Structural and thermal properties of Cu–Hf–Ti ternary metallic glasses

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Abstract

Cu–Hf–Ti ternary metallic alloys were prepared by melt spinning. The thermal stability of the alloys with various Ti contents was studied by differential scanning calorimetry. The evolution of short range order with annealing treatment was also investigated by means of perturbed angular correlation. The results for the initial as-spun alloys indicate that the short range order can be described by a dense packing of atoms. The variation of electric field gradient with alloy composition is comparable to that previously observed in binary and multi-component Zr- and Hf-based amorphous alloys.

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1. Introduction

Cu-based ternary metallic glasses are promising for practical applications since they combine high glass-forming ability with interesting mechanical properties, such as high strength and malleability, and also relatively low material cost \cite{1,2}. It was observed that the modifications of the concentrations and variety of constituents can improve some of the above properties against others \cite{3,4}. In particular, for the Cu–Zr(Hf)–Ti system, Ti addition increases the glass forming ability of the alloy, while it decreases the glass transition temperature, \( T_g \), but improves the mechanical properties. In order to rationalize the glass forming ability, it is useful not only to characterize the as-spun amorphous alloys structurally but also to determine the stable and metastable phases formed at each crystallization step. We are also interested, ultimately, in establishing a relationship between any short range order characteristic of various crystalline phases, which ultimately form on devitrification, and the mechanical properties of the glassy phase.

The perturbed angular correlation (PAC) technique, involving the determination of the electric-field-gradient (EFG), gives information about the atomic distribution around a given atom and thus can detect any local order. In previous studies, we investigated the thermal evolution of short range order in Zr- and Hf-based bulk metallic glasses using this hyperfine technique \cite{5,6}. In the present study we have studied the thermal stability of melt-spun Cu–Hf–Ti ribbons having various Ti contents by differential scanning calorimetry (DSC). The evolution of short range order with annealing treatments was also investigated by means of the PAC technique. The dependence of the EFG behavior on alloy composition is compared with that previously observed in binary and multi-component Zr and Hf-based amorphous alloys \cite{7}.

2. Experimental

Amorphous Cu\textsubscript{60}Hf\textsubscript{20}Ti\textsubscript{20}, Cu\textsubscript{55}Hf\textsubscript{30}Ti\textsubscript{15} and Cu\textsubscript{55}Hf\textsubscript{25}Ti\textsubscript{20} ribbons were prepared by melt spinning. Binary amorphous alloys Cu\textsubscript{100–x}Hf\textsubscript{x} (x = 40 and 45) prepared in the same way were also studied for comparison.

The as-prepared samples were analyzed by DSC in a Shimadzu TA50 calorimeter. The scans were carried out at a constant heating rate of 20 K/min under an argon flux.
All the samples for PAC measurements were irradiated with thermal neutrons in order to obtain the required activity of $^{181}$Hf by means of the nuclear reaction $^{180}$Hf(n,γ)$^{181}$Hf. The β decay of the $^{181}$Hf isotope populates the 133–482 keV γ−γ cascade in $^{181}$Ta. The PAC spectra were recorded at room temperature using a standard setup with four conical BaF$_2$ detectors arranged in a planar 90°–180° geometry, generating simultaneously 12 delayed coincidence spectra. The detector system had a time resolution of $\sim$600 ps.

After subtraction of chance coincidence background, time spectra corresponding to angles of 90° and 180° between detectors were combined to obtain the ratio

$$R(t) = \frac{2N(180°, t) - N(90°, t)}{N(180°, t) + 2N(90°, t)} = A_2^\text{exp}/G_2(t).$$

(1)

Theoretical functions of the form $A_2^\text{exp}(t)$, folded with the measured time resolution curve, were fitted to the experimental ratio $R(t)$.

3. Results and discussion

Fig. 1 shows DSC scans for the alloys studied. It can be observed that the Ti addition in binary alloys changes the crystallization mode from a single stage to two or more crystallization steps. At the same time, both the characteristic temperatures, $T_g$ and the crystallization temperature $T_x$, decrease. These features were observed previously in similar ternary alloys [1,8] although, for the Cu$_{60}$Hf$_{20}$Ti$_{20}$ sample, Louzguine et al. [9] reported three exothermic peaks. To our knowledge there are no reported data for the other compositions studied here.

