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Properties and atomic structure of amorphous early transition metals

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ABSTRACT

Recently, we studied the properties of amorphous Zr–TL alloys (TL = Ni, Cu) in order to obtain parameters associated with the electronic structure and interatomic bonding of amorphous Zr. Here, we provide new data for the magnetic, superconducting and mechanical properties of amorphous Hf–TL and Ti–TL alloys. We combine our results with published data in order to obtain parameters appropriate to hypothetical amorphous Hf and Ti. These parameters are very different from those of the stable crystalline phases (hcp) of Hf and Ti and indicate, as for Zr, an fcc-like short range order for amorphous Hf and Ti. This results in an enhanced electronic density of states at the Fermi level, but in weakened interatomic bonding.

1. Introduction

Amorphous TE–TL alloys (TE = Ti, Zr, Hf and TL = Ni, Cu) have been extensively studied in recent decades and interest in these alloys further increased following the discovery of TE–TL based bulk metallic glasses (BMGs) [1]. TE–TL alloys show wide glass-forming ranges which enables detailed study of the change in the electronic structure and properties on alloying and, thus a thorough comparison between the model and experimental data [2].

In amorphous TE–TL alloys the properties that are directly related to the electronic density of states (DOS) often show linear variations with TL content [2–5]. This finding correlates with ultraviolet photoemission spectroscopy (UPS) results [6] which show that, in these alloys, the DOS at the Fermi level (E_F), $N(E_F)$, is dominated by TE d-states and is reduced on increasing the TL content. Therefore, the effect of alloying with TL can be approximated by the dilution of amorphous TE [3,5]. Thus, one can extrapolate the data for glassy TE–TL alloys to zero TL content in order to deduce the properties of amorphous (a) TE. This method has been used to obtain the $N(E_F)$ and probable local atomic structure of a-Ti and a-Zr [2]. More recently, the same approach has been used to obtain the atomic volumes of a-TE [4] and the magnetic, superconducting and mechanical properties of a-Zr [5,7]. The derived parameters for a-Ti, Zr agree quite well with those calculated for cubic phases of these metals [8] and are quite different from those of the stable crystalline phases (hcp) of TEs. This result is plausible since the amorphous atomic arrangement is incompatible with the anisotropy of the hcp lattice.

The majority of the results for TE–TL metallic glasses have been obtained for Zr–TL alloys, so that a comparison between the alloy systems based on different TE is seldom possible [2,4,9]. Here, we report new results for the magnetic, superconducting and mechanical properties of several Ti–Cu and Hf–Cu glassy alloys and combine these results with the literature data for Ti–TL and Hf–TL metallic glasses in order to observe how a change in TE (Ti → Zr → Hf) affects these properties for glassy TE–TL alloys. We also estimate some parameters of hypothetical pure a-TE and compare them with those for crystalline phases of TE.

2. Experimental

The $Hf_{100-x}Cu_x$ ($30 \le x \le 70$) and $Ti_{100-x}Cu_x$ ($35 \le x \le 55$) glassy alloys were prepared in the form of thin ribbons by melt spinning of arc-melted alloys in a controlled He atmosphere. Casting with controlled parameters resulted in ribbons with closely similar cross-sections (~2 mm × 0.03 mm) and, thus, with the glassy phase having broadly the same degree of quenched-in disorder. As-cast samples were used for actual measurements and their fully amorphous structures were verified by X-ray diffraction [9]. The superconducting transition temperatures T_c were determined either resistively, or via ac susceptibility measurements [3,9]. The magnetic susceptibility was measured with a SQUID magnetometer MPMS [10] in a magnetic field $B \le 5.5$ T over the temperature range of 5–300 K. The Young's modulus, E, was calculated from the relationship $E = \rho v_E^2$, where ρ is the density of the alloy and v_E the velocity of ultrasonic waves along the ribbon. v_E was measured with a pulse-echo

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Table 1
The parameters of amorphous Ti, Zr and Hf compared with those for different crystalline phases of the same metals. The values for $N(E_F)$, χ_{exp} and χ_p of α(hcp) and fcc phase (calculated) are taken from [8].

	Structure	$N(E_F)$ (states/eV atom)	χ_{exp} ($\times 10^3$ JT^{-2} mol^{-1})	χ_p ($\times 10^3$ JT^{-2} mol^{-1})	T_c (K)	E (GPa)
Ti	Amorphous	2.0	2.11	1.2	2.0	80
	α(hcp)	1.03	1.40	0.44	0.4	116
	fcc	1.76	2	1.22		
Zr	Amorphous	1.55	1.58	0.84	5.5	40
	α(hcp)	0.84	1.08	0.42	0.8	68
	fcc	1.34	1.50	0.69		
Hf	Amorphous		1.2	0.7	3.5	60
	α(hcp)	0.68	0.71	0.29	0.1	78
	fcc	1.45	1.1	0.79		

technique at room temperature [7]. The density, ρ, of the samples was measured by the Archimedes method [3]. The estimated error was around ±2%.

