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Thermal rejuvenation of a heterogeneous metallic glass

Wei Guo[a,b,*], Rui Yamada[b], Junji Saida[b], Shulin Lü[a], Shusen Wu[a,*]

[a] State Key Lab of Materials Processing and Die & Mould Technology, Huazhong University of Science and Technology, 1037 Luoyu Road, Wuhan 430074, China
[b] Frontier Research Institute for Interdisciplinary Sciences, Tohoku University, Sendai 980-8578, Japan

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ABSTRACT

A relaxed heterogeneous metallic glass is successfully rejuvenated by using a recovery-annealing technique. It is found that the rejuvenation state is related to the final cooling rate and more nano-clusters are formed in the less rejuvenated heterogeneous metallic glass with a slower final cooling rate. Interestingly, the less rejuvenated heterogeneous metallic glass shows better plasticity than the more rejuvenated glass, which may result from the stress-induced crystallization (SIC) during deformation. The reasons for the SIC in the less rejuvenated sample are considered to be the evolution of nano-clusters, a more unstable glassy phase (easier to crystallize), and the high temperature rise in each shear band. These results suggest that not only the relaxation state of the amorphous phase, but also the heterogeneous microstructures, including nano-clusters, should be considered to improve the mechanical properties of metallic glasses.

1. Introduction

Bulk metallic glasses (BMGs) have attracted a lot of interest because of their superior mechanical properties such as high fracture strength and large elastic limit, which originate from their unique long-range disordered microstructures [1–3]. BMGs are always fabricated with a rapid quenching technique, which results in them possessing a high configurational potential energy and a tendency to progressively change their structures towards a lower potential energy state. Thus, the so-called structural relaxation occurs from low temperature annealing [4–6]. The relaxation of BMGs obviously degrades the properties such as embrittlement at room-temperature [7]. To overcome this problem, we have proposed a novel method (recovery-annealing) to rejuvenate the relaxed BMGs, in which the relaxed BMGs are heated to a certain temperature above the glass transition temperature (T_g) followed by a rapid quenching [8].

Recently, we observed an unusual relaxation-induced plasticization behavior of a structurally unstable or heterogeneous BMG ($Cu_{47.5}Zr_{47.5}Al_5$ (at.%)) [9]. The plasticization was considered to result from a cooperative contribution of the highly compacted energy in each shear band (SB) and the evolution of nano-ordered clusters. In this paper, we further applied the recovery-annealing technique to rejuvenate the relaxed heterogeneous metallic glass with the final cooling rate ranging from 100 K/min to 700 K/min. The microstructures, relaxation state and the mechanical properties of the recovery-annealed samples are investigated in detail to evaluate the influence of the cooling rate.

2. Experimental

The detailed methods to prepare the as-cast and relaxed $Cu_{47.5}Zr_{47.5}Al_5$ (at %) BMGs have been described in our previous study [9]. The relaxed sample was heated up to ~723 K (~1.05T_g) and held for 2 min, followed by a rapid quenching (see Fig. 1) as the recovery annealing process. The various final quenching rates investigated were 100 K/min, 300 K/min and 700 K/min, which were denoted as Rej100, Rej300 and Rej700, respectively. For Rej100 and Rej300, the thermal treatment was conducted in a differential scanning calorimeter (DSC, Perkin Elmer DSC8000). However, Rej700 was treated in an original quenching instrument that we developed. The details for this instrument have already been reported [10].

The structures of the samples were examined by X-ray diffraction (XRD; Bruker D8 Advance) with Cu Kα radiation, and transmission electron microscopy (TEM, JEOL JEM-2100F) with an acceleration voltage of 200 kV. The samples for TEM were cut from rod sample with thickness of 0.5 mm, and then polished with abrasive paper #2000 until 20 μm of thickness. After polishing, the samples were further thinned by ion milling (Gatan 691) with ion energy of 4 kV and milling angle of 4°. The T_g and the onset crystallization temperature (T_x) were measured by differential scanning calorimetry in argon at a heating rate of 20 K/min. The specific heat capacities of all samples were measured with a sapphire standard sample. The incubation time for crystallization (t_{in}) at

* Corresponding authors at: State Key Lab of Materials Processing and Die & Mould Technology, Huazhong University of Science and Technology, 1037 Luoyu Road, Wuhan 430074, China.
E-mail addresses: weiguo@hust.edu.cn (W. Guo), ssw636@hust.edu.cn (S. Wu).

