Enhanced superconductivity in Hf-base metallic glasses

Emil Tafra\textsuperscript{1}, Mario Basletic\textsuperscript{1}, Ramir Rustic\textsuperscript{2}, Emil Babic\textsuperscript{1} and Amir Hamzic\textsuperscript{1}

\textsuperscript{1} Department of Physics, Faculty of Science, PO Box 331, HR-10002 Zagreb, Croatia
\textsuperscript{2} Department of Physics, University of Osijek, PO Box 125, HR-31000 Osijek, Croatia

Received 4 April 2008, in final form 3 September 2008
Published 25 September 2008
Online at stacks.iop.org/JPhysCM/20/425215

Abstract
A systematic study of electrical resistivity of Hf\textsubscript{100}−\textit{x}Fe\textsubscript{x} (\textit{x} = 20, 25), Hf\textsubscript{100}−\textit{x}Cu\textsubscript{x} (\textit{x} = 30, 40, 50) and Ti\textsubscript{65}Cu\textsubscript{35} metallic glasses has been done in the temperature range 0.3–290 K, and in magnetic fields \textit{B} \leq 5 T. All Hf-base alloys are superconducting with \textit{Tc} \geq 0.44 K, which is well above the \textit{Tc} of pure crystalline Hf (0.13 K). From the initial slopes of the upper critical fields, (d\textit{Hc2}/d\textit{T})\textsubscript{\textit{Tc}}, and resistivities we determined the dressed electronic densities of states, \textit{N}(\textit{E_F}), for all alloys. Both \textit{Tc} and \textit{N}(\textit{E_F}) decrease with increasing \textit{x} (Fe and Cu content). The results are compared with those for corresponding Zr-base metallic glasses and ion-implanted Hf films.

1. Introduction
Glassy TE–TL alloys (TE and TL being the early and late transition metal, respectively) have been extensively studied in recent decades [1] and the interest in these alloys further increased after the discovery of TE–TL-base bulk metallic glasses [2–4]. These studies revealed several unusual phenomena [5–8], which has led to the development of novel concepts for the calculation of their properties [9, 10]. In TE–TL alloys the composition range for the formation of the amorphous state by rapid quenching from the melt is quite wide and in favourable cases it spans from 20 to 70 at.% of the TL component. Such a broad composition range enables a detailed study of the changes in the electronic band structure and properties on alloying through a comparison between the model and experiment [1, 11, 12].

In nonmagnetic amorphous TE–TL alloys, several properties which are related to the electronic density of states (DOS) show a simple, sometimes linear, variation with TL content [1, 6, 7, 11–16]. These simple variations of the properties correlate with ultraviolet photoemission spectroscopy (UPS) results for the same alloy systems [1, 17], which showed that DOS at the Fermi level (\textit{E_F}), \textit{N}(\textit{E_F}), is dominated by TE d-states. Accordingly, in amorphous TE–TL alloys, the effect of alloying with TL can be approximated with the dilution of amorphous TE [13]. So far, a majority of the results on TE–TL alloys has been obtained for Zr–TL metallic glasses, rendering a comparison between alloy systems based on different TE (e.g. Ti, Zr, Hf) rarely possible [11, 12, 18]. This is particularly true for superconductivity, with only a few results for superconducting transition temperatures \textit{Tc} of Ti-[19] and Hf-base [20, 21] metallic glasses.

Here we report the first, to the best of our knowledge, systematic study of superconductivity in Hf–Fe and Hf–Cu metallic glasses. Our results show that the variation of \textit{Tc} with \textit{x} in Hf\textsubscript{100}−\textit{x}Fe\textsubscript{x} and Hf\textsubscript{100}−\textit{x}Cu\textsubscript{x} glassy alloys is quite similar to that observed in the corresponding Zr\textsubscript{100}−\textit{x}Fe\textsubscript{x} and Zr\textsubscript{100}−\textit{x}Cu\textsubscript{x} metallic glasses [14, 15, 22]. In particular \textit{Tc} decreases with \textit{x} and the rate of decrease is much faster for \textit{x} = Fe than for Cu. The magnitudes of \textit{Tc} in Hf-base alloys are about two times lower than those in the corresponding Zr-base alloys [14, 15, 22]. The dressed density of states at the Fermi level, \textit{N}(\textit{E_F}), also decreases with increasing \textit{x}. Thus, superconductivity in Hf-base alloys is consistent with the ‘split-band’ electronic structure of glassy TE–TL alloys [1, 17, 20].

