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Rejuvenation and plasticization of metallic glass by deep cryogenic cycling treatment

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ABSTRACT

A Zr-based metallic glass is treated by a cryogenic- to room-temperature cycling treatment with 30 cycles. Though the structure after treatment maintains its monolithic amorphous structure, the treated sample exhibits a rejuvenation behavior contrasting with that of an untreated as-cast sample, including a higher relaxation enthalpy and a lower density. The atomic level core-shell heterogeneous microstructure is considered to contribute to the rejuvenation because of the internal stress generated during cycling. The microscopic deformation of the core region by the internal stress may be equivalent to the macroscopic shear band deformation by the external stress, which induces the evolution of the core region and an increased amount of excess free volume. The treated sample also exhibits lower hardness and better plasticity than the untreated sample. A lower shear plane formation energy and larger shear transformation zone volume and size are considered to promote shear band formation and to generate more multiple shear bands to accommodate the plastic deformation. The deep cryogenic cycling treatment is believed to be a feasible and non-destructive way to rejuvenate metallic glass and improve the mechanical properties.

1. Introduction

Bulk metallic glass (BMG) has attracted extensive research interest owing to its unique long-range disordered microstructures and superior properties such as high fracture strength and a large elastic limit [1,2]. However, the catastrophic fracture of most BMGs at room temperature limits their widespread application [3,4]. The non-equilibrium quenching during BMG fabrication induces them to be in a relatively high potential energy state, and its amorphous structure can be transformed to a lower energy state in a process called structural relaxation [5,6]. In contrast, if the structure transforms to a more metastable structure or to a higher potential energy state, this process is called structural rejuvenation [7,8]. At present, rejuvenation can be achieved via mechanical, thermal or thermo-mechanical treatments, where it is reported that the thermal treatment is a more feasible alternative owing to its sample size independence and its more homogenous rejuvenated structure [9]. Recently, Ketov et al. have found that thermal cycling between room and cryogenic temperatures can also induce rejuvenation in the BMGs [10]. However, a more accurate cycling treatment and a more detailed investigation of this phenomenon has yet to be undertaken. In this study, using our original developed thermal cycling treatment instrument, we investigated the structures and mechanical properties of a $Zr_{55}Cu_{30}Al_{10}Ni_5$ (at.%) BMG under a deep cryogenic cycling treatment (DCT) with 30 cycles. Hereafter, the thermally untreated and treated samples are denoted as As-cast and DCT30, respectively.

2. Experimental

2.1. Sample preparation

Master alloys were prepared by arc-melting high-purity Cu, Zr, Ni and Al metal pieces in a Ti-gettered Ar atmosphere in a water-cooled copper hearth. The alloy was re-melted four times to ensure chemical homogeneity. The BMG was fabricated by casting the master alloy into a copper mold to produce a 2-mm-diameter rod-shaped sample (denoted As-cast).

2.2. Deep cryogenic cycling (DCT) treatment

The schematic of original developed instrument for deep cryogenic cycling treatment (DCT) is shown in Fig. 1(a). The stage is connected

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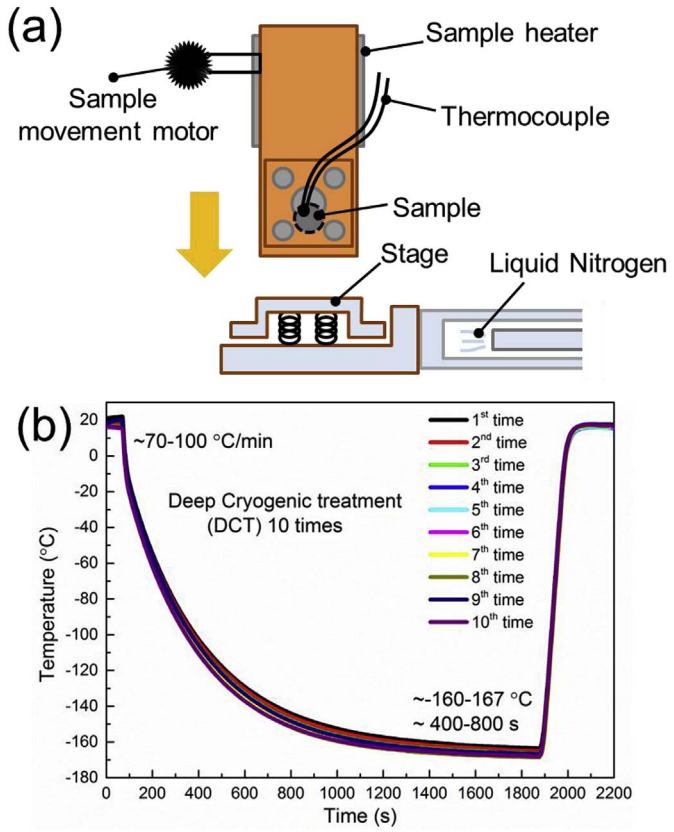

Fig. 1. (a) Schematic of original developed thermal treating instrument; (b) Sample temperature change in 10 cycles.