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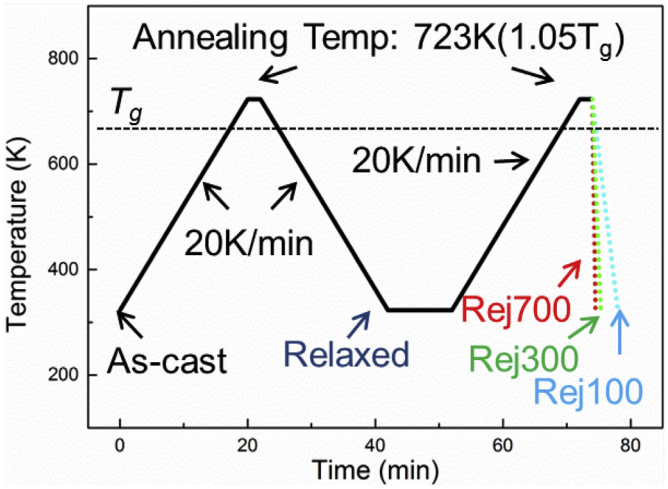

Fig. 1. Schematic illustration of thermal process to prepare the recovery-annealed samples.

723 K was measured by isothermal annealing in DSC with a heating rate of 20 K/min. The density was measured by using a gas pycnometer (AccuPyc II 1340, Micromeritics Co. Ltd). Compression tests were performed at a strain rate of $5 \times 10^{-4}\,s^{-1}$ at room-temperature using an Instron 5982 mechanical testing machine. The compression samples with the height of 4 mm and diameter of 2 mm were cut in parallel and carefully polished to ensure the end flatness. Multiple compression tests, using at least four samples each, were conducted to confirm the reproducibility. Fractured samples were observed by XRD, TEM and scanning electron microscopy equipped with energy-dispersive X-ray spectrometry (SEM-EDX; Carl Zeiss Ultra 55 with Bruker AXS).

3. Results and discussion

3.1. Heterogeneous microstructure of recovery-annealed samples

Fig. 2(a) shows the XRD patterns of Rej100, Rej300 and Rej700. All patterns exhibited a similar broad peak of the glassy phase without any obvious crystalline peaks, which indicated that no crystallization occurred during the recovery-annealing. Fig. 2(b) shows the DSC curves of Rej100, Rej300 and Rej700. All samples exhibited an endothermic glass transition followed by an exothermic crystallization peak [11]. Similar T_g and T_x for all the samples were obtained, which are summarized in Table 1. This clearly showed that varying the final cooling rates did not induce great changes in the amorphous structures.

For this specific structurally unstable BMG, it has been shown that the heterogeneity evolves, including nano-ordered clusters, after relaxation-annealing of the as-cast sample [9]. In this work, the recovery-annealed samples were thermally treated from the relaxed samples (see Fig. 1), thus they should also possess the heterogeneous microstructure. Fig. 3(a–c) show the bright-field TEM images of Rej100, Rej300 and Rej700, respectively. All samples exhibited a nano-sized heterogeneous structure. Even though the distribution of the heterogeneity is quite homogenous, here we referred to "heterogeneous structures" compared with relatively homogenous as-cast sample without any heat treatment. To evaluate the volume fraction of the nano-clusters (V_{nc}), we measured the crystallization enthalpy (ΔH_s) by DSC from Fig. 2(b) (the area of exothermic crystallization peak). Thus, V_{nc} can be calculated as [12]:

$$V_{nc} = 1 - \frac{\Delta H_s}{\Delta H_r} \tag{1}$$

where ΔH_r is the crystallization enthalpy of the fully amorphous state and here we used the data of a ribbon sample (55.6 J/g). The detailed data of ΔH_s and the calculated V_{nc} are summarized in Table 1. With a slower final cooling rate or a longer thermal treatment time (t_a), more

