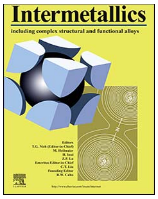
Intermetallics 93 (2018) 101–105

Contents lists available at ScienceDirect

Intermetallics

journal homepage: www.elsevier.com/locate/intermet



Two-step relaxations in metallic glasses during isothermal annealing

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ARTICLE INFO

Keywords:
β relaxation
α relaxation
Metallic glass
Isothermal annealing
Energy landscape

ABSTRACT

Isothermal annealing is a very useful strategy in modulating the properties and structures of metallic glasses, which has been regarded as a single relaxation progress. In this work, the enthalpy relaxation of Au-based metallic glasses are studied using a high-precision calorimetry. An intriguing transition from β relaxation to α relaxation was confirmed during isothermal annealing. Energy landscape model is proposed to quantitatively explain how the relaxation modes transform. It is found that a small enthalpy decrease (about 0.8 kJ/mol) in initial state causes an extremely large increase (about 100 kJ/mol) in relaxation barrier, which is attributed to the enhanced cooperative atomic motion. These results open a gate for precisely understanding the role of different relaxation modes in modifying the properties of metallic glasses.

1. Introduction

Relaxations are intrinsic characters of metallic glasses as a result of the far-from-equilibrium nature and play an important role in modulating the structure and physical properties. For examples, relaxation upon isothermal annealing below glass transition temperature (T_g) is applied to release the residual stress in metallic glasses [1,2] to enhance their soft magnetic performance [3]. Relaxation also plays an important role in modifying the mechanical properties of metallic glasses [4–6]. Upon optimal annealing, glasses can reach highly stable states with very low energy and high kinetic stability [7–9]. It has been found that relaxation has close relations with the atomic diffusion [10,11], the rearrangement of nearest-atoms [12,13] and nanoscale heterogeneity [14–16]. Upon continuous heating, a glass usually experiences two relaxation modes, known as secondary (β) relaxation and primary (α) relaxation [17–20]. The two relaxation modes usually split at low temperatures but merge at high temperatures in supercooled liquid states [21,22]. However, isothermal annealing at low temperatures was always regarded as single relaxation process, which can be fitted using extended exponential equation, i.e. Kohlrausch-Williams-Watts function [17,18,23–29].

Molecular simulations reveal that the glass may experience two relaxation stages upon isothermal annealing [21,30]. Such a two-stage relaxation phenomenon was confirmed experimentally in soft glasses, e.g. polymers and colloidal suspensions [31,32]. For rigid metallic glasses, a similar two-stage relaxation process are reported quite recently during stress relaxations [22,33]. The first-stage is a stress-driven relaxation process, while the second-stage is attributed to medium range ordering diffusion processes [34]. Our recent work [9] on the fabrication of highly stable bulk metallic glasses reported an abnormal non-linear relationship between the kinetic stability and thermodynamic stability. That is, for short time annealing at low temperatures, the glass transition temperature (T_g) decreases along with the decrease of enthalpy (contradiction in the evolutions of kinetic stability and thermodynamic stability), while when the annealing time is long enough T_g increases along with the decrease of enthalpy (consistency in the evolutions of kinetic stability and thermodynamic stability). It is worthwhile to study what is responsible for the change in relationship between T_g and enthalpy, and whether it is related to the recent findings of two-stage relaxations phenomenon.

For physical origins of relaxations, in the potential energy landscape (PEL) theory, it is proposed that α relaxation corresponds to the motion between "meta-basins" while β relaxations are identified as hopping events between the "sub-basins" [14,21,35]. But the quantitative relation between meta-basins and sub-basins in energy landscape has not been revealed yet.

