambda(t) = 0.615\lambda_L(0)(\xi_0/l)^{-1/2}(1-t)^{-1/2}\,, \qquad (4)$$

where $t = T/T_c$ and $\lambda_L(0)$ is the London penetration depth. Using the values of ξ_0 and l obtained above, we have $\xi(t) = 1.10\times10^{-6}(1-t)^{-1/2}$ for the $Be_{30}Zr_{70}$ alloy. The GLAG theory, on the other hand, yields $\xi(t) = [\phi_0/2\pi H_{c2}(t)]^{1/2}$ where ϕ_0 is the flux quantum.

Using the data of Fig. 4, we obtain $\xi(t)=0.71 \times 10^{-6}(1-t)^{-1/2}$ for $Be_{30}Zr_{70}$. Therefore, the above choice of values of ξ_0 and l is internally consistent. The Ginzburg-Landau parameter κ can now be estimated as ~60 from Eq. (3) and Eq. (4), suggesting a type II behavior with a high κ value. In the framework of the free-electron model, Eq. (1) can be rewritten as

$$\left.\frac{dH_{c2}(T)}{dT}\right|_{T\to T_c} = -4k_B c/\pi e D^*, \tag{5}$$

where $D^*=v_F^* l/3$ is the dressed diffusivity.[25] The values of D^* are determined from the data of Fig. 4 and are listed in Table I. In a study of several noncrystalline superconductors obtained by liquid quenching, Johnson and Poon[26] have obtained an empirical relation, $D^*=0.134d\ -0.014$, between D^* and the nearest-neighbor (nn) distance d. The results of nn distance obtained through this formula are listed in Table I. The relatively large values of the nn distance of 4–5 Å reflect the low density (~5.5 g/cm^3) of the Be-Zr alloys.

Based on the data presented here, several concluding remarks can be made: The glassy Be-Zr alloys can be classified as type-II medium-coupled superconductors with a large Ginzburg-Landau parameter ($\kappa \sim 60$). This differs from the case of the nontransition-metal amorphous films which have been identified as strong-coupled superconductors with λ in the vicinity of 2. The critical temperature of the glassy alloys ranges between 1 and 3 K. The increase of T_c as Be content decreases is attributed to the increase of the degree of structural disorder rather than a change in the electronic structure of the materials.

ACKNOWLEDGMENTS

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