Observations of distinct atomic packings in Cu–Nb metallic glasses synthesized by ion beam mixing

LETTER TO THE EDITOR

Observations of distinct atomic packings in Cu–Nb metallic glasses synthesized by ion beam mixing

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Abstract

The structural transformation and disordered atomic packing of metallic glasses in a selected immiscible system at equilibrium, i.e. the Cu–Nb system characterized by a positive heat of formation, are studied using ion beam mixing far from equilibrium. The experimental results indicate that the Cu–Nb metallic glasses could be formed in a composition range from 30 to 85 at.% of Nb and that the Cu–Nb metallic glasses are formed through two different structural phase transition routes, i.e. from the Nb-based body centred cubic and face centred cubic solid solutions, in which the two distinct predominant atomic packings have icosahedral and icositetrahedral orderings, respectively, revealed by the respective diffraction patterns. These observations not only help in formulating a general atomic structural spectrum for the binary metallic glasses, but also suggest an important concept of *structural heredity*: that the crystalline structure of the constituent metals plays a decisive role in determining the atomic structure of the resultant metallic glasses.

In the early 1980s, some new and powerful metallic glass-producing techniques were introduced, such as ion irradiation of multiple metal layers, alternatively named ion beam mixing (IBM) [1]. Formation of the metallic glasses by IBM is through a solid–solid phase transition, instead of a liquid-to-solid phase transition as in the traditional technique of liquid melt quenching (LMQ) [2]. It has been proved that IBM is capable of producing metallic glasses not only in those systems with negative heats of formation (ΔH_f), but also in those immiscible systems at equilibrium characterized by large positive ΔH_f. Because of the non-crystalline structure with no grain boundary, the metallic glasses have frequently shown unique properties in many respects [3]. A long standing basic scientific issue in the field of metallic glasses has been how to establish/develop a relevant correlation between the structure and

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properties, which requires one first to explore an exact description of the disordered atomic structure of the metallic glasses. In the past few decades, a number of structural models have been proposed, yet most of the proposed models are mainly based on geometrical/topological considerations, such as dense random packing, efficient local packing, network packing and fcc packing models [4–6]. Very recently, there has been an attempt to characterize the atomic structure of metallic glasses; e.g. in a recent paper published in *Nature*, Sheng *et al* have studied the effect of the relative size of the constituent metals on the atomic structure and claimed that the so-called 'icosahedral-type cluster' was the predominant structural unit of the metallic glasses [7]. It is noted that in Sheng's study, all the systems are equilibrium miscible and characterized by negative ΔH_f. It is therefore questionable that their argument is also valid for the metallic glasses obtained in the immiscible systems. In fact, the atomic structure of the metallic glasses formed in the positive ΔH_f systems has scarcely been studied and is almost unknown at present. Consequently, much effort is urgently needed to explore the description of the disordered atomic structure of the metallic glasses created with immiscible atoms. Until then, it would be possible to formulate a general atomic structural spectrum for the binary metallic glasses obtained in both miscible and immiscible binary metal systems.

In the present study, we investigate the atomic structure of the metallic glasses in an immiscible Cu–Nb system ($\Delta H_f = +4$ kJ mol^{-1}) [8] produced by IBM using 200 keV xenon ions. To match the irradiating ion range, the total thickness of the Cu–Nb multilayered films is calculated to be around 42 nm, according to the TRIM program [9]. Four Cu–Nb multilayered films are designed to have the overall compositions of $Cu_{70}Nb_{30}$, $Cu_{55}Nb_{45}$, $Cu_{30}Nb_{70}$ and $Cu_{15}Nb_{85}$, and to include adequate interfacial free energies; the films consist of 10, 11, 10 and 9 layers, respectively. As regards the details of the calculation of the interfacial free energy and design of the multilayered films, the readers are referred to some previous publications from the authors' group [10–12]. The Cu–Nb multilayered films are prepared in a high vacuum evaporation system and then irradiated in an implanter to a dose range from 8×10^{14} to 7×10^{15} Xe$^+$ cm^{-2}. During irradiation, the sample holder is cooled with liquid nitrogen and the ion current density is confined to being about 2 μA cm^{-2} to minimize an otherwise overheating effect. For structural characterization, all the Cu–Nb multilayered films are examined using x-ray diffraction (XRD), transmission electron microscopy (TEM), high resolution electron micrograph (HREM) and selected area diffraction (SAD). Energy-disperse spectrum (EDS) and x-ray fluorescence (XRF) examination were employed to ascertain the real compositions of the Cu–Nb films as well as the resultant alloy phases upon IBM.

