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Structural changes in amorphous metals from high-strain plastic deformation

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ABSTRACT

Structural changes in a bulk metallic glass subjected to high-strain plastic deformation was investigated. A zirconium-based bulk metallic glass was friction stir processed at different tool rotational speeds. The alloy retained its fully amorphous structure at lower speed. At higher tool rotational speed there was partial nano-crystallization with nearly three times increase in surface hardness. Changes in the glass transition temperature, relaxation and crystallization enthalpies were analyzed to explain the physics of high-strain deformation in amorphous metals.

1. Introduction

Understanding the influence of severe plastic deformation on thermodynamic and mechanical behavior of amorphous metals has fundamental and technological implications. Amorphous metals or metallic glasses typically show high elastic strain limit. However, plastic strain localization in the form of shear bands results in catastrophic failure in these materials. Deformation induced softening in metallic glasses has been attributed to the increase in free volume and structural relaxation [1–3]. Work hardening has been reported for certain metallic glasses, which was explained by high density of shear bands [4]. Structural heterogeneities nucleated during deformation affect the mechanical behavior of metallic glasses [5]. Therefore, its deformation behavior is strongly affected by free volume evolution, strain localization, and nucleation of secondary phases.

There are numerous studies on severe plastic deformation of crystalline materials [6–10]. Thermo-mechanical processing methods, including friction stir processing (FSP), refine the microstructure and contribute towards enhanced mechanical properties for crystalline materials. However, there are very limited studies on severe plastic deformation of bulk metallic glasses (BMG) [11–13]. There are a few reports on welding/joining of metallic glasses to crystalline materials using friction stir processing [14–16]. However, the primary emphasis in these studies was the assessment of microstructural characteristics and mechanical properties of the amorphous–crystalline interface region. A previous study on FSP of metallic glass [12] investigated the effect of nanocrystallites volume fraction on the mechanical properties. A nominal increase in hardness of the processed metallic glass was reported [12]. However, there is no systematic study on the relaxation behavior, detailed thermal analysis, and variation in surface mechanical properties of amorphous metals subjected to high strain deformation. We report on the unusually high hardness, relaxation behavior in the context of free volume theory, and structural modification in a zirconium-based bulk metallic glass after friction stir processing at different strain rates. We evaluated the change in glass transition and crystallization enthalpy for plastically deformed metallic glass at different tool rotational speeds. The change in thermodynamic properties for the deformed metallic glass compared to as-cast materials is explained within the context of creation and annihilation of free volume. The unusual increase in hardness of the metallic glass after FSP is explained by the interaction of shear bands.

2. Materials and methods

The material used in the current investigation is a Zr-based bulk metallic glass, $Zr_{44}Ti_{11}Cu_{10}Ni_{10}Be_{25}$. This is one of the best known glass formers in the Zr-based system (with a supercooled liquid region of ~120 °C) [17]. Friction stir processing was

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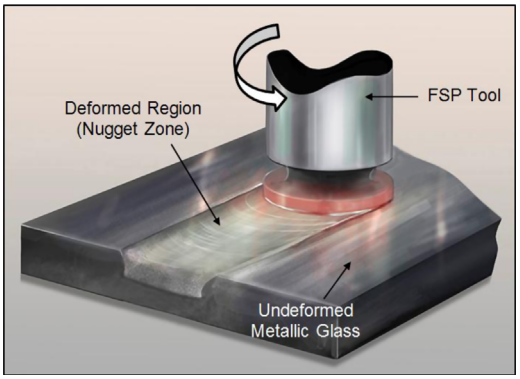

Fig. 1. Schematic of friction stir processing (FSP). A rotating tool traverses along the length of the specimen and results in severe plastic deformation of the material. To avoid any non-homogeneity, specimens for thermal analysis were taken from the center of nugget zone.

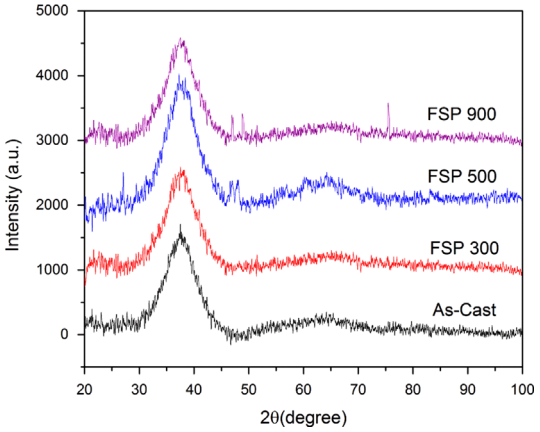

Fig. 2. XRD analysis of zirconium-based metallic glass (as-cast), metallic glass friction stir processed at 300 rpm (FSP 300), 500 rpm (FSP 500) and 900 rpm (FSP 900). As-cast and FSP 300 specimen show a fully amorphous structure, whereas FSP 500 and FSP 900 show partial devitrification.

