ARTICLE IN PRESS

Available online at www.sciencedirect.com

ScienceDirect

Acta Materialia xxx (2013) xxx–xxx

Acta MATERIALIA

www.elsevier.com/locate/actamat

Evolution of shear bands, free volume and hardness during cold rolling of a Zr-based bulk metallic glass

M. Stolpe [a,*], J.J. Kruzic [b], R. Busch [a]

[a] Metallic Materials, Campus C6.3, Saarland University, Saarbrücken, Germany

[b] Materials Science, School of Mechanical, Industrial, and Manufacturing Engineering, Oregon State University, Corvallis, OR, USA

Received 29 April 2013; received in revised form 11 October 2013; accepted 14 October 2013

Abstract

Two-dimensional cold rolling was performed on a bulk metallic glass (BMG) with composition $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$. The average shear band density continuously increased with plastic strain. By comparing with published data, a common relation is proposed whereby the average shear band density scales with the square root of the induced true plastic strain, independent of changes in BMG composition or loading mode. Also, the measured exothermal heat release preceding the glass transition, and thus also the free volume, was found to increase linearly with shear band density. Based on an analysis of the measured shear band densities and enthalpy changes, it is concluded that the free volume of both the matrix and the shear bands must evolve continuously during deformation. Finally, the measured hardness during cold rolling was found to decrease initially within the low deformation regime and then increase at higher deformations with a minimum at a strain of ~0.073. By recognizing the commonality in the shear band formation among different loading modes, the contributions of shear band generation and residual stresses to the hardness changes were separated. The initial decrease in hardness was attributed to free volume generation and a softening of the material, while the subsequent increase in hardness was related to the evolution of compressive residual stresses during cold rolling. It is suggested that these competing mechanisms affecting hardness may help to explain the different observations in the literature concerning the influence of pre-deformation.

Keywords: Bulk metallic glasses; Free volume; Shear bands; Residual stresses; Hardness

1. Introduction

In recent decades, considerable effort has been made to develop strategies to overcome the fracture instabilities that limit metallic glasses to low or negligible tensile and compressive ductility. Generally, approaches to increasing deformability are based on increasing the number of shear bands by increasing the capacity for shear band formation [1–5] and/or by hindering propagation of activated shear bands [6–11]. Following the models of Spaepen and Argon [12,13], plastic flow is considered as a net balance of shear-induced atomic rearrangement creating free volume and diffusive-like processes annihilating free volume. Within this context, the enthalpic state of the material is thought to be crucial in determining the plastic behavior of metallic glasses. A higher enthalpic state is characterized by a higher excess volume (or free volume) of the material. Owing to the kinetic nature of the glass transition, the enthalpy, and thus the free volume, of a glass is determined by its thermal history. Therefore, there is no unique glass structure but, rather, a variety of states that may be achieved. Hence, plastic deformation will be strongly determined by the distinct enthalpic state of a glass, whereby it is predicted that a higher initial free volume results in larger capacity for ductility.

It has been verified experimentally that a reduction in free volume (e.g., via structural relaxation by slow cooling or annealing) leads to embrittlement of the material, manifested as an increase in hardness and elastic modulus along

* Corresponding author. Tel.: +49 681 302 3278; fax: +49 681 302 4385. *E-mail address:* m.stolpe@mx.uni-saarland.de (M. Stolpe).

1359-6454/$36.00
http://dx.doi.org/10.1016/j.actamat.2013.10.035

with a reduced capacity for shear band formation and lower fracture toughness [14–17]. Conversely, an increase in free volume (structural rejuvenation) results in a decrease in hardness and stiffness coupled with an enhanced capacity for shear band formation and increased capacity for ductility [5,18,19]. For example, by simply changing the casting current during processing, Tan et al. have shown that higher free volume states lead to an increase in plasticity and in Poisson's ratio as well as an decrease in hardness and elastic constants (shear and Young's modulus) [5].

