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Free-volume dependent atomic dynamics in beta relaxation pronounced La-based metallic glasses

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ABSTRACT

The atomic dynamics and its structure dependence in a glass are fundamental issues but still little understood for decades. Through state-of-the-art experiment and simulation, we reveal that the annihilation of excess free volume in a β-relaxation pronounced La–Al–Ni metallic glass slows down the atomic motion by one order of magnitude upon annealing, which is mainly caused by the change of subatomic cavities and enhanced network structure resulting from the presence of Ni atoms, showing significant difference from a β-relaxation unpronounced La–Al–Cu glass. Our findings provide insights into the dynamics and atomic structure of La-based metallic glasses and will be helpful in understanding the microscopic dynamic behavior of metallic glasses in general.

1. Introduction

As a metastable system, the stability of metallic glasses (MGs) lies in the possibility for bringing the system into deep minima of the potential energy landscape (PEL) by annealing at temperatures below the glass transition (T_g) [1,2]. It is commonly believed that two distinct relaxation processes exist in glasses [3,4], *i.e.*, (1) hopping across "sub-basins" of the PEL named as the secondary β-relaxation discovered by Johari and Goldstein (JG) [5] and (2) the global structural change between megabasins due to the primary α-relaxation. It was shown that the α-relaxation depends strongly on the thermal history of the glass [6]. Usually, the higher the quenching rate, the shorter the relaxation time, possibly due to the presence of a larger amount of free volume in the material. With free volume changing, the properties of MGs can be tuned accordingly [7]. It is thus important to understand how the free volume affects the atomic dynamics and how the structure evolves with aging.

Recent reports revealed that the pronounced β-relaxation in MGs may pertain to the strong and comparable interactions among all the constituent atoms [8] as well as the mobility of small atoms [9]. However, the correlation of the β-relaxation and the dynamics of the primary α-relaxation process during aging remains unclear. Thanks to the development of modern synchrotron radiation techniques, X-ray photon correlation spectroscopy (XPCS) [10] has recently emerged as a powerful tool to probe the out-of-equilibrium relaxation dynamics of structural glasses [6,11]. Also, local atomic environment changes can be traced *in situ* by using the X-ray absorption fine structure (XAFS) [12]. For instance, Ruta et al. used XPCS to measure the α-relaxation in an Mg–Cu–Y and a Zr–Ni MG [6,13]. A dynamical crossover between the supercooled liquid and the metastable glassy state has been observed, which leads to a complex hierarchy of aging regimes in the glassy state. However, those MGs do not have pronounced β-relaxation, which could be amendable to the atomic dynamics associated with the primary α-relaxation. Here we combine XPCS with differential scanning calorimetry (DSC) and *in situ* XAFS measurements to study the concurrent structural and dynamical changes occurring in both $La_{70}Al_{15}Ni_{15}$ and $La_{70}Al_{15}Cu_{15}$ MGs under two different thermal protocols. We select La-based MGs as a prototype to study since La–Al–Ni MGs have been reported to exhibit pronounced β-relaxation [14,15], which however becomes insignificant if Ni atoms are replaced by Cu in La–Al–Cu MGs. The structural origin of the different dynamic behaviors of both MGs has been interrogated by analyzing the atomic structure of structural models derived from reverse Monte Carlo (RMC) [16] constrained with classic molecular dynamics simulations.

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2. Materials and methods

Ribbons of $La_{70}Al_{15}M_{15}$ (M = Ni and Cu) MGs were prepared by melt spinning at a speed of 30 m/s in argon atmosphere. Part of the as-prepared ribbons was vacuum-sealed in quartz tubes then annealed at about $0.9T_g$ of their own for 7 days (358 K for $La_{70}Al_{15}Cu_{15}$ and 388 K for $La_{70}Al_{15}Ni_{15}$). The atomic dynamics was measured at the ID10 beamline (XPCS) at ESRF. The data were collected for a wave vector q_0 corresponding to the position of the first maximum in the static structure factor $S(q)$, where q_0 is of about 2.10–2.13 $Å^{-1}$ for these MGs. In this way we probed directly the dynamics on a spatial scale of $2\pi/q_0$ in MGs, which is difficult to access by using other experimental techniques. The data were collected by two two-dimensional IkonM charge-coupled devices (CCD) (1024 × 1024 pixels and 13 × 13 μm^2 pixel size) installed vertically symmetric with respect to the incoming beam. Sets up to ~1300 images were collected with an exposure time of 3 s per image and analyzed following the procedure described in Ref. [17]. A Perkin-Elmer Pyris Diamond DSC was used to measure the thermal behavior changes in argon atmosphere at a heating rate of 20 K/min. A TA-Q800 DMA was adopted to probe the α and β-relaxations by using tension film clamps with constant force 0.8 N, frequency 1 Hz and heating rate of 3 K/min under the nitrogen-flushed atmosphere. The XAFS spectra at Cu and Ni K edges (8979 eV and 8333 eV) were collected in transmission mode at the beamline 1W1B-XAFS of BSRF, Beijing. Standard data analysis was conducted by using the software package of IFEFFIT [18], and the FEFF-8 code [19] being used to calculate the scattering amplitudes and phase shifts.

