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Abnormal devitrification behavior and mechanical response of cold-rolled Mg-rich Mg-Cu-Gd metallic glasses

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ABSTRACT

Abnormal devitrification behavior and mechanical response of $Mg_{75}Cu_{15}Gd_{10}$ (relatively strong glass former with higher structural stability) and $Mg_{85}Cu_5Gd_{10}$ (relatively fragile glass former with lower structural stability) metallic glasses, fabricated by repeated forced cold rolling, have been investigated. When metallic glasses were cold-rolled up to a thickness reduction ratio of ~33%, the heat of relaxation ($\Delta H_{relax.}$) below T_g of the cold-rolled specimens was reduced, which indicates the formation of local structural ordering via cold rolling due to stress-induced relaxation. The local structural ordering results in abnormal devitrification behavior, such as higher resistance of glass-to-supercooled liquid transition and delayed growth, in the following heat treatment due to increased nuclei density and pinning site. In particular, the fragility index, *m*, could assist in understanding structural stability and local structural variation by mechanical processing as well as compositional tuning. Indeed, we examine the shear avalanche size to rationalize the variation of the deformation unit size depending on the structural instability before and after cold rolling. The deformation mode in $Mg_{85}Cu_5Gd_{10}$ metallic glass might change from self-organized critical state to chaotic state by cold rolling, which results in unique hardening behavior under the condition for coexisting well distributed local structural ordering and numerous thinner shear deformed areas. These results would give us a guideline for atomic scale structural manipulation of metallic glasses, and help develop novel metallic glass matrix composites with optimal properties through effective mechanical processing as well as heat treatment.

1. Introduction

Metallic glasses (MGs) exhibit local plastic deformation, suggesting that strong metallic bonding remains even though there is no long-range order (or translational periodicity) of constituting elements. It is of interest to know whether the atomic arrangement during deformation undergoes a change towards more crystallinity by relaxation phenomena or towards greater randomness by shear deformed area. The general consensus is that elemental process of deformation in the MGs is a local rearrangement of atoms to accommodate local strains incurred through the redistribution of free volume and the operation of shear transformation zone, which can lead to nucleation and propagation of shear bands [1], although there has been considerable debate as to whether shear localization in MGs is mainly due to thermal effects or shear-induced disordering such as dilation. On the other hand, the room-temperature mechanical deformation of MGs with structural instability can induce local structural ordering with relatively lower energy levels by promoting a so-called structural relaxation due to annihilation of frozen-in "defect", especially in the shear bands with increased atomic mobility [2]. Recent investigations of the structural variation in MGs via severe deformation process [3–7] have shown that partially devitrified MGs with fine nanocrystals embedded in the shear bands or the amorphous matrix exhibit controllable microstructures and mechanical properties. Thus, it has been understood that deformation of MGs may be a way of generating unique nanostructures with denser and softer regions by annihilation and creation of free volume as a microstructural response, which is not a simple alternative to thermal annealing. Although it appears that the devitrification process of MGs via simple heat treatments is relatively well understood, the correlation between deformation–induced structural change and following devitrification behavior of the MGs has not been fully understood [1,7–9].

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Among existing previous studies of the question, deformation-induced structural changes and following devitrification behavior of Al-based MGs have been relatively well defined in severe deformation environments such as tensile/compressive tests or rolling process and the following heat treatment [8,9]. For example, the presence of quenched-in-nuclei of alpha Al in an amorphous matrix can enhance local structural ordering in severe deformation environments, especially under compressive force [8], and minimize the size of precipitates after 1st crystallization behavior in the following heat treatment. However, other glass-forming systems such as Zr- [5,10], Fe- [8], Cu- [11] or Mg-based [12] MGs often show different responses to applied deformation. For example, some of them did not exhibit a consistent devitrification process after cold-rolling, implying that the applied deformation on MGs does not necessarily exhibit a similar structural change at room temperature for all MGs. Also, the trends of the DSC peak shift (or reduction of crystallization enthalpy) were not consistent even at a similar amount of deformation [9,12], suggesting that the crystallization behavior in the following heat treatment after cold rolling might be closely dependent on structural instability of MGs [13–16]. In this regard, it is useful to scrutinize the devitrification behavior by cold rolling and following heat treatment in various glass-forming systems, which allows manipulation of the nanostructure as well as the structural instability of MGs. However, very little attention has been focused on the local structural variations in the relaxation regime and mechanical responses of MGs with different levels of structural instability via cold rolling.

In the present study, two Mg-Cu-Gd glass-forming alloy compositions [17–20] on either side of the border of bulk metallic glass (BMG)-forming alloy compositions have been selected; $Mg_{75}Cu_{15}Gd_{10}$ with a GFA of 2 mm (relatively strong glass former) and $Mg_{85}Cu_5Gd_{10}$ with a GFA of less than 1 mm (relatively fragile glass former). In order to identify the devitrification behaviors and mechanical responses of the MG ribbons depending on cold rolling and the following heat treatment, the selected MG ribbons were investigated with a Transmission Electron Microscope (TEM) equipped with heating facilities both before and after cold rolling together with DSC analyses and nanoindentation test.