performed on a CNC vertical milling machine. The FSP tool used was pin-less with shoulder diameter of 10 mm. Three different tool rotational speeds of 300 rpm, 500 rpm and 900 rpm were used at constant transverse speed of 60 mm/min. For microstructural studies and hardness measurements, the processed samples were sectioned normal to the processing direction using slow speed diamond cutter. Temperature of the surface during FSP was measured using K-type thermocouple. Microstructural studies were done using scanning electron microscope (SEM) and transmission electron microscope (TEM). X-ray diffraction (XRD) was used to determine the amorphous structure of specimens. A differential scanning calorimeter (DSC), in which samples were heated at 20 K/min, was used to determine glass transition temperature (T_g), crystallization temperature (T_x), and enthalpy changes. Microhardness testing was done at 300 gf load to determine hardness as a function of depth from the surface. A schematic of the FSP set up is shown in Fig. 1. The figure shows the plastically deformed nugget zone. To avoid any non-homogeneity, specimens for thermal analysis were taken from the center of nugget zone.

3. Results and discussion

XRD analysis of the as-cast metallic glass and all the processed specimens are shown in Fig. 2. A broad peak for the as-cast and FSP 300 specimens indicate fully amorphous structure. FSP 500 and FSP 900 specimens show a few sharp crystalline peaks indicating partial devitrification. TEM images of FSP 300, FSP 500 and FSP 900 specimens are shown in Fig. 3. FSP 300 specimen shows a fully amorphous structure without any evidence of crystalline phases. In contrast, nano-crystallites are clearly seen for FSP 500 and FSP 900 specimen, indicating partial devitrification of the metallic glass. The microstructure for FSP 500 and FSP 900 are similar, with FSP 900 having larger fraction of the crystalline phase.

DSC curves for all the investigated cases are shown in Fig. 4(a) and the results are summarized in Table 1. All specimens show a single crystallization peak, indicating no change in the crystallization mechanism. A small temperature window around glass transition for all specimens is shown separately in Fig. 4(b). Just prior to glass transition, there is an exothermic peak in the DSC curve for all specimens, as clearly seen in Fig. 4(b). This exothermic peak is associated with the decrease in free volume due to structural relaxation during heating [18–20]. The enthalpy change (ΔH) during structural relaxation is directly proportional to the free volume change ($\Delta\nu_f$) [19] as shown by the expression, $C_p = dh/dT = Adv_f/dT$ [20], where C_p is the specific heat, h is enthalpy, T is the temperature and A is a scaling factor. The free volume continues to annihilate until it reaches a critical value, the equilibrium free volume for the supercooled liquid. The enthalpy of structural relaxation was calculated by integrating the area under the peak obtained by subtracting the 2nd heating curve from the 1st heating curve in DSC. From Table 1, it is seen that the enthalpy change for structural relaxation is highest for FSP 500 (13.74 J/g), followed by FSP 300 (11.84 J/g), the as-cast metallic glass (11.04 J/g) and FSP 900 specimen (9.96 J/g). Thus, the structural relaxation enthalpy for the specimens processed at lower rotational speed of 300 rpm and 500 rpm is higher compared to the as-cast alloy. However, with further increase in tool rotational speed, the structural relaxation enthalpy decreased.

The amount of free volume is influenced by the strain rate and peak temperature reached during processing. During FSP, the metallic glass is severely deformed and its free volume increases. However, with increase in tool rotational speed, the amount of heat generated also increases. The peak temperatures for FSP 300, FSP 500 and FSP 900 specimens were measured by a thermocouple to be nearly 170 °C, 300 °C and 430 °C respectively. The free volume in metallic glasses tends to annihilate with increase in temperature [21]. Therefore, strain rate and temperature can have opposing effects on the free volume in metallic glasses. Further, the fraction of crystalline phase also increases at higher tool rotational speed. The crystallization enthalpy was used to calculate the fraction of crystalline phase in the processed specimens and is given in Table 1. It is seen that FSP 900 has highest fraction of the crystalline phase while enthalpy of structural relaxation is the lowest. Lower structural relaxation for FSP 900 specimen may be attributed to rapid annihilation of free volume at the higher temperature reached during processing. An initial increase in the structural relaxation energy with strain and its subsequent reduction due to crystallization has been reported previously [22]. The crystallization enthalpy change for the FSP 300 specimen is nearly same as that of the as-cast metallic glass, indicating retention of the fully amorphous structure. The crystallization temperature, T_x, for the investigated metallic glass is around 451 °C (Table 1), which is higher than the peak temperature reached during FSP under all processing conditions. This implies that the partial devitrification of FSP 500 and FSP 900 specimens may have been induced by the higher strain rate. From the thermal analysis, it is clearly seen that FSP resulted in a minor shift in the onset (T_g^{onset}) and end (T_g^{end}) of the glass transition temperature (Table 1). T_g^{onset} increases for FSP 300 specimen and decreases for FSP 500 and FSP 900 specimens.