In the $Cu_{30}Nb_{70}$ multilayered films, at an irradiation dose of 1×10^{15} Xe$^+$ cm^{-2}, an Nb-rich FCC phase was obtained firstly as shown in figure 1(a) and its lattice constant was determined as around 0.423 nm. Increasing the irradiation doses to a range from 2×10^{15} to 5×10^{15} Xe$^+$ cm^{-2}, partial amorphization took place in the Nb-rich fcc matrix as evidenced by figure 1(b). Upon further irradiation to a dose of 7×10^{15} Xe$^+$ cm^{-2}, as the SAD pattern displayed in figure 1(c) shows, the sharp diffraction lines from the fcc phase disappeared and transformed into diffuse halos, indicating that a unique amorphous phase is formed.

For the $Cu_{15}Nb_{85}$ multilayered film, figure 2(a) shows a SAD pattern taken at a dose of 2×10^{15} Xe$^+$ cm^{-2}, and it confirms that a unique Nb-rich bcc phase is obtained. Increasing the irradiation dose to a range from 3×10^{15} Xe$^+$ cm^{-2} to 5×10^{15} Xe$^+$ cm^{-2}, an amorphous phase is gradually formed from the bcc phase as shown in figure 2(b) and at a dose of 7×10^{15} Xe$^+$ cm^{-2}, a uniform amorphous phase was obtained as evidenced by the SAD pattern in figure 2(c). Similar results were obtained for the $Cu_{70}Nb_{30}$ and $Cu_{55}Nb_{45}$ multilayered films; i.e. after ion irradiation to a dose of 7×10^{15} Xe$^+$ cm^{-2}, a uniform amorphous phase could be obtained, as evidenced by the respective SAD patterns (not shown, as they are similar to that of figure 2(c)).
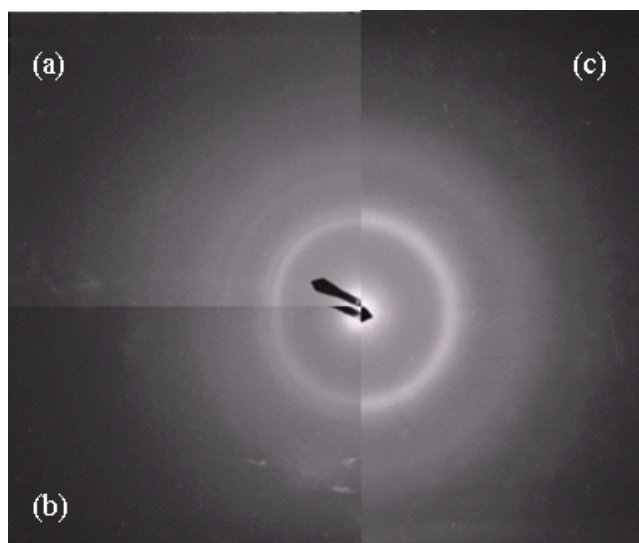
Figure 1. SAD patterns for the $Cu_{30}Nb_{70}$ multilayered samples upon 200 keV xenon ion irradiation (a) at an irradiation dose of 1×10^{15} Xe^+ cm^{-2}, (b) at an irradiation dose of 5×10^{15} Xe^+ cm^{-2}; (c) a unique amorphous phase formed at an irradiation dose of 7×10^{15} Xe^+ cm^{-2}.

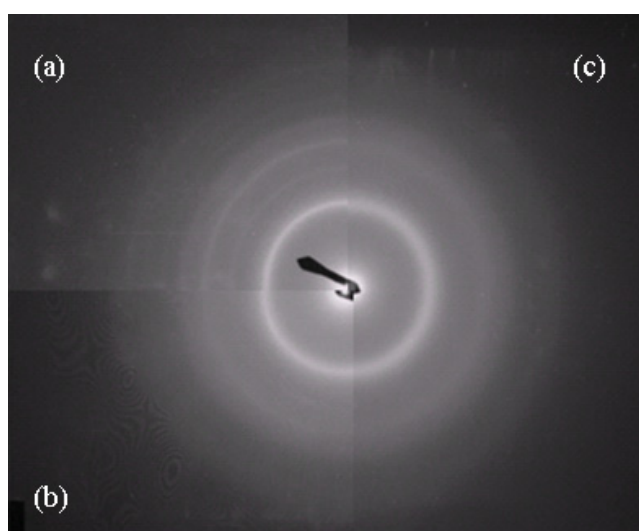**Figure 2.** SAD patterns for the $Cu_{15}Nb_{85}$ multilayered samples upon 200 keV xenon ion irradiation (a) at an irradiation dose of 2×10^{15} Xe^+ cm^{-2}, (b) at an irradiation dose of 5×10^{15} Xe^+ cm^{-2}; (c) a unique amorphous phase formed at an irradiation dose of 7×10^{15} Xe^+ cm^{-2}.