with a liquid nitrogen flow pipe and it can be cooled down to and held at −180 °C. The sample is fixed in a copper sample-holder and contacted with a thermocouple to record the sample temperature. Then by moving down the sample-holder to fully contact the cryogenic stage, the sample will be cooled down to very low temperature, together with the stage. After a certain time (30 min in this study), by moving up and heating the sample-holder, the sample will be heated up to room-temperature. Repeating this step can thermally and cyclically treat the sample between room-temperature and cryogenic temperature. The sample temperature change in 10 cycles is shown in Fig. 1(b). The initial cooling rate is about 70–100 °C/min, the sample is cooled down to about −165 °C and kept there for ~8 min. A very good reproducibility can be obtained by using this instrument. Moreover, the sample is treated in vacuum (5×10^{-4} Pa) during DCT. The sample treated by DCT with 30 cycles is denoted DCT30.

2.3. Sample characterization

The structure was 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 glass transition temperature (T_g) and the onset crystallization temperature (T_x) were measured by differential scanning calorimeter (DSC, Perkin Elmer Pyris Diamond DSC) in Ar at a heating rate of 20 K/min. The specific heat capacities were measured by comparing them with a sapphire standard sample. The density was measured using an Ar gas pycnometer (AccuPyc II 1340, Micromeritics Co. Ltd.).

2.4. Mechanical test

The samples used for nanoindentation were cut into small discs 2 mm thick and mechanically polished to mirror faces. The

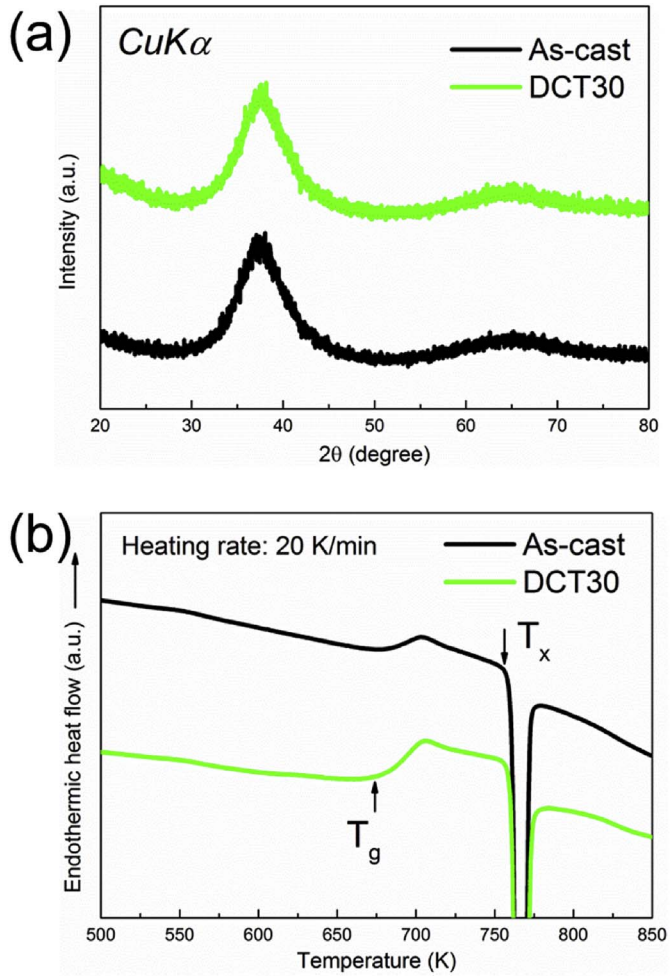

Fig. 2. (a) XRD and (b) DSC curves for both As-cast and DCT30.

nanoindentation test was performed with the load control mode at a peak load of 100 mN (MZT-500, Mitutoyo Co. Ltd.), where the loading and unloading rates varied (5, 10 and 20 mN/s). For each sample, at least ten indents were made. The cylindrical compression samples with a height of 4 mm and a diameter of 2 mm were cut in parallel and carefully polished to ensure that their ends were flat. The compression test was performed at a strain rate of 5×10^{-4} s^{-1} at room temperature using an Instron 5982 mechanical testing machine. Multiple compression tests using at least four samples each were conducted to confirm the reproducibility. Fractured samples were observed by both XRD and scanning electron microscopy with energy-dispersive X-ray spectrometry (SEM-EDX; Carl Zeiss Ultra 55 with Bruker AXS).

3. Results and discussion

3.1. Glassy nature after DCT

Fig. 2(a) shows X-ray diffraction (XRD) patterns for both the As-cast and DCT30 samples, which exhibit similar single broad peaks of the glassy state without crystallization. The glass transition (T_g) and onset crystallization (T_x) temperatures for both samples are measured by a differential scanning calorimeter (DSC), as shown in Fig. 2(b), and are found to be 673 and 761 K for As-cast, respectively, and 669 and 760 K for DCT30, respectively.

Fig. 3(a) and (b) show the bright-field transmission electron microscope (TEM) images for both samples, which reveal no crystallization occurred before and after DCT. Moreover, high-resolution TEM images and selected area diffraction patterns (SAD) of As-cast and