Au-based metallic glasses are good model materials for investigating the relaxation kinetics, because of their good glass forming ability, high oxidation resistance and low glass transition temperature [13,29,36,37]. The kinetics of β relaxation and glass transition for Au-based metallic glasses have been studied in-situ using high-rate differential scanning calorimetry (DSC) [9,38]. In this paper, we studied the

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https://doi.org/10.1016/j.intermet.2017.11.016
Received 17 October 2017; Received in revised form 1 November 2017; Accepted 27 November 2017

isothermal relaxation kinetics of $Au_{49}Cu_{26.9}Ag_{5.5}Pd_{2.3}Si_{16.3}$ (at.%) metallic glass by measuring the enthalpy evolution of Au-based metallic glasses using a high-precision and high-rate DSC. A transition from β relaxation to α relaxation was identified by measuring the relaxation activation energy. Quantitative analysis based on energy landscape model is proposed to explain the transition mechanism between different relaxation modes.

2. Materials and methods

Master alloy with nominal composition of $Au_{49}Cu_{26.9}Ag_{5.5}Pd_{2.3}Si_{16.3}$ (at.%) was prepared by arc melting the pure elements (> 99.9 wt%) under the protection of high-purity Ar gas. The master alloy was then remelt in a quartz tube and injected on a fast spinning copper roller (tangent speed ~40 m/s) to obtain metallic glass ribbons. A small piece of sample with dimensions about 50 μm × 50 μm × 30 μm was cut from the ribbon under an optical microscope. The small sample was then transferred to the sample chip for DSC measurement under an optical microscope. Annealing experiments were performed using a high-precision and high-rate differential scanning calorimeter (Flash DSC 1, Mettler Toledo). During measurement, a flow of high-purity Ar gas (40 ml/min) was applied to protect the sample from oxidation. The relaxation behaviors were measured at different annealing temperatures for various time.

3. Results and discussions

The thermal protocol is shown in Fig. 1a. To obtain a fully glassy sample, the melt is cooled at a rate of 6000 K/s, which is much faster than the critical cooling rate (~1000 K/s[9]) for glass formation. Fig. 1b shows the typical DSC traces of as-cooled and relaxed samples. After the relaxation at 363 K for 0.1 s, an excess endothermic peak appears before glass transition. The endothermic peak is obtained by subtracting heat flow of as-cooled sample, as shown in the inset of Fig. 1b. To reveal the evolvement of relaxation peak, a 2-dimensional contour of the heat flow versus temperature and annealing time is given in Fig. 1c. The relaxation peak T_p (solid circles in Fig. 1c) experiences two stages as the yellow lines indicate. T_p increases very fast at the first stage upon annealing while it increases slowly at the second stage.

To study the relaxation kinetics, the heating rate dependent behavior of the relaxation peaks is studied, as shown in Fig. 2a. At higher heating rates, the relaxation peak shift to higher temperatures. In Fig. 2b, the activation energy (ΔE) for relaxation is calculated from the slope of Kissinger plot [39,40], which is almost equal to that determined by Arrhenius fitting (see Fig. S1 in supplementary materials). The ΔE is plotted versus annealing time in Fig. 2c and a 3-dimensional plot for ΔE versus annealing time and annealing temperature is shown in Fig. 2d. At initial annealing stage, ΔE is small and almost a constant, about 75–95 kJ/mol. When the annealing time is long enough at a given annealing temperature, ΔE increases to a much larger value and remains constant, about 160–175 kJ/mol. The transition time from small ΔE to large ΔE behavior is consistent with the transition time of T_p observed in Fig. 1c, which confirms the two-step relaxation phenomenon. Furthermore, ΔE at initial annealing stage is about (25.5 ± 2) RT_g (given T_g = 401 K at 20 K/min [37]), which is almost equal to the β relaxation activation energy $\Delta E_\beta \approx 26RT_g$ [28]. It is noteworthy that this activation energy is larger than the fast relaxation process during stress relaxation [22]. ΔE at the second annealing stage is about (50 ± 2) RT_g. Considering the relaxation peak temperature (i.e. 450 K measured at 1000 K/s for the glass annealed at 363 K for 1000 s) is much higher than T_g (=401 K at 20 K/min) and the non-Arrhenius character of α relaxation, ΔE at the second annealing stage is close to the α relaxation activation energy (ΔE_α, see Fig. S2). The β-to-α transition time ($t_{\beta\text{-}\alpha}$) exhibits strong temperature-dependent character. $t_{\beta\text{-}\alpha}$ decreases when T_a increases, suggesting a thermal activated character. Fig. 2d shows that β relaxation dominates at low annealing temperature for short annealing time, while α relaxation takes over at high annealing temperature for long annealing time.