2. Experimental details
Hf\textsubscript{100}−\textit{x}Fe\textsubscript{x} (\textit{x} = 20, 25), Hf\textsubscript{100}−\textit{x}Cu\textsubscript{x} (\textit{x} = 30, 40, 50) and Ti\textsubscript{65}Cu\textsubscript{35} amorphous ribbons were prepared by melt spinning of master alloys with the predetermined concentration in either a pure Ar [23] or He [24] atmosphere. The ribbons were typically 10 \textmu m (Hf–Fe) and 20 \textmu m (all other alloys) thick and 25 T superconducting magnet. The current...
and Ti65Cu35 agree quite well with our results (table 1).

values for resistivities and TCRs of the corresponding Hf–Cu temperature coefficients of resistivity (TCR). The literature resistivity, $\rho$, for Ti 65Cu35 and selected Hf–Cu, Fe glassy alloys. As propagated into the values of the density of states

$\rho(\text{Alloy}) = 206 \mu\Omega \text{cm}$

$\alpha = -1.2 \times 10^{-4} \text{K}^{-1}$

$T_c = 1.86 \text{K}$

$(d\rho/dT)_{T_c} = 38 \text{K/\Omega K}^{-1}$

$N_f(E_F)$ is the dressed density of states obtained from (1).

Table 1. Measured and calculated parameters for Hf–Fe and Hf–Cu metallic glasses. $\rho$ is resistivity at 2 K, $\alpha$ is the temperature coefficient of resistivity, $T_c$ is the superconducting transition temperature, $(d\rho/dT)_{T_c}$ is the initial slope of the upper critical field and $N_f(E_F)$ is the dressed density of states obtained from (1).

| Alloy      | $\rho$ (\(\mu\Omega\) cm) | $\alpha$ (10^{-4} \text{K}^{-1}) | $T_c$ (K) | $(d\rho/dT)_{T_c}$ (K/\Omega K^{-1}) | $N_f(E_F)$ (states/eV atom) |
|------------|-----------------------------|-----------------------------------|-----------|-------------------------------------|-----------------------------|
| Hf60Fe20   | 206                         | -1.2                              | 1.86      | 38                                  | 2.27                        |
| Hf75Fe25   | 200                         | -2.0                              | 1.12      | 35                                  | 2.14                        |
| Hf60Cu30   | 206                         | -1.3                              | 1.36      | 28.5                                | 1.64                        |
| Hf60Cu50   | 212                         | -1.2                              | 0.82      | 26.1                                | 1.40                        |
| Hf60Cu70   | 210                         | -1.1                              | 0.44      | 23.7                                | 1.16                        |

Figure 1. Temperature dependence of normalized resistance for representative Hf-based metallic glasses and Ti65Cu35 amorphous alloy.

Figure 2. Resistive transitions for Hf-based metallic glasses. For Hf75Fe25 alloy transitions curves in a magnetic field 0 and 0.5 T are shown.

3. Results and discussion

Figure 1 shows the variation of resistance with temperature for Ti65Cu35 and selected Hf–Cu, Fe glassy alloys. As is usual for glassy TE100−xTLx alloys with high resistivity ($\rho > 140 \mu\Omega$ cm) [6, 13, 26] all our samples had negative temperature coefficients of resistivity (TCR). The literature values for resistivities and TCRs of the corresponding Hf–Cu and Ti65Cu35 [6, 26] agree quite well with our results (table 1).