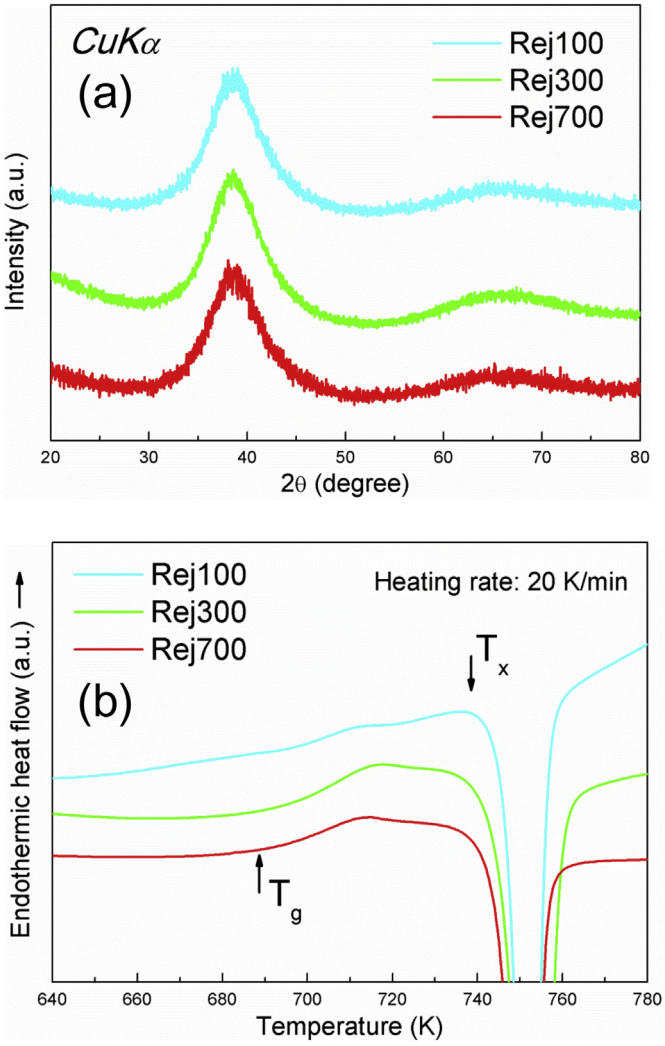

Fig. 2. (a) XRD patterns and (b) DSC curves of Rej100, Rej300 and Rej700.

nano-clusters were formed because of the additional supplied thermal energy during annealing (see Fig. 3(d)), that is, V_{nc} (Rej100) > V_{nc} (Rej300) > V_{nc} (Rej700) was confirmed. Furthermore, the relation between t_a and V_{nc} could be fitted by using a power exponential function, which indicated that the formation rate of nano-clusters increased with treatment time. This relationship has also been reported previously [13, 14].

3.2. Relaxation state of recovery-annealed samples

To investigate the relaxation state of a glassy structure, the enthalpy of relaxation (ΔH_{relax}) is generally used [4, 15], which is given as.

$$\Delta H_{relax} = \int_{RT}^{T} \Delta C_p dT \tag{2}$$

where $\Delta C_p = C_{p,s} - C_{p,r}$, and $C_{p,s}$ and $C_{p,r}$ are the specific heats of the initial glassy state and its relaxed state, respectively. In the present study, the relaxed state was obtained by annealing the sample at 723 K (~$1.05T_g$) for 2 min followed by 20 K/min cooling. We measured the specific heat up to T = 723 K (~$1.05T_g$) and plotted the specific heat curves of Rej100, Rej300 and Rej700 in Fig. 4(a). The data of the as-cast and relaxed samples were also included from Ref. [9]. By using Eq. (2), ΔH_{relax} for each sample was calculated as 15.9 J/g for as-cast (Ref. [9]), 2.1 J/g for Rej100, 4.9 J/g for Rej300 and 7.5 J/g for Rej700. Obviously, the sample exhibited a larger ΔH_{relax} with a faster final cooling rate, which meant that the sample was rejuvenated to a more