2. Experimental

A Cu-Gd master alloy was prepared by arc melting Cu and Gd (purity > 99.9%) under a Ti-gettered argon atmosphere in a water-cooled copper crucible. The master alloy was then alloyed with Mg (99.9%) in a boron nitride (BN) coated graphite crucible under a dynamic Ar atmosphere using an induction furnace. The alloy ingots were melted several times to help improve compositional homogeneity. After complete melting, the liquid alloy was poured into a Cu mold in air. The copper mold was cone-shaped, 45 mm in height, 15 mm in diameter at the top, and 6 mm in diameter at the bottom. Rapidly solidified ribbon specimens were prepared by re-melting the alloys in quartz tubes with over-pressure of 50 kPa through a nozzle onto a Cu wheel rotating with a surface velocity of 40 m/s. To exclude structural relaxation of Mg-Cu-Gd MGs at room-temperature (corresponding to a homologous temperature T/T_g of about 0.7) like Mg-Cu-Y MGs [21], all experiments were done after 10 days to exclude room temperature relaxation effect. The amorphous ribbons were cold-rolled by a twin roll in order to examine the structural bias of severe deformation. The rolling process was performed by electric motor-controlled twin roll with a diameter of 20 cm at a constant speed of ~2.0 radians/sec. A single amorphous ribbon sandwiched by two clean stainless steel plates was repeatedly cold rolled. The thicknesses of the amorphous ribbons were measured after final pass. After rolling, the specimen was elongated towards the rolling directions due to the formation and propagation of shear bands. The thickness of the ribbon was reduced from ~30 μm to ~20 μm (~33% in thickness reduction) after cold rolling.

The structures of the samples were confirmed by X-ray diffraction (XRD: Rigaku CN2301) for the as-spun and cold-rolled ribbon samples using monochromatic Cu Kα radiation. The thermal history of the as-spun and cold-rolled specimens was investigated by differential scanning calorimetry (DSC; Perkin Elmer DSC8500) using various heating rates between 5 K/min and 80 K/min. The microstructures of the MGs were examined by TEM (JEOL 300KVJEM-3011) with single tilting heating holder (Gatan model 628). To evaluate devitrification behavior of the Mg-based MGs, the holder was quickly heated up to 423 K and was kept at the temperature for 10 min. Then the temperature was increased up to ~523 K with a 10 K interval. To stabilize the temperature at each step, we kept the temperature at each step under isothermal condition for 3 min. To minimize thermal drift, a water cooling of the outer part of the sample holder was installed. The thin foil TEM specimens were prepared by ion milling (Gatan 695 PIPS II) with liquid nitrogen cooling after mechanical thinning process. Extreme care was taken with the HRTEM analysis since Mg-based MG thin foils oxidize readily upon exposure to air. And, the nanoindentation tests were performed using a nanomechanical tester (Hysitron TI 750 TriboIndenter). Indenting force was loaded up to a maximum load of 5 mN using a conical type indenter with a 2 μm radius by load control mode at a constant loading rate of 1 mN/s.

3. Results

The $Mg_{65}Cu_{25}Gd_{10}$ alloy exhibits significantly improved GFA with at least 8 mm in diameter (D_{max}) by conventional Cu-mold casting method in air atmosphere [17]. The critical cooling rate for glass formation (R_c) was estimated to be approximately 10 K/s by the following equation: $\log R_c = -2.52 \log Z_{max} + 3.27$ [22]. Fig. 1 shows a map of D_{max} with border line of BMG formation in $Mg_{100-x}Cu_xGd_{10}$ alloys (x = 5–30 at.%). As shown in Fig. 1, with increasing Mg contents up to 85 at.%, the D_{max} gradually deceases down to 0.5 mm ($R_c \sim 10^4$ K/s [22]). In particular, the border of BMG-forming alloy composition is located between $Mg_{80}Cu_{10}Gd_{10}$ and

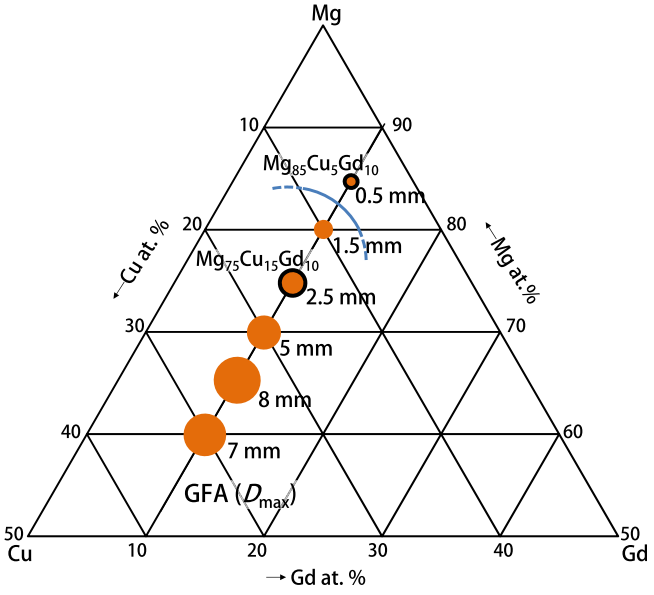

Fig. 1. Map of maximum diameter (D_{max}) for glass formation with border line of BMG formation in $Mg_{100-x}Cu_xGd_{10}$ alloys (x = 5–30 at.%).