The experimental procedures used to obtain published data can be found in the original papers. The (extrapolated) values for some properties of pure amorphous Ti, Zr and Hf are compared with those of the respective crystalline phases of these metals in Table 1.

3. Results and discussion

As pointed out in Section 1, the band structure of amorphous TE–TL alloys results in DOS with d-states for TE at E_F and those for TL well below E_F [2,6]. Such a DOS results in an approximately linear decrease of $N(E_F)$ with increasing TL content x, for $x \leq 65$ [2]. In Zr–TL and Ti–TL alloys [2] the values of $N(E_F)$ were obtained from the measurements of low temperature specific heat (LTSH) and superconducting transition temperature, T_c. LTSH yields the Debye temperature, θ_D, and dressed DOS at E_F, $N_\gamma(E_F) = (1 + \lambda_{ep})N(E_F)$ (with λ_{ep} the electron–phonon enhancement), while T_c enables [2] the calculation of λ_{ep}. $N_\gamma(E_F)$ can also be calculated from the normal state resistivity r, density ρ, and the temperature dependence of the upper critical field, $H_{c2}(T)$ [9]:

$$N_\gamma(E_F) = \frac{-\pi M}{4k_B N_A \rho r}\left(\frac{dH_{c2}}{dt}\right)_{t=1}, \tag{1}$$

where k_B is the Boltzmann constant, N_A the Avogadro's number, M the molecular weight and $t = T/T_c$. We applied this method to Hf–Cu alloys for which there are no LTSH results. As shown in Fig. 1, $N_\gamma(E_F)$ for all TE–TL glassy alloys decreases linearly with TL content (x). Since λ_{ep} also decreases approximately linearly [2] with x, the corresponding variation of $N(E_F)$ in TE–TL alloys should be qualitatively the same as that of $N_\gamma(E_F)$. The $N_\gamma(E_F)$ values in Fig. 1 decrease in the sequence Ti → Zr → Hf, which is mainly due to increasing bandwidth in the same sequence [8]. At low TL contents, $N_\gamma(E_F)$ values for all the TE–TL glassy alloys are substantially larger than those of corresponding pure crystalline (hcp) TEs (Fig. 1). The enhanced $N_\gamma(E_F)$ and $N(E_F)$ in a-TEs is probably due to absence of a local minimum in the DOS at E_F which occurs in hcp phases of crystalline TE and is absent in cubic phases of the same metals [8]. Indeed, the values of $N(E_F)$ for a-Ti [2] and a-Zr [5] are close to those calculated for fcc phases of these metals [8] (Table 1). The absence of any hcp atomic arrangements in a-TEs and their alloys has a profound influence on their DOS and interatomic bonding and, hence, affects all properties of glassy TE–TL alloys.

Quite large $N(E_F)$ and its simple variation with x strongly affect the magnetic and superconducting properties of glassy TE–TL alloys [5,9]. As shown in Fig. 2, in paramagnetic alloys with TL = Ni, Cu magnetic susceptibility, χ_{exp}, decreases approximately linearly with x and for the same x χ_{exp} decreases in the sequence Ti → Zr → Hf. Also, the extrapolations of χ_{exp} plots in Fig. 2 to $x = 0$ ($0 = $ TE) yield values which are considerably larger than those for hcp TE, but agree quite well with those calculated [8] for fcc phases of these metals (Table 1). In spite the apparent similarity between $N(E_F)$ vs. x [2] and χ_{exp} vs. x (Fig. 2) plots, the description of χ_{exp} for transition metals is somewhat more involved:

$$\chi_{exp} = \chi_p + \chi_{ion} + \chi_{orb}, \tag{2}$$

where χ_{ion} and χ_{orb} are, respectively, the temperature-independent ionic core diamagnetism and the orbital paramagnetism. The Pauli paramagnetism of the d-band, χ_p, is enhanced over the free-electron value, χ_p^0, due to exchange interaction. $\chi_p = S\chi_p^0$, where S is the Stoner enhancement factor [5,15] and, in TE, χ_p is only weakly dependent on temperature [8].

