Correlation Between Electronic Structure, Mechanical Properties and Stability of TE-TL Metallic Glasses*

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Abstract. Mechanical properties (Young's modulus and hardness) of TE-Ni,Cu (TE = Ti, Zr and Hf) amorphous alloys increase approximately linearly with Ni, Cu fraction, \( x \), over a wide composition range (fraction of Ni, Cu atoms \( \leq 66 \% \)). This correlates with the observed increase of the Debye temperatures with \( x \) and shows that the strength of interatomic bonding increases with \( x \) in these alloys. The thermal stability (e.g., the crystallization temperatures) of these alloys also increases with \( x \), thus with increasing interatomic bonding. Since in all these alloys the electronic density of states at the Fermi level, \( N(E_F) \), decreases linearly with \( x \) within the same \( x \)-range, a very simple relationship exists between the electronic structure and mechanical and thermal properties. We also estimate the mechanical properties of amorphous TEs (by extrapolating the properties of alloys to \( x = 0 \)) and compare them with those of crystalline TEs.

Keywords: metallic glasses, electronic structure, mechanical properties, thermal stability, transition metals

INTRODUCTION

Amorphous TE-TL alloys (TE = Ti, Zr, Hf and TL = Co, Ni, Cu) have been extensively studied1 and interest in these alloys further increased upon the discovery of TE-TL based bulk metallic glasses (BMG).2 These alloys show wide glass-forming range (fraction of TL atoms usually 20–70 %) which enables detailed study of the change in the electronic structure and properties on alloying, thus a thorough comparison between the model and experiment.3

In nonmagnetic amorphous TE-TL alloys the properties that are directly related to electronic density of states (DOS) show often linear variation with TL fraction1,3–7 This finding correlates with Ultraviolet photoemission spectroscopy (UPS) results3,8 which showed that in these alloys DOS at the Fermi level (\( E_F \)), \( N(E_F) \), is dominated by TE d-states and is reduced on increasing TL fraction. Therefore, the effect of alloying with TL can be approximated with the dilution of amorphous TE.9 Thus, one can extrapolate the data for glassy TE-TL alloys to zero TL fraction in order to obtain the atomic volumes of a-TE7 and magnetic and superconducting properties of a-Zr.9 The obtained parameters for a-TE agree well with those calculated for cubic crystalline phases of these metals10 and are quite different from those of stable crystalline phases (hcp) of TEs. This result is plausible since the amorphous (random) atomic arrangement is incompatible with a high anisotropy of the hcp lattice.

Very recently, a simple relationship between the electronic structure (DOS) and mechanical (Young's modulus and hardness) and thermal properties of glassy Zr-TL alloys has been found.11 This finding is quite surprising since the observations of a direct relationship between the mechanical properties (especially hardness) of materials and their electronic band structure are very rare.12,13 Therefore, it is of interest to check whether similar relationships exist in other glassy TE-TL alloys, or not. Unfortunately, most of the results for TE-TL metallic glasses are obtained on Zr-TL alloys, so that a comparison between the alloy systems based on different TE is rarely possible.3,7,14,15 Here, we report new results for mechanical properties (Young's modulus and hardness) of several Ti-Cu and Hf-Cu glassy alloys and combine these results with the literature data for mechanical properties, Debye temperatures3 and thermal stability of Ti-TL and Hf-TL alloys in order to see how

Dedicated to Professor Boran Leontić on the occasion of his 80th birthday.
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a change of TE (Ti → Zr → Hf) affects these properties of glassy TE-TL alloys. We also estimate some parameters of hypothetical pure a-TE and compare them with those of crystalline TE.

EXPERIMENTAL

The Hf_{100-x}Cu_{x} (30 ≤ x ≤ 60) and Ti_{100-x}Cu_{x} (x = 35 and 50) glassy alloys were prepared in a form of ribbons by melt spinning of master alloys with a predetermined composition in either pure Ar\(^{16}\) or He\(^{17}\) atmosphere. Controlled casting conditions resulted in ribbons with nearly the same cross-sections (≈ 2 × 0.025 mm\(^2\)) and, thus, with probably the same degree of quenched in disorder. As-cast samples were used for actual measurements and their amorphousness was verified by X-ray diffraction.\(^{15}\)

The microhardness, H\(_m\), was measured at room temperature using a standard E. Leitz (Wetzlar, Germany) Miniload II apparatus supplied with a 136° diamond pyramid indenter.\(^{12}\) A load of 0.981 N was used and the loading time was 10 s. The estimated value of microhardness is obtained from ten or more indentations on each studied sample, and the standard deviation was about 5–10 % of the mean value. The measurements were performed on the shiny (upper) surface of the ribbons, but occasional checks on the lower surface (in contact with roller) gave the same H\(_m\) values. Altogether, six different alloys with 30 ≤ x ≤ 60 were measured. The values of H\(_m\) were measured in kgf/mm\(^2\) and, finally, converted in Pa units by multiplying results in kgf/mm\(^2\) with 9.81 \times 10\(^6\).