Comparing the SAD patterns in figures 1(c) and 2(c), one sees that the radius of the halo in figure 1(c) for the $Cu_{30}Nb_{70}$ metallic glass is obviously smaller than that observed from figure 2(c) for the $Cu_{15}Nb_{85}$ metallic glass as well as for the $Cu_{70}Nb_{30}$ and $Cu_{55}Nb_{45}$ metallic glasses. In addition, HREM and XRD examinations also provided confirmation of the formation of the Cu–Nb metallic glasses and, interestingly, the halo peak positions in the XRD patterns from the ion mixed $Cu_{70}Nb_{30}$, $Cu_{55}Nb_{45}$ and $Cu_{15}Nb_{85}$ metallic glasses locate
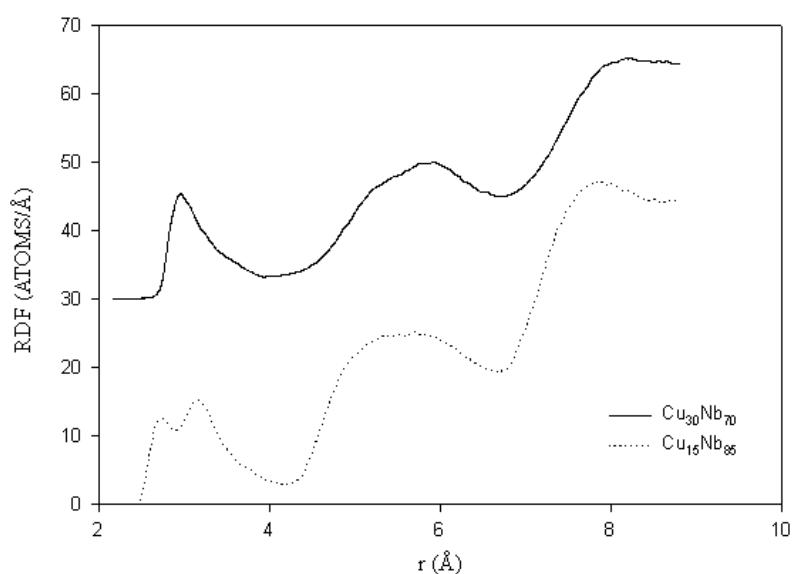
Figure 3. Radial distribution functions for the two Cu–Nb samples, calculated from the x-ray diffraction spectra data. Note: the curve for the $Cu_{30}Nb_{70}$ sample has been displaced vertically by +20.

at $2\theta \approx 39°$–$42°$, while the halo peak position of the $Cu_{30}Nb_{70}$ metallic glass locates at $2\theta \approx 37.5°$, showing clearly a shift in halo peak position. In fact, the $Cu_{30}Nb_{70}$ metallic glass is formed from the fcc Nb-based solid solutions, while the $Cu_{15}Nb_{85}$ metallic glass is formed from a bcc Nb-based solid solution. Obviously, the crystalline structure of the solvent metal Nb in the initial and/or intermediate states plays a decisive role in determining the atomic structure in the resultant metallic glasses.