Each ternary alloy was analyzed by PAC in its as-prepared state and after annealing in vacuo at the temperatures indicated in Fig. 1. All the initial, as-spun alloys display a wide distribution of quadrupole frequencies well described by a Czjzek distribution which represents a short range order based on dense random packing of ‘hard sphere’ atoms (DRP) [10].

Following a least squares fitting procedure, using a perturbation factor described elsewhere [5], we obtain the quadrupole frequencies related with the EFG sensed by the probe atom. The variation of the quadrupole frequency with Hf content is shown in Fig. 2, together with previous results for other Hf-based amorphous alloys [7,11]. A similar trend is observed for the Cu–Hf binary alloy (full stars), with the central $\omega_Q$ value decreasing with the Ti addition (open stars).

3.1. Cu$_{60}$Hf$_{20}$Ti$_{20}$ alloy

The composition of this alloy corresponds to that of the intermetallic phase Cu$_{10}$Hf$_7$ (orthorhombic Ni$_{10}$Zr$_7$ structure) if Hf and Ti are grouped together. Although a polymorphic crystallization process is expected, a single exothermic peak is not observed. PAC spectra, together with the resulting theoretical fits, are shown in Fig. 3. Isothermal annealings at 500°C ($\sim T_x$), with times increasing by 10 min increments, each show the effects of the crystallization of the alloy, with results similar to those for a binary Hf$_{41}$Cu$_{59}$ amorphous [11]: four quadrupole interactions are identified as the crystallographic sites in the intermetallic compound Cu$_{10}$Hf$_7$ [7]. Heat treatments at higher temperatures result in reorganization of the local atomic environments, which leads to a slight modification in the individual fractions and to a reduction in the distribution width.
3.2. Cu55Hf30Ti15 and Cu55Hf25Ti20 alloys

Figs. 4 and 5 show the PAC spectra obtained for Cu55Hf30-xTx, with x = 15 and 20, respectively. Both samples were annealed at 420 °C, well below the first crystallization peak. The spectra for annealing times up to 1 h can be fitted with three quadrupole interactions. One of these represents a wide distribution of frequencies characterizing an amorphous phase. The other two can be associated with crystalline environments (nuclei) of the intermetallic phases CuHf2 and Cu10Hf7. At higher annealing temperatures (above the second exothermic peak) four interactions are needed to fit the spectra: one low quadrupole frequency (13 Mrad/s), which represents a rather symmetric environment, characteristic of t-Hf2Cu, and the other three similar to the ones found in the compound Cu10Hf7 [11,12]. The final crystallized states achieved in these alloys differ mainly in the relative fraction for each component, as can be appreciated from their Fourier transforms (Figs. 4 and 5).

4. Conclusions

Ti addition to binary amorphous alloys Cu1-xHf with x = 15 and 20, induced various changes in thermal stability and in the crystallization process. However, the crystallization proceeds as if Hf and Ti were equivalent atoms—a polymorphic

Fig. 3. PAC spectra (left) and their corresponding Fourier transforms (right) for amorphous Cu60Hf20Ti20. The full line represents the results of least-squares fitting.

Fig. 4. PAC spectra (left) and their corresponding Fourier transforms (right) for amorphous Cu55Hf30Ti15. The full line represents the results of least-squares fitting.

Fig. 5. PAC spectra (left) and their corresponding Fourier transforms (right) for amorphous Cu55Hf25Ti20. The full line represents the results of least-squares fitting.
transformation to Cu_{10}Hf_{7} in the case of Cu_{60}Hf_{20}Ti_{20} and primary crystallization for Cu_{55}Hf_{30}Ti_{15} and Cu_{55}Hf_{25}Ti_{20}. The variation of the EFG in the amorphous state with Hf content followed a trend similar to that observed in binary alloys but Ti addition diminished its main value. This fact may be analyzed by taking into account the role played by each atom in the various EFG contributions.

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References