Journal of Alloys and Compounds 504S (2010) S45–S47

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Improvement in mechanical properties of a Zr-based bulk metallic glass by laser surface treatment

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ARTICLE INFO

Article history:
Received 6 December 2009
Received in revised form 31 March 2010
Accepted 9 April 2010
Available online 24 April 2010

Keywords:
Metallic glasses
Laser processing
Mechanical properties
Synchrotron radiation

ABSTRACT

In this work, surface modification of $Zr_{55}Cu_{30}Al_{10}Ni_5$ bulk metallic glass for improving the mechanical properties was carried out by employing laser surface melting (LSM) treatment. The structures and thermal properties of the as-cast and LSM treated samples were characterized with high energy synchrotron diffraction and differential scanning calorimeter, respectively. After the laser surface remelting, the $Zr_{55}Cu_{30}Al_{10}Ni_5$ alloy still consisted of fully amorphous structure. In comparison to the as-cast Zr-based alloy without distinct plasticity, the LSM treated one exhibited compressive plastic strain of 5.3% prior to fracture. The improvement in mechanical behavior of the LSM treated metallic glass may be resulted from complex residual stress distributions and increase in free volume in the surface layer induced by LSM treatment.

1. Introduction

Bulk metallic glasses (BMGs) have attracted great attentions due to their high strength, low Young's modulus, superplasticity in supercooled liquid region and unique physical and chemical properties [1–5]. However, most BMGs exhibit zero or limited plastic strain during deformation at room temperature, which limits the practical applications as structure materials. Great efforts have been devoted on studying the deformation behavior and mechanism and improving the plasticity of bulk metallic glasses in the last two decades. It has been widely recognized that the ductility improvement of BMGs virtually depends on the suppression of the localized strain softening caused by shear bands [6]. Some criteria for the intrinsic ductility of some bulk metallic glasses, such as high Poisson's ratio [7–9], nanocrystallization during deformation [10–12] and low glass transition temperature have been proposed in recent years. The situation of surface also influences mechanical properties of materials as diverse as silicate glasses and alloys. It has been reported that shot-peening can improve BMGs' plasticity in bending and in compression due to the induced compressive residual stress in the samples and the pre-existing shear bands in the surface [13]. Laser surface melting (LSM) is also expected to be a surface modification technique of metallic glasses because the high energy density of laser makes rapid heating and cooling possible. During the laser surface melting at a fast scanning speed on a metallic glass, cooling rate of 10^5–10^8 K/s which is even higher than the critical cooling rates of bulk glassy alloys can be reached [14,15]. On the other hand, LSM can also change the residual stress state of alloy surface, which may have effects on the mechanical properties of metallic glasses. In our recent work, it was found that, after laser surface melting, the $Zr_{55}Cu_{30}Al_{10}Ni_5$ BMG still consisted of fully amorphous structure and the treated metallic glass exhibited distinctly improved plasticity in compression as compared to the as-cast one. This paper presents the structure, thermal properties and compressive mechanical properties of $Zr_{55}Cu_{30}Al_{10}Ni_5$ BMG before and after LSM treatment. The origin of the effect of LSM on mechanical properties of metallic glasses is discussed.

2. Experimental

Alloy ingot with a nominal composition of $Zr_{55}Cu_{30}Al_{10}Ni_5$ (at.%) was prepared by arc melting the mixture of the pure metals of Zr (99.8 mass%), Cu (99.9 mass%), Al (99.99 mass%) and Ni (99.8 mass%) under a purified Ar atmosphere. From the ingot, cylindrical rods of 3 mm in diameter and 50 mm in length were prepared by copper mould casting under a purified Ar atmosphere and their glassy structure was confirmed by X-ray diffraction and differential scanning calorimeter (DSC). Laser melting on the surface of the glassy rods was carried out using a 180 W Nd:YAG laser at a beam scanning speed of 1000 mm/min with defocused beam (diameter = 1 mm), laser working voltage of 175 V and laser frequency of 8 Hz. During the laser melting process, a helium jet flow was used for preventing surface oxidation. Along the axial direction on the surface of the glassy cylindrical rod, the laser remelted spots with a diameter of 1 mm were overlapped one by one, which composed a laser-treated-spot line. The whole surface of the 3 mm diameter rod was covered by 11 overlapped laser-treated spot lines.

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doi:10.1016/j.jallcom.2010.04.053

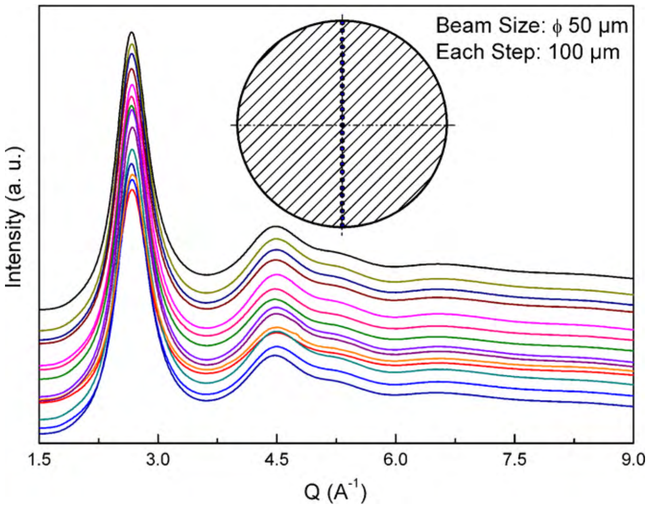

Fig. 1. Synchrotron diffraction patterns of the LSM treated $Zr_{55}Cu_{30}Al_{10}Ni_5$ bulk metallic glass of 3 mm in diameter. The diffraction patterns shown here correspond to the points from the edge to the center of the metallic glass plate, schematically illustrated in inset.