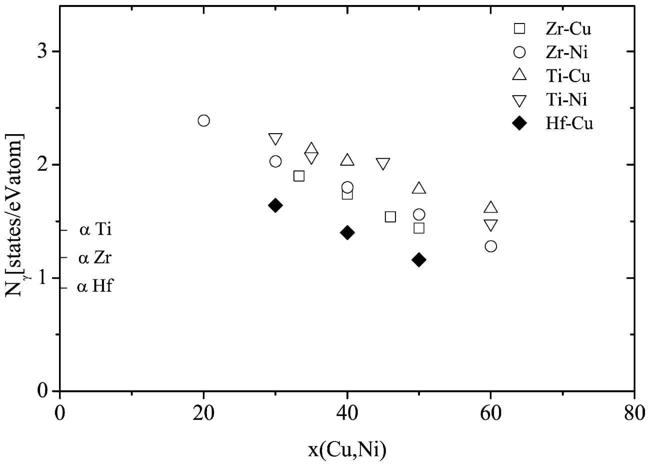

Fig. 1. Dressed densities of states $N_\gamma(E_F)$ of Zr–Cu [11], Zr–Ni [12], Ti–Cu [13], Ti–Ni [14] and Hf–Cu alloys vs. Cu,Ni content x. Full symbols denote present data.

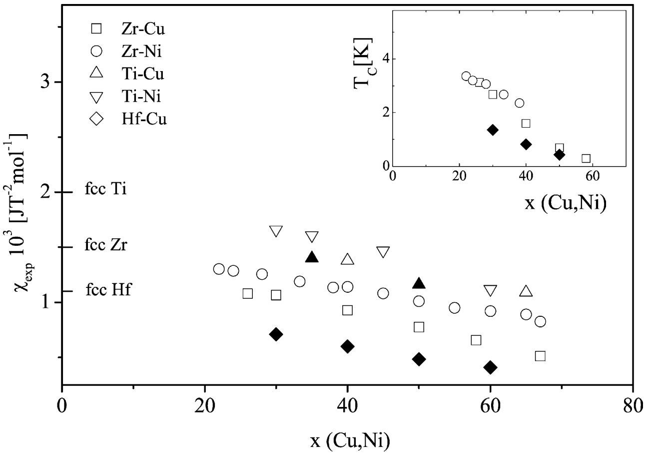

Fig. 2. Magnetic susceptibility χ_{exp} of Zr–Cu [3], Zr–Ni [3,15], Ti–Cu [13], Ti–Ni [14], and Hf–Cu alloys vs. Cu, Ni content x. Susceptibilities of pure fcc Ti, Zr and Hf [8] are shown for comparison. (Inset) Superconducting transition temperatures T_c of Zr–Cu [3], Zr–Ni [3] and Hf–Cu alloys vs. Ni,Cu content x. Full symbols denote present data.

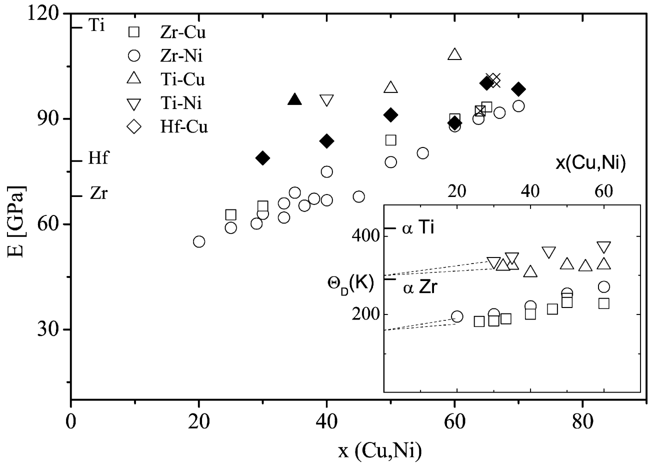

Fig. 3. Young's modulus E for Zr–Cu [16,17], Zr–Ni [16,18], Ti–Cu [19], Ti–Ni [17], $Hf_{34}Cu_{66}$ [20], $Zr_{36}Cu_{64}$ [21], Hf–Cu and $Ti_{65}Cu_{35}$ alloys vs. Cu,Ni content x (crossed symbols are bulk alloys). E of pure (α) Ti, Zr and Hf are also shown. (Inset) Debye temperatures θ_D of Zr–Cu [11,22], Zr–Ni [12], Ti–Cu [13] and Ti–Ni [14] alloys vs. Cu,Ni content x. θ_D for pure (α) Ti and Zr are also shown. Full symbols denote present data.

The expression (1) can also be applied to glassy TE–TL alloys, with χ_{ion} and χ_{orb} of the constituents scaled to their atomic fractions in the alloy [5], which enables one to extract χ_p from χ_{exp}. For TE = Ti, Zr, Hf, the bandwidth increases in the sequence Ti → Zr → Hf which leads to a decrease of both χ_p (via the decrease of the bare DOS at E_F, $N(E_F)$, in χ_p^0) and χ_{orb} [8], in the same order. The lack of reliable $N(E_F)$ data for Hf-based alloys [2,9] prevents a detailed analysis of their χ_{exp} in terms of Eq. (1). The values of χ_p for all a-TEs agree well with those calculated for fcc phases of corresponding TEs [8] and are substantially larger than those of their α-phases (hcp) (Table 1). In particular, χ_p for a-Zr is double that for α-Zr.

