



Linking electronic structure to beta relaxation of La-based bulk metallic glasses

Wei Jiang, Jili Wu, Bo Zhang*

Institute of Amorphous Matter Science, School of Materials Science and Engineering, Hefei University of Technology, Hefei 230009, PR China



ARTICLE INFO

Keywords:

Electronic structure
Beta relaxation
Bulk metallic glass

ABSTRACT

This work investigates the correlation of electronic structure and β relaxation of $\text{La}_{70}\text{Ni}_{15}\text{Al}_{15}$, $\text{La}_{70}\text{Co}_{15}\text{Al}_{15}$ and $\text{La}_{70}\text{Cu}_{15}\text{Al}_{15}$ bulk metallic glasses. X-ray photoelectron spectroscopy measurements discovered that the activity of electrons around Fermi level of $\text{La}_{70}\text{Ni}_{15}\text{Al}_{15}$ and $\text{La}_{70}\text{Co}_{15}\text{Al}_{15}$ glasses with peak-like strong β relaxation are more intense than $\text{La}_{70}\text{Cu}_{15}\text{Al}_{15}$ glass with shoulder-like weak β relaxation and correspondingly the core levels of electronic states of Ni and Co elements are seriously split whereas that of Cu is not. This work might provide a different route to understand the origin of β relaxation rather than the normal thinking of atomic packing structure.

1. Introduction

Bulk metallic glasses (BMGs) usually display a secondary relaxation (β relaxation) [1–4] which favors understanding their properties, such as physical aging [5,6], diffusion [7], heterogeneity [8,9], and mechanical properties including plastic deformation behaviors [9,10]. On the other hand, BMGs are as simply effective model material for understanding of β relaxation, although their random structures also cause the complexity [11]. In the past years, it has been discovered that β relaxation usually performs in different types, such as peak (in La-Ni-Al and La-Co-Al *etc.* [12,13]), shoulder (in Pd-Ni-P-Cu and binary Cu-Zr BMGs *etc.* [4,14–16]) and excess wing (in Cu-Zr-Al, Zr-based and Ce-based BMGs *etc.* [17–20]). Nevertheless, in the view of microstructures, the causes regarding to different types are the unsolvable puzzles. That is, the origin of β relaxation is still a long-standing and elusory topic in the area of amorphous systems [3].

In macroscopic thermodynamic theory, peak-type β relaxation behaviors are related to the fluctuations of chemical interactions (mixing enthalpy, H_{AB}) and chemical affinity ($\Delta H_{\text{chem}} = 4\sum_{A \neq B} c_A \cdot c_B \cdot H_{AB}$, where c_A and c_B are the molar percentage of the elements A and B, respectively.) [15,21]. By using prototypical BMGs, Yu et al. [15] found out that peak-type β relaxations are associated with that all the atomic pairs, in the BMGs, have large similar negative mixing enthalpy, whereas positive or significant fluctuations in mixing enthalpy suppress β relaxations. Furthermore, this scenario was also separately demonstrated in Y-Ni-Al [21], La-Ga-Ni [22] and Fe-Zr-B [23] systems. In a desirably imaginary picture, regarding the structural origin of β relaxation is, summarily, that strong and comparable interactions among

all the constituting atoms easily maintain a string-like atomic configuration for the excitations of β relaxation, *i.e.* the formation of molecule-like metallic glasses [15,24].

From the viewpoint of atomic scale clusters/atom pairs, on the other hand, highly ‘mobile’ atomic pairs, such as the La–Ni pair in La–Ni–Al MGs [13], and low interacted bonding atom pairs, such as La–Ga pair in La–Ga-based MGs [22], which lowers down the onset temperature for β relaxation and thus promote the peak-type β relaxation. Yu et al. [25] disclosed that the β relaxation behavior and its onset temperature can be consecutively changed accompanying with the ratio of La/Ce atoms, and deduced two types of atomic pairs to trigger the succession of β relaxation in Ce-doped La-based MGs. More than that, atom pairs with various onset temperatures favor the multiple β relaxation [11,26]. Obviously, the atom pairs, with high ‘mobility’, strongly control the β relaxation below glass transition temperature (T_g).