In particular, our $T_c = 2 \text{K}$ resistivities, $\rho(2 \text{K})$, are a few percent higher than the room temperature resistivities, $\rho(290 \text{K})$, of other authors [6, 26, 27].

Figure 2 shows the variations of normalized resistance $R(T)/R(2 \text{K})$ with temperature below 2.5 K for all studied alloys. All Hf–Cu, Fe samples become superconducting within the explored temperature range ($T > 0.3 \text{K}$). Except for the Hf75Fe25 alloy, all other samples show very narrow superconducting transitions with typical widths (from 0.1 to 0.9$\rho(2 \text{K})$) $\Delta T_c \lesssim 0.04 \text{K}$, which can be regarded as an indication of good quality (homogeneity) of the studied samples [13–15, 20, 27]. The transition width for the Hf75Fe25 alloy, $\Delta T_c \cong 0.14 \text{K}$, is somewhat larger but not unusual for amorphous alloys. As illustrated in figure 2 the resistive transition of this alloy became narrower in an applied field, which allowed reliable determination of the variation of the upper critical field with temperature, $H_{c2}(T)$, also for this alloy. The values of superconducting transition temperatures (defined as midpoints of resistive transitions) are given in table 1. Sample Ti65Cu35 showed no sign of superconductivity down to 0.3 K, which is consistent with the reported $T_c \cong 0.06 \text{K}$ for this alloy [19].

In figure 3 we compare the variations of zero-field $T_c$s with concentration $x$ for our Hf100-xFex and Hf100-xCu alloys, with the literature results for Zr–Fe and Zr–Cu alloys [14, 15, 22]. Also shown are the maximum $T_c$s (i.e. the highest attainable $T_c$ in the given TE100−xTLx series) of presumably amorphous Ti–Cu, Hf–Cu and Zr–Cu thin films, obtained by low temperature ion implantation [28], which seem to extrapolate the results for metallic glasses quite well to lower Cu contents. Since there are no previous results for $T_c$ of Hf–Fe, Cu glassy alloys, we can compare our results only with those for splat cooled Hf60Ni30 foil [20] with $T_c = 1.5 \text{K}$. 

2
Judging by the relation between $T_c^{0.8}$ of similar Zr–Ni and Zr–Cu alloys [12, 14, 15, 22], $T_c$ of the Hf$_{70}$Ni$_{30}$ alloy [20] is consistent with $T_c = 1.36$ K for our Hf$_{70}$Cu$_{30}$ alloy. The transition temperatures of pure crystalline (hcp) Zr and Hf (figure 3) are about an order of magnitude lower than the maximum $T_c^{0.8}$ of Zr–Cu and Hf–Cu amorphous alloys. This is qualitatively consistent with the observed [1, 12, 16, 17] and calculated [11, 12] higher $N(E_F)$ in dilute amorphous TE–TL alloys than those of pure crystalline (hcp) TE metals. As seen from figure 3 the variations of $T_c$ with $x$ in Zr–Fe, Cu and Hf–Fe, Cu amorphous alloys are qualitatively very similar; the main difference is that $T_c$'s of Hf–Fe, Cu alloys are about two times lower than those of the corresponding Zr–Fe, Cu alloys. Like in Zr-base alloys the rate of decrease of $T_c$ with $x$ in Hf-base alloys is much faster for Fe than for Cu alloy. This is due to the onset of magnetic correlations such as the spin fluctuations and/or formation of magnetic moments/clusters which cause strong pair-breaking [14, 15, 20, 25].