The Young's modulus, E, was calculated from the relationship \(E = \rho v_E^2\) where \(\rho\) 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 technique at room temperature.\(^{11}\) The density, \(\rho\), of the samples was measured by the Archimedes method.\(^6\) The estimated error was around 2 %.

The experimental procedures used to obtain the literature data for mechanical properties and thermal stability can be found in original papers.

RESULTS AND DISCUSSION

As pointed out in the Introduction, the band structure of amorphous TE-TL alloys results in DOS with d-states of TE at \(E_F\) and those of TL well below \(E_F\).\(^{1,8}\) Such DOS combined with weak tendency for the formation of chemical short range order (CSRO) at TL fraction \(x \leq 65\)\(^{1,7}\) yields approximately linear decrease of \(N(E_F)\) with increasing \(x\) of TL.

In superconducting alloys the value of \(N(E_F)\) can be obtained from the measurements of low temperature specific heat (LTSH) and superconducting transition temperature, \(T_c\).\(^{3,9,15}\) LTSH yields the Debye temperature, \(\theta_D\), and dressed DOS at \(E_F\), \(N(E_F) = (1 + \lambda_{ep}) N(E_F)\) (with \(\lambda_{ep}\) the electron-phonon enhancement), while \(T_c\) via the McMillan equation\(^{16}\) enables the calculation of \(\lambda_{ep}\). \(N(E_F)\) can also be calculated from the normal state resistivity, density, and the temperature dependence of the upper critical field, \(H_{c2}(T)\).\(^{15}\) As shown in the upper part of Figure 1, \(N(E_F)\)\(^{15}\) for all TE-TL glassy alloys decreases linearly with the increase of TL fraction. Since \(\lambda_{ep}\) also decreases approximately linearly\(^3\) with \(x\) the variation of \(N(E_F)\) in TE-TL alloys is qualitatively the same as that of \(N(E_F)\) (Figure 1). The \(N(E_F)\) values in Figure 1 decrease in order Ti → Zr → Hf alloys which is mainly due to increasing bandwidth in the same order.\(^{10}\) At lower TL fractions (\(x\)) \(N(E_F)\) values of Ti and Zr-base glassy alloys are sizably larger\(^3\) than those of pure crystalline (hcp) Ti and Zr.\(^{10}\) This enhancement of \(N(E_F)\) in glassy state of TE is due to absence of local minimum in DOS at \(E_F\) which occurs in stable (hcp) phases of crystalline TE and is absent in cubic phases (fcc, bcc) of the same metals.\(^{10}\) Thus, the

Figure 1. a) Young's modulus E of Zr_{100-x}Cu_{x} (□),\(^{11}\) Zr_{100-x}Ni_{x} (○),\(^{11}\) Ti_{100-x}Cu_{x} (△),\(^{19}\) Ti_{60}Ni_{40} (▽),\(^{20}\) Hf_{100-x}Cu_{x} (◇),\(^{15}\) and (full symbols) of bulk metallic glasses Hf_{55}Cu_{45} (●),\(^{21}\) Zr_{60}Cu_{50} (■)\(^{22}\) and Zr_{50}Cu_{50} (▲)\(^2\) alloys vs. fraction of Cu, Ni atoms, x. E of pure (a) Ti, Zr and Hf are also shown. b) Dressed densities of states \(N(E_F)\) per atom of Zr_{100-x}Cu_{x} (○),\(^3\) Zr_{100-x}Ni_{x} (○),\(^3\) Ti_{100-x}Cu_{x} (△),\(^3\) Ti_{60}Ni_{40} (▽)\(^3\) and Hf_{100-x}Cu_{x} (◇)\(^{15}\) alloys vs. fraction of Cu or Ni atoms, x, expressed in percents.
absence of a hcp atomic arrangements in a-TEs and their alloys has profound influence on their DOS and interatomic bonding, hence affects all properties of glassy TE-TL alloys.7,9,11,15

In Figure 1 we compare the variations of the Young’s modulus, E, in TE-TL glassy alloys with TL fractions x (lower part of the Figure)11,19,23 with those of Nf (Ef) with x (upper part). In all alloy systems a linear decrease of Nf(Ef) (also N(E)) at least in Zr and Ti-base alloys)3,11 is accompanied with approximately linear increase of E with x. Thus, a simple relationship between DOS at Ef and stiffness (E) first observed in Zr-TL metallic glasses11 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 atoms3,7,9 suggests direct link between their alloys has profound influence on their DOS and interatomic bonding, hence affects all properties of glassy TE-TL alloys.3,7,9,11,15