Even so, chemical interaction and mobile clusters/atom pairs just present an imaginative routine to realize the origin of β relaxation. More fundamental understanding of β relaxation of BMGs has been progressively, and interesting results has met the string-like atomic configuration viewpoint [27,28]. Underlying this atomic configuration, electronic structure and atomic structure interrelations are expected to give more fundamental insights into the understanding of β relaxation. In this work, we experimentally investigated the electronic basis, by using X-ray photoelectron spectroscopy (XPS), referring to three La-based BMGs and aims to conclude the electronic viewpoint of β relaxation. The electronic state of core level and density of state of electrons explored that the Ni and Co elements play a key role in the peak-type β relaxation of La-based BMGs and also indicated that the

* Corresponding author.

E-mail address: bo.zhang@hfut.edu.cn (B. Zhang).

split electronic states of atoms are responsible for peak-type β relaxation.

2. Experiments

2.1. Preparation and characterization

The alloy ingots with nominal compositions of $\text{La}_{70}\text{Ni}_{15}\text{Al}_{15}(\text{N})$, $\text{La}_{70}\text{Co}_{15}\text{Al}_{15}(\text{O})$ and $\text{La}_{70}\text{Cu}_{15}\text{Al}_{15}(\text{U})$ (in at.%) were prepared by arc-melting mixtures of pure metals (purity not less than 99.9 at.%) in Ti-gettered argon atmosphere. Each ingot was melted at least four times to ensure chemical homogeneity and then cast into a water-cooled copper mold to obtain a rectangular plot with the dimension of $\sim 80 \text{ mm} \times 10 \text{ mm} \times 1 \text{ mm}$.

The amorphous structure of the as-cast alloys were ascertained by X-ray diffraction using $\text{Cu-K}\alpha$ radiation and DSC under a flow of purified nitrogen in a Perkin-Elmer Diamond DSC with a heating rate of 20 K min^{-1} .

2.2. Dynamic mechanical analysis

The relaxation behaviors of three La-based BMGs were characterized by a TA Q800 dynamic mechanical analyzer(DMA). The dynamic modulus (loss modulus) was measured as a function of the temperature, in the range from 300 to 500 K at a constant heating rate of 3 K min^{-1} . Prior to DMA tests, the rectangular specimens ($30 \text{ mm} \times 2 \text{ mm} \times 1 \text{ mm}$) were gripped to an oscillating system and subject to sinusoidal single cantilever-bending strains with the limited amplitude of $\sim 0.02\%$.

2.3. X-ray photoelectron spectrum

The bonding states were evaluated by X-ray photoelectron spectroscopy (XPS, Escalab 250Xi) with a monochromic Al $\text{K}\alpha$ X-ray source ($h\nu = 1486.6 \text{ eV}$). The base pressure of the analysis chamber was lower than $5 \times 10^{-12} \text{ Torr}$. All spectra were calibrated using the binding energy (BE) of C_{1s} (284.8 eV) as a reference. For the pure components, we use polycrystalline plates of La, Co, Ni, Cu and Al. Before the XPS experiments, all specimens were cleaned by Ar-ion sputtering to obtain oxygen-free surfaces.

3. Results

Fig. 1 shows the XRD patterns of as-cast N, O and U plates with thickness of 1 mm. For each XRD pattern, a broad diffraction peak without any distinct sharp crystalline peak indicates the amorphous nature of as-cast alloys, that is, forming monolithic BMGs. The glass transition temperatures (T_g) of as-cast N, O and U BMGs are 422 K, 434 K and 398 K, respectively(Fig. S1). The distinct glass transition and sharp crystallization behaviors further confirm the glassy structures of as-cast alloys. The DMA spectra indicate that as-cast N and O BMGs display a peak-like β relaxation but as-cast U BMG clearly presents a shoulder-like β relaxation(Figs. S2 and S3). It has been well known that Co, Ni and Cu have a very similarity in atomic size and electronegativity because they are in a same period and contiguous sites of the elements period table [29].

Regarding the origin of β relaxation of these three BMGs, Wang et al. [12] emphasized that mixing enthalpy of Cu with Al (-1 kJ/mol) are positively larger than Ni or Co with Al (-22 kJ/mol and -19 kJ/mol , respectively.), and suggested that the variation of composition can change the proportion and structure of loose-packing regions, and thus affect the relaxation mode. Stevenson et al. [24] considered β relaxation as reversibly and cooperatively back-and-forth-moving atomic chain within the confinement of surrounding elastic matrix and theoretically predicts β relaxation is related to the excitations of string-like configurations. And also, “weak” and “strong” interaction/bonding act