Since inhomogeneous deformation of metallic glasses is dilatational, plastic deformation leads to an increase in free volume and enthalpy. Accordingly, plastic deformation should shift the state of the material away from the supercooled liquid state towards a softer and potentially more ductile higher enthalpy state. However, reported observations are inconsistent in their findings with respect to both enthalpy and hardness changes. Concerning the measured enthalpy differences between cold-rolled and as-cast plates, Flores et al. [20] found an increase in relaxation enthalpy in the early stage of deformation via cold rolling (thickness reduction <10%), while afterwards a decrease was observed in the $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$ bulk metallic glass (BMG). In contrast, Liu et al. [21] found a continuous increasing trend of the measured relaxation enthalpy of cold-rolled plates in the $Zr_{64.13}Cu_{15.75}Ni_{10.12}Al_{10}$ and $Zr_{46.5}Cu_{45}Al_7Ti_{1.5}$ BMG alloys. Similarly, Haruyama et al. [22] found an increasing trend in both relaxation enthalpy and measured volume with cold rolling for a BMG with composition $Zr_{55}Cu_{30}Ni_5Al_{10}$. With respect to hardness, experimental observations are also not in agreement [21,23–25]. Song et al. [23] found that cold rolling (thickness reduction of 2.9%) resulted in an increase in the measured Vickers microhardness number from 545 HV to 600 HV on the ground and polished top sample surface while, in contrast, Liu et al. [21] found essentially no change in hardness on that surface with deformation. Both those results are in strong contrast to the observations of a continuous decrease in hardness with plastic strain during uniaxial compression tests [24]. Therefore, it is necessary to examine further the effect of cold deformation on the evolution of free volume and hardness. The purpose of this paper is to focus especially on separating the contributions of two competing mechanisms expected to affect hardness during cold rolling. These include (1) decreases in hardness due to the increase in free volume and (2) increases in hardness due to residual compressive stresses that may emerge at the cold-rolled surfaces as a result of the inhomogeneous deformation through the thickness.

2. Experimental

2.1. Sample preparation

Master alloys of the $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$ BMG-forming alloy were produced from high-purity elements in an arc melter under a high-purity, Ti-gettered atmosphere. The master alloys were then remelted in an arc melter and suction cast into water-cooled copper molds to form plates of $2.3 \times 10 \times 50\ mm^3$. Prior to cold rolling, the as-cast plates were ground and polished on each surface to a thickness of 2.0 mm to (1) minimize the influence of casting residual stresses on hardness results, (2) minimize the influence of surface roughness on hardness results and (3) facilitate observations of the evolution of shear bands after each cold-rolling thickness reduction.

2.2. Cold rolling

Cold rolling was performed by stepwise decreasing the roller separation distance in increments of 0.01 mm until the desired degree in thickness reduction was reached. A two-dimensional (2-D) rolling process was applied whereby the plates were turned by 180° after each pass. When the desired degree of pre-deformation was reached, samples were cut from the plates and the accurate degree of the pre-deformation plastic strain was determined by measuring the thickness of the cold-rolled plates using an optical microscope. By this method, the accuracy in measured thickness reduction was estimated to be within ∼0.3%. Thickness reduction was then converted to true plastic strain ε by the following relation:

$$\varepsilon = |\ln(h/h_0)| \tag{1}$$

where h is the thickness at a given deformation, h_0 is the initial thickness of the plate. Note that, for reasons of clarity and comprehensibility, the true plastic strain ε is defined as a positive value, even though cold rolling actually results in a reduction in thickness.

2.3. X-ray diffraction

Diffractograms of the material in the as-cast state as well as at several degrees of pre-deformation ($\varepsilon = 0.14$, 0.286, 1.394) were measured and compared to determine whether crystallization occurred in the pre-deformed samples during cold rolling. X-ray diffraction was carried out using a PANalytical XPert Pro diffractometer. Measurements were performed in a theta-theta configuration from 20° to 80° with a step size of 0.02°.

2.4. Shear band evolution

In order to monitor shear band evolution during cold rolling, optical micrographs of the shear band patterns appearing on the ground-and-polished side surfaces of the cold-rolled plates were taken using a binocular microscope. The average shear band spacing λ_{SB} was determined from at least five micrographs taken at different positions along the side surface of samples at a given degree of deformation. The average shear band line density ρ_{SB} therefrom was derived as the inverse of the measured average shear band spacing, in accordance with Ref. [24].