Since the amorphous alloys are macroscopically homogenous and isotropic systems, their elastic constants are correlated. Thus, the shear modulus, G, and the bulk modulus, B, can be calculated from known E and Poisson ratio ν.9,11 Furthermore, very little variation of ν in alloys8,20 leads to proportionality between the elastic constants E, G and B in glassy alloys.9,11 Therefore,
in TE-TL alloys \( H_c \) is proportional to all elastic constants and simultaneously all elastic constants and \( H_c \) show simple relationship with the electronic structure represented by DOS at \( E_F \). This finding differs markedly from the situation encountered in TE carbonitrides\(^{13} \) where \( H_c \) is proportional to \( G \) only. As discussed elsewhere, this difference is associated with a more complex electronic structure of TE carbonitrides.\(^{11} \) Taken together, all mechanical properties and Debye temperatures of TE-TL glassy alloys indicate large reduction in the strength of interatomic bonding on approaching pure a-TEs.

We expect that this progressive weakening of the interatomic bonding in TE-TL alloys on decreasing TL fraction (\( x \)) affects their thermal stabilities and glass-forming abilities.\(^{28} \) Indeed, as shown in Figure 4 the variation of the first crystallization temperatures \( T_c \) of all glassy TE-TL alloys with \( x \) support this prediction. In particular, the available literature data\(^{11,27-31} \) for \( T_c \) decrease rapidly with decreasing the fraction of TL. The progressive decrease of thermal stability as \( x \to 0 \) (Figure 4) is accompanied with rapid decrease of glass-forming ability (GFA)\(^{11,20} \) with result that TE-TL metallic glasses with \( x < 18 \) have not been prepared so far.\(^{15,26} \) The findings from Figure 4 extend the simple relationship between the electronic structure (Figure 1) and mechanical properties also to thermal stability and GFA of TE-TL glassy alloys.

**CONCLUSION**

Recent analysis\(^{11} \) of the relationship between the electronic structure and mechanical and thermal properties of Zr\(_{100-x}\)TL\(_x\) glassy alloys \((20 \leq x \leq 70)\) has been extended to include corresponding Ti-TL and Hf-TL alloys. New results for mechanical properties of these alloys have been combined with literature data in order to obtain an insight into the electronic structure/mechanical property relationship for all TE-TL metallic glasses.

Both Young's modulus and hardness (Figures 1 and 3) and the Debye temperatures (Figure 2) of TE-TL glassy alloys increase with the increase of TL fraction (\( x \)). Due to amorphous atomic structure and the absence of crystal slip all these properties reflect the strength of interatomic bonding. Thus, low extrapolated elastic moduli and Debye temperatures of amorphous (a) TEs compared to those of their stable crystalline modifications indicate very weak interatomic bonding in a-TEs, atypical of transition metals. This softening of the interatomic bonding on decreasing \( x \) probably affects the thermal stability (Figure 4) and the glass forming ability of TE-TL alloys which rapidly decrease as \( x \to 0 \).

Rather simple electronic structure of TE-TL metallic glasses\(^{1,3,8} \) results in simple variations of their several properties with the composition. This enables one to predict the properties of as yet unprepared amorphous alloys, including those of pure amorphous TEs. Since many bulk metallic glasses (BMG) are based on TE and TL components the results of systematic studies of binary TE-TL metallic glasses may be useful for the understanding and development of such BMGs.

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**SAŽETAK**

**Međuovisnost elektronske strukture, mehaničkih svojstava i stabilnosti amorfnih legura ranih i kasnih prijelaznih metala**

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Elastičnost i tvrdoća amorfnih slitina tipa TE-Ni,Cu (TE = Ti, Zr i Hf) rastu približno linearno s udjelom (x) Ni i Cu u širokom kompozicijskom području (udjeli Ni,Cu atoma, \( x \leq 66 \% \)). Taj porast povezan je s porastom Debye-vih temperatura istih slitina s \( x \) te pokazuje da jakost međuatomskog vezanja raste s \( x \). Termička stabilnost tih slitina (npr. temperature kristalizacije) također raste s \( x \) dakle s međuatomskim vezanjem. Budući da u svim tim slitinama elektronska gustoća stanja na Fermijevoj razini \( N(E_F) \) opada linearno s \( x \), postoji vrlo jednostavna veza elektronske strukture s mehaničkim svojstvima i stabilnosti amorfnih slitina TE-Ni,Cu. Ocjениli smo i mehanička svojstva amorfnih TE (ekstrapolacijom svojstava slitina u \( x = 0 \)) te ih usporedili s onima kristalnih TE.