In energy landscape theory [21,35], relaxation can be illustrated as jumping between different energy minima, as shown in Fig. 3a. The β relaxation has a small energy barrier while α relaxation has a large energy barrier. It is curious to know whether the enthalpy decrease account for the large increase in relaxation energy barrier. The enthalpy is given by $\Delta H = \int_{T_a}^{T_0} C_p dT$, with T_0 is the integral upper limit (in supercooled liquid state), C_p is specific heat. As shown in Fig. 3b, ΔE is plotted versus ΔH. It is surprising that a small decrease of about 0.8 kJ/mol for ΔH causes an extremely large increase of about 100 kJ/mol for ΔE. In elastic model, the activation energy ΔE can be expressed in harmonic approximation as $\Delta E = 0.5MV_m\gamma$ [2,41–44], where M is the elastic modulus, V_m is the molar volume and γ is the elastic strain. It is well known that the elastic moduli and molar volume usually change less than 10% after annealing [36,45,46], which should not contribute much to the increase of ΔE. The large increase of ΔE from β relaxation to α relaxation is attributed to the increase of relaxation strain. The shear modulus G and molar volume V_m of this Au-based MG is about 26.5 GPa and 10.9 cm^3/mol [37,44], respectively. According to the elastic model, the transformation strain increase from 0.721 to 1.053 after β relaxation transform to α relaxation, which is consistent with atomic cooperative model [34,47].

The transition time (t_{tran}) from β relaxation to α relaxation exhibits a clear dependence on temperature, as shown in Fig. 2c. The energy barrier for the transition (ΔE_{tran}) can be determined by $t_{tran} = t_0\exp(\Delta E_{tran}/RT)$, where t_0 is a prefactor and R is gas constant. As shown in Fig. 4a, ΔE_{tran} is determined to be about 164 kJ/mol, which is almost equal to the ΔE_α. As illustrated in Fig. 4b, before annealing, the atoms in region with lower packing density (liquid-like zone or flow unit [48–53]) perform β relaxation that involves less atoms moving cooperatively. After deep annealing, the atoms with high packing density (solid-like zone [48–53]) perform α relaxation that requires large-scale

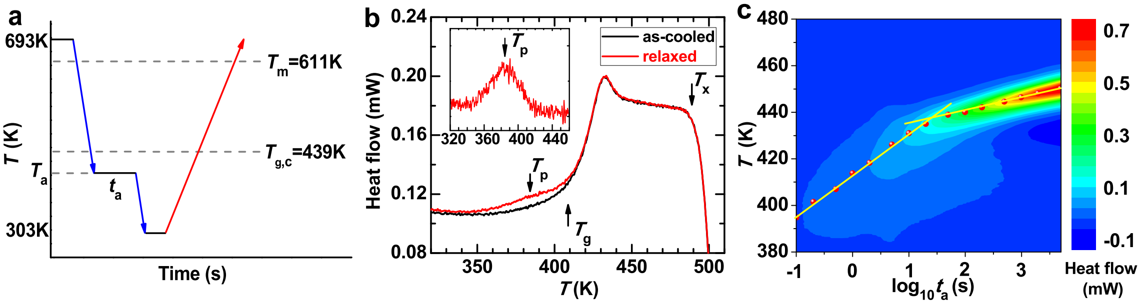

Fig. 1. (a) Schematic illustration of thermal progress. (b) The DSC traces for as-cooled sample (black) and the sample relaxed at 363 K for 0.1 s (red). The heating rate is 500 K/s. T_p is relaxation peak temperature, T_g is glass transition temperature, T_x is onset crystallization temperature. Inset is the relaxation peak by subtracting the two DSC traces. (c) 2D contours of the relaxation heat flows, the peak values (red full circles) exhibit two-step relaxation behaviors that is highlighted by yellow lines.(For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)