The enhanced $N(E_F)$ for a-TEs is also the main reason that the T_c's for Zr and Hf-based glassy alloys are well above those for pure crystalline Zr and Hf (inset to Fig. 2). The approximately linear variations of T_c with x in these alloys extrapolate to T_c's of amorphous Zr and Hf which are about an order of magnitude higher than those of crystalline Zr and Hf (Table 1). The larger ionic mass of Hf than that of Zr contributes to lower T_c's of Hf-based alloys. Surprisingly, glassy Ti-based alloys having the highest $N(E_F)$ show the lowest T_c's, which implies very inefficient electron–phonon coupling in these alloys [9].

In Fig. 3 we show the variations of the Young's modulus, E, in TE–TL glassy alloys with TL content x. Comparing Fig. 3 with Fig. 1, we note that, in all these alloy systems, a linear decrease of $N_\gamma(E_F)$ (also $N(E_F)$) is accompanied by an approximately linear increase of E with x. Thus, a simple relationship between DOS at E_F and the elastic stiffness (E), first observed in Zr–TL metallic glasses [7], seems to hold also for other TE–TL glassy alloys. In binary amorphous metal–metal alloys such as the TE–TL glassy alloys the dense random packing of constituent atoms [2,4] suggests a direct link between their Young's modulus and the strength of the interatomic bonding [7,24]. Thus, an approximately linear increase of E with x implies an increase in the strength of bonding, which correlates with the simultaneous decrease of the DOS at E_F ($N_\gamma(E_F)$, $N(E_F)$) with x (Fig. 1). Accordingly, the enhanced DOS at E_F in a-TE is associated with a Young's modulus which is substantially smaller than that of the corresponding crystalline (hcp) TE (Fig. 3 and Table 1). We note that the values of E for binary BMG alloys in the Zr–Cu and Hf–Cu systems fall well within the ranges of the data for other compositions from the same alloy systems (Fig. 3).

Since the amorphous alloys are approximately isostructural [23], their vibrational spectra should be quite similar [24], thus their Debye temperatures, θ_D, should also be directly related to the strength of interatomic bonding. Indeed, as illustrated in the inset to Fig. 3, the variations of θ_D for Zr–TL and Ti–TL glassy alloys with TL content are qualitatively similar to those of E with x (Fig. 3) for alloys in these systems. The extrapolated values of θ_D for a-Zr and a-Ti are much lower than those of crystalline Zr and Ti (Fig. 3), which is consistent with weak interatomic bonding in a-TEs.

Since the amorphous alloys are macroscopically homogenous and isotropic systems, their elastic moduli are correlated. Thus, the shear modulus, G, and the bulk modulus, B, can be calculated from the known E and the Poisson's ratio σ [5,7]. Furthermore, the absence of extended crystal defects [23] in metallic glasses leads to very large hardness, H_v, and also to a direct relationship between H_v and the strength of the interatomic bonding [7]. Thus, the H_v for TE–TL glasses should be proportional to the elastic moduli [7,17] and, therefore, should increase with TL content within the explored concentration range. This was verified for Zr–TL alloys [7]; measurements of H_v for Hf–Cu and Ti–TL alloys are in progress.

4. Conclusion

New results for the properties of Ti–TL and Hf–TL alloys are presented and have been combined with literature data in order to obtain an insight into the electronic structure/property relationships for all the TE–TL metallic glasses and to predict, by extrapolation, the properties of pure amorphous TE (Table 1). Density of states, $N(E_F)$ for TE-rich glassy alloys is considerably larger than for the pure corresponding crystalline TE, which shows that the local atomic structure in glassy alloys is different from that in hcp TE [2,5]. Indeed, $N(E_F)$ and related magnetic and superconducting parameters of a-TEs agree quite well with those calculated for cubic phases of these metals [8] and are very different from those of hcp TEs. Simultaneously, such atomic structure results in reduced strength of interatomic bonding which shows up in low elastic moduli and Debye temperatures of a-TEs and TE-rich TE–TL glassy alloys (Fig. 3).

The relatively simple electronic structure of TE–TL metallic glasses [2] results in simple variations of several of their properties with composition. This enables one to predict the properties of, as-yet, unprepared amorphous alloys. Since many bulk metallic glasses (BMGs) are based on TE and TL components the systematic studies of binary TE–TL metallic glasses may be useful for the development of such BMGs.

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