Thermal expansion of La-based BMG studied by in situ high-energy X-ray diffraction

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**Abstract**

The present work focuses on the study of the thermal stability of La\(_{62}\)Al\(_{14}\)(Cu\(_{5/6}\)Ag\(_{1/6}\))\(_{14}\)Ni\(_5\)Co\(_5\) (at.\%) bulk metallic glass (BMG) using the state-of-the-art high temperature in situ hard X-ray scattering techniques available at the undulator beamline ID11 of ESRF (Grenoble, France). Constant-rate heating experiments using a fast X-ray camera (time resolution of 3 s) reveal detailed information about the thermal stability of the La-based BMG. Analyzing diffraction patterns in a reciprocal space yields thermal expansion of amorphous alloy providing insight about the thermally activated relaxation effects and glass transition. We found that in the region 20 K below the glass transition (\(T_g = 420\) K) thermal expansion curve exhibits negative slope which indicates annealing-out of the quenched-in free volumes. The glass transition appears as a brake in the value of coefficient of the volume thermal expansion \(\alpha_v\). Furthermore, real space analysis based on reduced pair distribution function \(G(r)\) allows to trace the changes in the local atomic structure of amorphous material during constant-rate heating.

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1. Introduction

Bulk metallic glasses represent relatively new class of materials exhibiting unique mechanical, chemical, electronic and magnetic properties which strongly differ from the ones of their crystalline counterparts [1]. These multi-component metallic alloys combine high glass-forming ability with low cooling rates below 100 K/min which allow formation of few mm thick samples by conventional mould casting [2,3]. Structurally, bulk metallic glasses can be classified as disordered materials. X-ray diffraction (XRD) using high-energy photons has proven to be well suited for describing the structure of disordered systems such as BMGs. Time-resolved in situ X-ray diffraction experiments may nowadays be performed at high-brilliance synchrotron radiation sources for a variety of conditions which help to elucidate the structure–property relations.

Aim of this work is to study the thermal stability of La\(_{62}\)Al\(_{14}\)(Cu\(_{5/6}\)Ag\(_{1/6}\))\(_{14}\)Ni\(_5\)Co\(_5\) BMG in the temperature range 300–800 K using in situ high-energy X-ray diffraction. The special emphasis is placed at the study of its thermal expansion.

2. Experimental procedures

Amorphous ingots with nominal composition of La\(_{62}\)Al\(_{14}\)(Cu\(_{5/6}\)Ag\(_{1/6}\))\(_{14}\)Ni\(_5\)Co\(_5\) (at.\%) were prepared by suction-casting into copper mold (with diameter of 0.9 mm) under a purified argon atmosphere. The purities of the elements ranged from 99.5 to 99.98 at.\%. A differential scanning calorimeter (NETZSCH DSC 404C) was used to detect the crystallization and melting behavior of as-prepared BMG under a continuous argon flow at a heating rate of 20 K/min. Temperature evolution of the as-casted rods was continuously followed using a high-energy monochromatic beam on the ID11 undulator beamline at the ESRF (Grenoble, France). The rod sample having diameter of 0.9 mm and length of 4 mm was sealed into quartz capillary. Annealing was done in Ar-protective atmosphere using a computer-controlled Linkam THMS 600 hot stage. Heating and cooling rates were 20 K/min. The synchrotron radiation wavelength was set to \(\lambda = 0.01469\) nm (photon energy 88 keV). The sample was illuminated with well collimated incident beam having a cross-section of 0.7 mm \(\times\) 0.3 mm. The diffracted photons were collected up to a maximum 20 vector momentum transfer \(q = 120\ \text{nm}^{-1} (q = 4\pi \sin(\theta/2))\) using a fast two-dimensional CCD detector (FRELON 2K16, 2048 \(\times\) 2048 pixels, each pixel having effective size of 50 \(\mu\)m \(\times\) 50 \(\mu\)m) carefully aligned orthogonal to the X-ray beam. The delay between consecutive patterns, due to read-out time of the CCD and write-time to hard-disc was 3 s. Two-dimensional diffraction patterns were integrated using the FIT2D software package [4]. The observed X-ray scattering intensities \(I(q)\) were corrected for background, absorption, polarization, incoherent and multiple scattering effects (all procedures are described in reference [5]). Using the Faber–Ziman formalism [6] the total structure factor \(S(q)\) is obtained from the coherently scattered intensity.
where \( T_h \) = one third the volume thermal expansion coefficient \( \alpha_v \) of amorphous material as in