The atomic packings of as-cast $La_{70}Al_{15}Ni_{15}$ and $La_{70}Al_{15}Cu_{15}$ MGs are constructed by using classical molecular dynamics (MD) LAMMPS [20] with newly-developed embedded atom method (EAM) potentials [21] to simulate the rapid quenching process. A cubic box containing 10,000 atoms (7000 La, 1500 Al and 1500 Cu/Ni) with periodic boundary conditions in three directions is initially relaxed at 2000 K for 2 ns then quenched to 300 K at a cooling rate of 10^{11} K/s with a canonical NPT ensemble (Constant atom number, pressure and temperature). The RMC simulation [16] is further adopted to optimize the MD-produced configurations by initially setting relatively high convergence accuracy.

3. Results

3.1. Thermal difference

Fig. 1 shows the DSC traces of the as-cast and annealed $La_{70}Al_{15}Ni_{15}$ and $La_{70}Al_{15}Cu_{15}$ MGs at a heating rate of 20 K/min. At temperatures below T_g, there is a broad exothermic event with heat release of about −7.6 J/g starting from 363 K for the as-cast $La_{70}Al_{15}Ni_{15}$. After 7-day annealing at 388 K (~$0.9T_g$), the exothermic event below T_g totally disappears with the appearance of a distinct endothermic peak above T_g due to enthalpy recovery [22]. At higher temperatures, the crystallization behavior of the annealed sample remains similar to the as-cast one. In comparison, for the as-cast and annealed $La_{70}Al_{15}Cu_{15}$ MGs, the sub-T_g annealing significantly promotes the first crystallization event in addition to a relatively small enthalpy recovery of about −2.3 J/g below T_g.

3.2. Atomic dynamics by XPCS measurements

Fig. 2a shows the temperature dependence of the intensity autocorrelation function, $g_2(q,t) = \frac{\langle I_p(q,t_1) I_p(q,t_1+t)\rangle_p}{\langle I(q,t_1)\rangle_p \langle I(q,t_1)\rangle_p}$, of the as-cast $La_{70}Al_{15}Ni_{15}$ MG upon heating at different isothermal steps, where $\langle \ldots \rangle_p$ denotes the ensemble average over all the pixels of the detector and $\langle \ldots \rangle$ is the temporal average. The intensity correlation

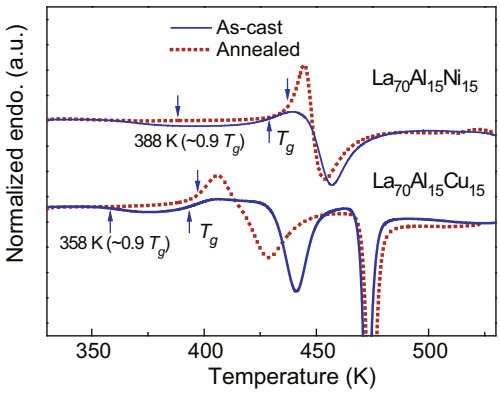

Fig. 1. DSC measurements for the as-cast and annealed $La_{70}Al_{15}Ni_{15}$ and $La_{70}Al_{15}Cu_{15}$ MGs, showing the pronounced excess free volume annihilation in the as-cast $La_{70}Al_{15}Ni_{15}$ MG.

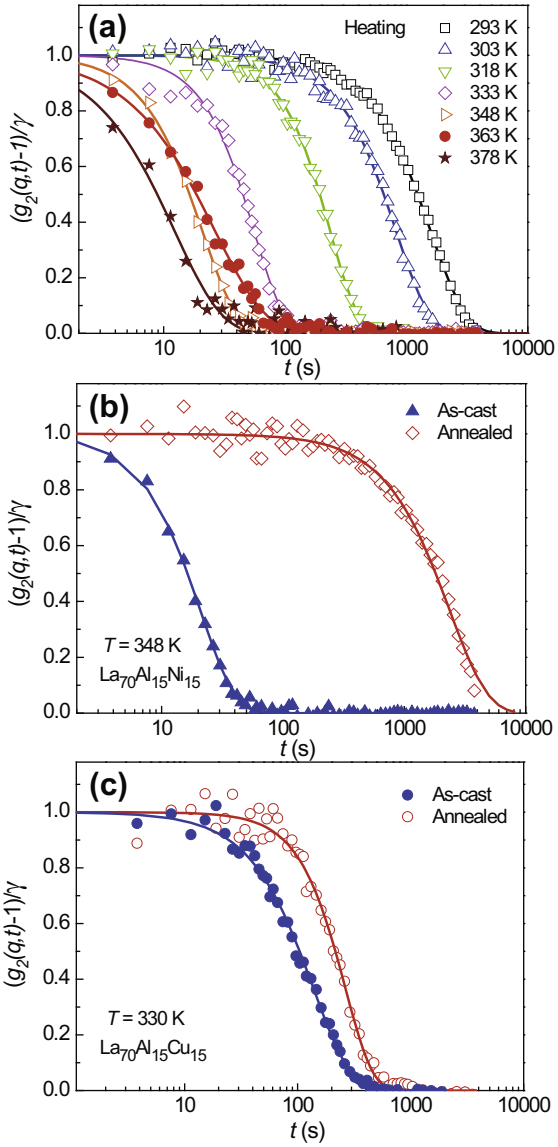

Fig. 2. (a) Temperature dependence of correlation functions measured at q_0 = 2.11 $Å^{-1}$ for the as-cast $La_{70}Al_{15}Ni_{15}$ MG upon heating (b) and (c) are comparisons between the correlation function measured in as-cast and annealed $La_{70}Al_{15}Ni_{15}$ (T = 348 K) and $La_{70}Al_{15}Cu_{15}$ (T = 330 K) MGs, respectively. The lines are the best fits using the KWW model function.