Lower $T_c$'s of Hf–Fe, Cu alloys, compared to those of Zr–Fe, Cu, are consistent with a decrease of $N(E_F)$ on going from Zr to Hf (due to the increase of the bandwidth), but may also be affected [29] by the different Debye temperatures of Zr- and Hf-base alloys. Unfortunately, there are no measurements of the low temperature specific heat (LTSH) of Hf-base metallic glasses [12] which are necessary in order to explain the difference between $T_c$'s of Zr-base and Hf-base alloy systems. In the absence of LTSH, useful information about the nature of superconductivity in metallic glasses can be obtained from the measurements of upper critical field $H_{c2}(T)$ [14, 15, 20–22, 27, 30]. The variation of $H_{c2}$ with temperature in TE–TL metallic glasses is usually well described by the Werthamer–Helfand–Hohenberg theory [31] and a fit of experimental results to the model enables one to determine the spin–orbit interaction parameter, $\lambda_{so}$, and the Maki paramagnetic limitation parameter $\alpha$ [32]. However, such fits yield reliable results for the above parameters (especially $\lambda_{so}$) only if the measurements extend to sufficiently low temperature, $T/T_c \leq 0.1$ [21]. The $H_{c2}(T)$ variations for our Hf–Fe, Cu alloys are shown in figure 4. $H_{c2}$ was defined with $0.9\rho(2K)$, but—as illustrated for the Hf$_{70}$Fe$_{20}$ alloy—the variation of $H_{c2}$ with $T$ for the $0.5\rho(2K)$ criterion was virtually the same. Due to the low $T_c$ of alloys we have studied, our measurements are limited to $T/T_c \geq 0.2$ which is not sufficient for the accurate estimate of both $\lambda_{so}$ and $\alpha$. Instead, we can use rather well-defined initial slopes of $H_{c2}$, $(dH_{c2}/dT)_{T_c}$, for our alloys (table 1) in order to estimate their dressed densities of states, $N_F(E_F)$ [14, 15, 20, 22, 27]. $N_F(E_F)$ can be calculated from [31]

$$N_F(E_F) = \frac{\pi M 1}{4k_B^2 N_A \rho_d} \left( \frac{dH_{c2}}{dT} \right)_{T_c}, \quad (1)$$

where $k_B$ is the Boltzmann constant, $N_A$ the Avogadro number, $M$ the molecular weight, $d$ the mass density and $t = T/T_c$. The product $\rho_d$ can be expressed via resistance $R$, length $l$ and mass $m$ of the sample, $\rho_d = (mR/l^2)$ [14, 15, 27]. The values of $N_F(E_F)$ for Hf–Fe, Cu alloys calculated by using (1) decrease with increasing Fe, Cu content (table 1) in the same fashion as $N_F(E_F)$ in the corresponding Zr–Fe, Cu alloys [14, 15]. However, the magnitudes of $N_F(E_F)$ in Hf-base alloys are some 10–12% lower than those in the corresponding Zr-base alloys [14, 15]. As in Zr-base alloys [14, 15, 20] a clear correlation exists between the values of $N_F(E_F)$ and $T_c$. In metallic glasses the values of $N_F(E_F)$ calculated from (1) usually agree well with those obtained more directly from the coefficient of a linear term in LTSH, $\gamma$ [12, 14, 15, 20–22, 27, 30]:

$$N_F(E_F)_{\text{LTSH}} = \frac{3\gamma}{\pi^2 k_B^2}. \quad (2)$$

The dressed density of states is enhanced by many-body interactions in respect to a band (bare) density of states, $N(E_F)$. In particular, $N_F(E_F) = (1 + \lambda_{ep} + \lambda_{esf})N(E_F)$, where $\lambda_{ep}$ and $\lambda_{esf}$ are the electron–phonon and electron–spin fluctuation interaction parameters, respectively. Since our Hf-base alloys were paramagnetic [25] with magnetic susceptibilities well below of those for the corresponding Zr-base alloys [14, 15] we expect $\lambda_{esf}$ to be small for Hf–Fe, and
negligible for Hf–Cu alloys. For a reliable estimate of $\lambda_{ep}$ the LTSH measurements are required [12]. Since at present no LTSH results for Hf-base glassy alloys exist [12] we cannot make accurate estimates of $N(E_F)$ for the alloys studied.