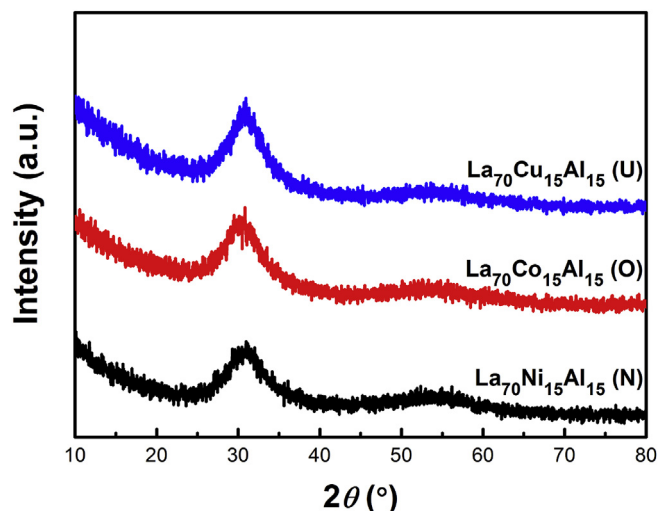


Fig. 1. XRD patterns of as-cast $\text{La}_{70}\text{Ni}_{15}\text{Al}_{15}(\text{N})$, $\text{La}_{70}\text{Co}_{15}\text{Al}_{15}(\text{O})$ and $\text{La}_{70}\text{Cu}_{15}\text{Al}_{15}(\text{U})$ BMGs.

as ‘cutters’ or ‘anti-glue’ to the string-like configurations and then to complete cooperative β process [15]. Summarily, the origin of β relaxation can boil down to bonding/packing state, global enthalpy of the system and reversibly cooperative motion.

More importantly, β relaxation is closely correlated with structural heterogeneity of BMGs. The heterogeneity is usually as free volume or flow units, which are currently considered as “defect” in BMGs [30,31,35]. To simplify the illustration of heterogeneity of a BMG, in thermodynamics, the heterogeneity can be evaluated with the enthalpy before T_g [32]. Fig. 2(a) displays the local curves of DSC of as-cast N, O and U BMGs. It can be clearly seen that the enthalpy, before T_g , of as-cast U BMG is remarkably smaller than two others. Evidently, it demonstrates that as-cast U BMG is packed closer than two others in structure, and, on this point, as-cast U BMG should to undergo a weak β relaxation process. Furthermore, underlying this mediate feature, electronic structure and atomic structure interrelations are expected to give more fundamental insights into the understanding of β relaxation.

Fig. 2(b) illustrates the density of states (DOS) of as-cast N, U and O BMGs. To simplify the comparison among three BMGs and highlight the difference around Fermi level(E_f), the curves were normalized by being scaled with corresponding peak at $\sim 19 \text{ eV}$. A remarkable difference can be found around E_f (inset of Fig. 2(b)). Specifically, as-cast N and O BMGs have a higher relative DOS, around E_f , than as-cast U BMG. In general, the lower intensity for a BMG around E_f usually indicates a close packed structure of this BMG [33]. Alternatively, compared with the DOS of pure Co and Ni, the pure Cu have a nearer bonding energy to pure La and thus the outer electronic orbit of these two elements can easily hybridize with the outer orbit of principal element La in the counterpart alloy(Fig. S4). Therefore, the structure of as-cast U BMG is denser than as-cast N and O BMGs; and also, as-cast U BMG has relatively lower free volume/flow unit quantity, regarding to as-cast N and O BMGs. This also is agreed with the analysis of enthalpy before T_g .

Fig. 3 indicates the core level of La and Al elements of as-cast N, O and U BMGs. For the La element(Fig. 3(a)), bonding energies of La $3d_{3/2}$ (851 eV) and La $3d_{5/2}$ (834 eV) in as-cast U BMG are lower than other two BMGs. It is worth noticing that the alloy with highly close-packed atomic structure may possess a decreased size of the valence electron cloud, which strengthen the attractive Coulomb force between the atomic nucleus and the valence electrons, and thus increase the binding energy of the valence electrons [33,34]. However, for Al element(Fig. 3(b)), the bonding energies of Al $2p$ of as-cast N, O and U BMGs do not indicate non-ignorable disparity. Therefore, as-cast U BMG packed in a denser state than two other ones. On the other hand, it is also reasonable that the differences in the structure of three BMGs are

Download English Version:

<https://daneshyari.com/en/article/7988283>

Download Persian Version:

<https://daneshyari.com/article/7988283>

[Daneshyari.com](https://daneshyari.com)