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\left( \frac{Q(T_0)}{Q(T)} \right)^{3/2} = \left( \frac{V(T)}{V(T_0)} \right) = 1 + \alpha_v (T - T_0)
\]

where \( V(T)/V(T_0) \) is the reduced mean atomic volume at \( T \), with the reference temperature \( T_0 \) (in this work \( T_0 = 320 \) K). Furthermore it was shown that the atomic volume change computed using Eq. (3) is equivalent to the macroscopic volume change obtained by dilatometry [7]. It should be noted here that for isotropic materials, the length thermal expansion coefficient \( \beta_{th} \) is one third the volumetric coefficient \( \alpha_v \), i.e. \( \alpha_v = 3\beta_{th} \). Since observed changes in the principal peak position \( Q \) with the temperature are relatively small and thus quite sensitive to the noise in data, one should include in the peak position (center of mass) determination procedure as many points so that the influence of an individual datapoint on the resulting peak position is minimized. In the present study the principal diffuse peak \( q \)-range between 15 and 30 nm\(^{-1} \) was modelled using the pseudo-Voigt function and linear background. Tracing the peak position of the principal diffuse peak below crystallization temperature \( T_x \) we obtained the thermal expansion of La-based BMG. As can be seen from Fig. 2a an early stages of heating can be characterized as the linear volume expansion coefficient of volume thermal expansion \( \alpha_v = 3.8 \pm 0.1 \times 10^{-5} \) K\(^{-1} \). After reaching 400 K curve exhibits negative slope which indicates the volume contraction. The most probable explanation of such behavior is structural relaxation by annealing-out of the quenched-in free volumes which are introduced when casting the rod sample [8]. Similar results on different metallic glasses were reported in [7]. Negative volume changes last until reaching the glass transition temperature \( T_g \) at which an abrupt increase of the slope is observed. The volume expansion between \( T_g \) and \( T_x \) is linear and it yields the slope of \( \alpha_{th} = 14.6 \pm 0.3 \times 10^{-5} \) K\(^{-1} \), which is almost four times larger as compared with the slope obtained below 400 K. After reaching \( T_x \) expansion curve reveals discontinuity which has no physical meaning and indicates that the position of the principal diffuse peak has dramatically changed due to superposition with the Bragg peaks. Further one can observe that the values for \( T_g \) and \( T_x \) obtained from DSC and in situ XRD are in perfect agreement. Fig. 2b shows the thermal expansion curve obtained by tracing the peak position of the principal diffuse peak when heating and cooling in the molten state, above the melting temperature \( T_m \). One may conclude that the linear behavior of the volume expansion...
reveals no traces of thermal hysteresis and suggests that heating and cooling of La-based BMG above liquidus temperature \( T_L \) is fully reversible process. Obtained coefficient of the volume thermal expansion \( \alpha_{th} = 9.6 \pm 0.1 \times 10^{-5} \text{K}^{-1} \) is one and half times smaller than the value obtained within the supercooled liquid region \( \Delta T_s \).

So far we discussed results based on analysis in reciprocal space, utilizing only part of a data in the vicinity of the principal diffuse peak. In order to get the local atomic structure of the as-casted sample and observe how it is affected upon applying thermal load with time we conducted real space analysis by observing the changes on reduced pair distribution function \( G(r) \) defined by Eq. (2). Fig. 3 shows reduced pair distribution function \( G(r) \) of as-casted La-based rod at the room temperature, prior heating experiment. For ing and cooling of La-based BMG above liquidus temperature \( T_L \) reveals no traces of thermal hysteresis and suggests that heating and cooling of La-based BMG above liquidus temperature \( T_L \) is fully reversible process. Obtained coefficient of the volume thermal expansion \( \alpha_{th} = 9.6 \pm 0.1 \times 10^{-5} \text{K}^{-1} \) is one and half times smaller than the value obtained within the supercooled liquid region \( \Delta T_s \).

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4. Conclusions

In situ X-ray diffraction experiments on La-based BMG provided data about its thermal stability. Obtained results are in a good agreement with DSC measurements. Tracing the position of the principal diffuse peak we obtained the thermal expansion curve. About 20 K below \( T_g \) expansion curve exhibits strong deviation from linearity which suggests contraction of the mean atomic volumes. Such behavior can be explained by annealing-out of the quenched-in free volumes which are introduced when casting the rod sample. Reaching glass transition temperature \( T_g \) is accompanied by an abrupt change of the volume thermal expansion coefficient \( \alpha_{vol} \). Real space analysis reveals the change of the first coordination shell suggesting redistribution of atoms in the nearest neighborhood.

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References