In amorphous TE–TL alloys the electron–phonon enhancement factor can also be estimated from the temperature variation of the thermopower, $S(T)$ [6]. Such an estimate for the amorphous Hf$_{75}$Cu$_{25}$ alloy yields $N_F(E_F)/N(E_F) \approx 1.4$, nearly the same as that obtained for the Zr$_{50}$Cu$_{50}$ alloy [33]. Another estimate of $\lambda_{ep}$ in Hf–Cu glassy alloys can be obtained by dividing our results for $N_F(E_F)$ with the calculated values of $N(E_F)$ for amorphous Hf$_{100-x}$Cu$_x$ alloys [12, 34]. The ratio between our $N_F(E_F)$ and (interpolated) values of $N(E_F)$ decreased from about 1.4 ($x = 30$) to $\approx 1.2$ ($x = 50$). This calculation gave $N(E_F)$ values for amorphous Hf–Cu alloys about 10% lower than the values of $N(E_F)$ in the corresponding Zr–Cu alloys [12].

In principle, $\lambda_{ep}$ can also be obtained from the approximate proportionality between $\lambda_{ep}$ and $N(E_F)$ derived for disordered transition metal alloys of a given series [35] which was found applicable to several 4d (Zr, Mo)-base metallic glasses [20]. There, the coefficient of $\lambda_{ep}$ versus $N(E_F)$ variation for 4d and 5d series was found to be quite similar [35], whereas for 3d series was sizeably smaller. This result is in qualitative agreement with the estimates of $\lambda_{ep}$ from $S(T)$ [33] for equiatomic Ti–Cu, Zr–Cu and Hf–Cu amorphous alloys. Thus, the electron–phonon enhancement in Hf–Cu glassy alloys is probably quite similar to that in Zr–Cu alloys and the main reason for lower $T_c$ in the former system may be higher ionic mass of Hf (lower Debye temperature, $\Theta_D$ [36]) and lower $N(E_F)$ [12].

The near absence of superconductivity in Ti-base metallic glasses [12, 19], also confirmed by us (figures 2 and 3), is puzzling. Since in these systems both $N_F(E_F)$ and $\Theta_D$ are higher than those in the corresponding Zr-base and Hf-base metallic glasses [12], an inefficient electron–phonon coupling is required to explain their low $T_c$ values [34].

4. Conclusion

The first systematic study of superconductivity in Hf-based metallic glasses has been reported. A clear correlation between the values of $T_c$ and the dressed density of states $N_F(E_F)$ has been established. With the exception of the Hf$_{75}$Fe$_{25}$ alloy, higher $N_F(E_F)$ corresponds to higher $T_c$. More rapid suppression of $T_c$ with x in Hf$_{100-x}$Fe$_x$ alloys than in Hf$_{100-x}$Cu$_x$ is probably caused by magnetic effects. In general, the variations of $T_c$ and $N_F(E_F)$ in Hf–Fe, Cu metallic glasses with Fe, Cu content are qualitatively the same as those in the corresponding Zr–Fe, Cu glassy alloys which is consistent with the very similar electronic structures of these alloys. Considerably lower values of $T_c$ in Hf-based metallic glasses than those in the corresponding Zr-based alloys are probably due to the lower Debye temperatures $\Theta_D$, and electronic densities of states $N(E_F)$ in the former system. For a more detailed insight into the superconductivity of Hf-based metallic glasses the additional measurements of the low temperature specific heat (yielding $\Theta_V$) and perhaps tunnelling experiments (giving more directly electron–phonon coupling) are required.

Acknowledgments

The samples Hf$_{50}$Cu$_{30}$ and Hf$_{50}$Cu$_{40}$ have been prepared by Dr L Varga and Dr I Bakonyi from the Research Institute for Solid State Physics and Optics, Hungarian Academy of Sciences. This work was supported by the Croatian Ministry of Science, Education and Sports projects nos. 119-191458-1023 and 119-191458-1019.