In order to further reveal the atomic structures of the Cu–Nb metallic glasses, we also calculate the radial distribution function [13] from the above experimentally determined intensities of the respective x-ray diffraction spectra of the $Cu_{30}Nb_{70}$ and $Cu_{15}Nb_{85}$ metallic glasses. The calculated results are shown in figure 3. Comparing the RDF curves qualitatively from figure 3, one sees that the $Cu_{30}Nb_{70}$ and $Cu_{15}Nb_{85}$ metallic glasses are indeed in different atomic structures. By integrating the first peak of the RDF curves, we found that the coordination number (CN) of the $Cu_{15}Nb_{85}$ metallic glass is around 14, whereas the CN of the $Cu_{30}Nb_{70}$ metallic glass is around 12, indicating two distinct atomic packings as local units in the short range. Naturally, a specific atomic configuration (or ordering) corresponds to a specific coordination number (CN), e.g. icositetrahedral and icosahedral atomic configurations correspond to CN = 14 and 12 [7], respectively. Topologically, a local packing unit could be defined as a polyhedron, which includes a specific atom together with its first nearest neighbouring atoms. In reality, the polyhedra may be distorted a little to fill the three dimensional space of the metallic glass. In the present case of the Cu–Nb system, the ground state of the Nb metal is in a bcc structure, in which one Nb atom has eight first and six second neighbouring atoms, and if the two neighbours, under some specific conditions, are squeezed into a mixed one, an effective coordinate number would be 14. Interestingly, in our IBM experiments, the predominant short range local packing unit in the $Cu_{15}Nb_{85}$ metallic glasses formed from the bcc Nb-based solid solution is indeed of icositetrahedral atomic configuration with CN $\approx$ 14. Similarly, if the Nb atoms are in a metastable state of fcc structure, the dominant

packing unit in the corresponding resultant metallic glasses would be an icosahedral atomic configuration with CN $\approx$ 12, which is indeed observed in the $Cu_{30}Nb_{70}$ metallic glass formed by IBM. Incidentally, a first principles calculation showed that the energy difference between the Nb atoms in fcc and bcc structures is only 0.32 eV/atom, which could explain why the Nb metal could be in either a fcc or a bcc structure in IBM experiments, resulting in two distinct atomic configurations as the corresponding dominant local packing units in the respective Cu–Nb metallic glasses. Moreover, the structures of the metallic glasses studied by He *et al* were all characterized by an icosahedral short range ordering, because those glasses were all from solvent metals with an fcc structure [14]. It can be deduced that if the two constituent metals of a system are both fcc structures, the dominant atomic configuration of the metallic glasses formed in the system is expected to be icosahedral ordering, matching well with that reported for the Ni–Ag system [15].

According to the atomic collision theory [16], the process of IBM is commonly known to occur as follows: initially, a sequence of ballistic collisions is triggered in the Cu–Nb multilayered films by 200 keV xenon ions and is responsible for intermixing of the Cu and Nb layers. During the mixing, the Cu and Nb atoms are most probably in a highly energetic state and in a disordered structure. When the atomic collision cascade is eventually terminated, the highly energetic state has to relax towards equilibrium. However, because the relaxation period is extremely short, i.e. lasting for 10^{-10} s, only very minor atomic rearrangement could take place. Consequently, either a simple structured crystalline phase, such as fcc, bcc and hcp, could be grown or the disordered structure prefers to preserve, thus forming an amorphous phase. Unlike other glass-producing quenching techniques, formation of the metallic glasses by IBM is through a solid–solid phase transition, instead of a liquid-to-solid phase transition. It is reasonable to deduce that the atomic configuration of the synthesized amorphous alloy is closely related with the crystalline structure of the metal in the initial and/or intermediate states. In the present $Cu_{30}Nb_{70}$ and $Cu_{15}Nb_{85}$ case, we first obtain an fcc/bcc Nb-based solid solution and after further ion irradiation, the metastable fcc/bcc crystalline phases collapse into two amorphous alloys with distinct atomic configurations, which, in fact, have been observed in experiments.

To establish an atomistic model of the Cu–Nb metallic glasses, an N-body Cu–Nb potential is first derived, based on the embedded atom method and then applied in molecular dynamics (MD) simulation under the Parrinello–Rahman scheme. The primary results obtained so far strongly confirm the above argument and the details will be published later.

In summary, on the basis of the design of the interfacial free energy stored in the Cu–Nb multilayered films, the unique amorphous phases and metastable fcc/bcc solid solution in a broad composition range from 30 to 85 at.% Nb were obtained in the Cu–Nb system by ion beam mixing. More importantly, two distinct atomic packings as local units are found: icosahedral and icositetrahedral atomic configurations with coordinate numbers of 12 and 14. These findings suggest an important concept of *structural heredity*: that the structure of the constituent metals plays a decisive role in determining the atomic structure of the resultant metallic glasses.

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