References

[1] Beck H and Güntherodt H J (ed) 1994 Glassy Metals III (Springer Topics in Applied Physics vol 72) (Berlin: Springer) and references therein
[2] Peker A and Johnson W L 1993 Appl. Phys. Lett. 63 2342
[3] Das J, Tang M B, Kim K B, Theissmann R, Baier F, Wang W H and Eckert J 2005 Phys. Rev. Lett. 94 205501 and references therein
[4] Inoue A, Zhang W, Zhang T and Kurosaka K 2001 Acta Mater. 49 2645
[5] Gey W, Eschner W and Galperin Y M 1993 Phys. Rev. B 48 15666 and references therein
[6] Howson M A and Gallagher B L, 1988 Phys. Rep. 170 265
[7] Marońič Z, Babić E, Guberović M and Morgan G J 1988 J. Non-Cryst. Solids 105 303
[8] Whang S H, Polk D E and Giessen B C 1982 4th Int. Conf. on Rapidly Quenched Metals (Sendai) ed T Masumoto and K Suzuki p 1365
[9] Jank W, Hausleitner Ch and Hafner J 1991 Europhys. Lett. 16 473
[10] Hausleitner Ch and Hafner J 1990 Phys. Rev. B 42 5863
[11] Mankovsky S, Bakonyi I and Ebert H 2007 Phys. Rev. B 76 184405 and references therein
[12] Bakonyi I 1995 J. Non-Cryst. Solids 180 131 and references therein
[13] Babić E, Ristić R, Miljak M, Scott M G and Gregan G 1981 Solid State Commun. 39 139
[14] Altounian Z and Strom-Olsen J O 1983 Phys. Rev. B 27 4149
[15] Batalla E, Altounian Z and Strom-Olsen J O 1985 Phys. Rev. B 31 577
[16] Ristić R and Babić E 2007 Mater. Sci. Eng. A 449–451 569
[17] Oelhafen P, Hauser E and Güntherodt H-J 1979 Solid State Commun. 35 1017
[18] Bakonyi I 2005 Acta Mater. 53 2509
[19] Hickey B J, Greig D and Howson M A 1986 J. Phys. F: Met. Phys. 16 L13
[20] Tenhoven M and Johnson W L 1983 Phys. Rev. B 27 1610
[21] Nordström A, Dahlborg U and Rapp O 1993 Phys. Rev. B 48 12866
[22] Samwer K and Lohneysen H v 1982 Phys. Rev. B 26 107 and references therein
[23] Revesz A, Cziraki A, Lovas A, Padar J, Ledvai J and Bakonyi I 2005 Z. Metallk. 96 874
[24] Babić E, Butcher S, Day R K and Dunlop J B 1985 Phys. Rev. B 32 4149
[25] Pajić D, Zadro K, Ristić R, Živković I, Skoko Ž and Babić E 2007 J. Phys.: Condens. Matter 19 296207 and references therein
[26] Pavan D 1985 Solid State Commun. 54 771
[27] Karkut M G and Hake R R 1983 Phys. Rev. B 28 1396
[28] Meyer J D and Stritzker B 1983 Z. Phys. B 54 25
[29] Collings E W and Ho J C 1971 Phys. Rev. B 4 349
[30] Poon S J 1983 Amorphous Metallic Alloys ed F E Luborsky (London: Butterworths) p 432
[31] Werthamer N R, Helfand E and Hohenberg P C 1966 Phys. Rev. 147 295
[32] Maki K 1966 Phys. Rev. 148 362
[33] Gallagher B L and Hickey B J 1985 J. Phys. F: Met. Phys. 15 911
[34] Cyrot-Lackmann F, Mayou D and Nguyen Manh D 1988 Mater. Sci. Eng. 99 245
[35] Dynes R C and Varma C M 1976 J. Phys. F: Met. Phys. 6 L215
[36] McMillan W L 1968 Phys. Rev. 157 331