The microstructure of the LSM treated Zr-based BMG with a diameter of 3 mm was investigated by high energy synchrotron diffraction radiation. The radiation on the ID11 beam line of the European Synchrotron Radiation Facilities (ESRF) was monochromatized using a nitrogen-cooled double crystal silicon monochromator. The photon energy was 70 keV corresponding to a X-ray wave length of 0.17615 Å. The diffraction spectra were acquired in transmission by a 2D CCD camera. The radiated acquisition points were along the diameter of the cross-section of the LSM treated specimen, and the distance between each neighbored points was 100 μm. Thermal stability of the as-cast and the LSM treated samples was examined by DSC at a heating rate of 0.33 K/s. Vickers microhardness were measured under 200 g load. Compressive tests were performed on a material test system (MTS) at a strain rate of $2.1 \times 10^{-4}\ s^{-1}$ at room temperature using the glassy rods with a gauge dimension of 3 mm in diameter and 6 mm in height. The samples after the compressive tests were observed by scanning electron microscopy (SEM).

3. Results and discussion

Synchrotron diffraction patterns taken from the cross-section of the LSM treated $Zr_{55}Cu_{30}Al_{10}Ni_5$ BMG of 3 mm in diameter at fast beam scanning speed (1000 mm/min) are shown in Fig. 1. The 14 curves correspond to 14 radiated points from the edge to the center along the diameter of the sample, respectively (see the insert schematic illustration). The patterns exhibit no Bragg peak corresponding to a crystalline phase, indicating that the $Zr_{55}Cu_{30}Al_{10}Ni_5$ metallic glass kept glassy structure after the LSM treatment. The thickness of the molten and heat affected region of the present LSM treated Zr-based BMG was about 170 μm.

During the LSM process, a thin molten zone is produced on the surface, but hardly any energy of the laser is conducted into the interior of the metal. This leads to large temperature gradient between the molten layer and the matrix. When the laser beam is removed, extremely high cooling rate can be achieved (10^8 K/s) [16,17]. An estimation of the cooling rates, $\partial T/\partial t$, obtained during laser surface melting at high scanning speeds can be made using the Rosenthal solution for a moving heat point source, as proposed by Steen [14,18]:

$$\frac{\partial T}{\partial t} = -2\pi k \left[\frac{V_1}{P_d A}\right] \quad \Delta T^2 \tag{1}$$

where k is the thermal conductivity, V_1 the laser scanning speed, P_d the laser power density, A the area of the laser beam at the surface and ΔT is the range of temperature variation during cooling. For the calculations, it was assumed that the maximum temperature in the melt pool is the melting temperature of the alloy [14]. In this work, when appropriate parameters were chosen, the cooling rate of the LSM treatment is estimated to be about 3×10^6 K/s, which is several orders of magnitude larger than the cooling rate necessary for the vitrification of the Zr-based alloy. The results indicate that during the present LSM process, crystallization can be avoided due to the high cooling rate.

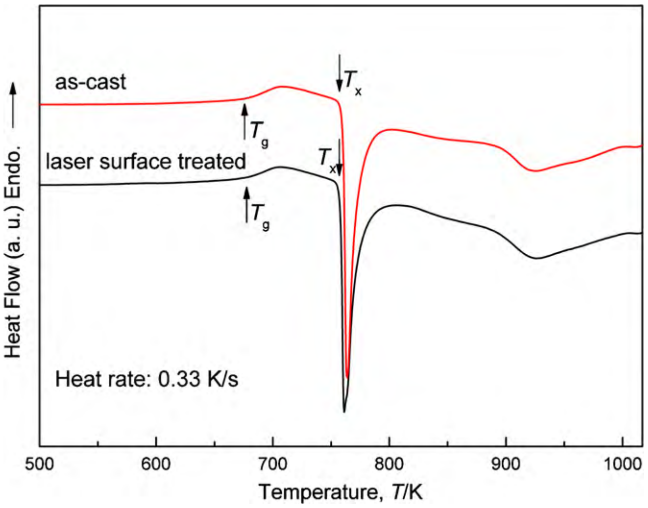

Fig. 2. DSC curves of the as-cast and the LSM treated $Zr_{55}Cu_{30}Al_{10}Ni_5$ glass rods with a diameter of 3 mm.

Fig. 2 shows DSC curves of the as-cast and LSM treated $Zr_{55}Cu_{30}Al_{10}Ni_5$ specimens with a diameter of 3 mm. It is seen that both the alloys exhibit a distinct glass transition at 677 K, followed by a supercooled liquid region of 81 K prior to crystallization at 758 K. No distinct difference in glass transition temperature (T_g), crystallization temperature (T_x) and the total heat release of the main crystallization peaks (ΔH_x) between the as-cast and the LSM treated samples is detected. Combined with the synchrotron diffraction results, it is confirmed that the LSM treatment on the Zr-based bulk metallic glass did not induce the crystallization and the alloy kept glassy structure.

Compressive stress-strain curves of the as-cast and the LSM treated $Zr_{55}Cu_{30}Al_{10}Ni_5$ rods with a diameter of 3 mm are shown in Fig. 3. Both the curves exhibit an elastic strain of ~2% in compression, which is typical for bulk metallic glasses. The as-cast BMG

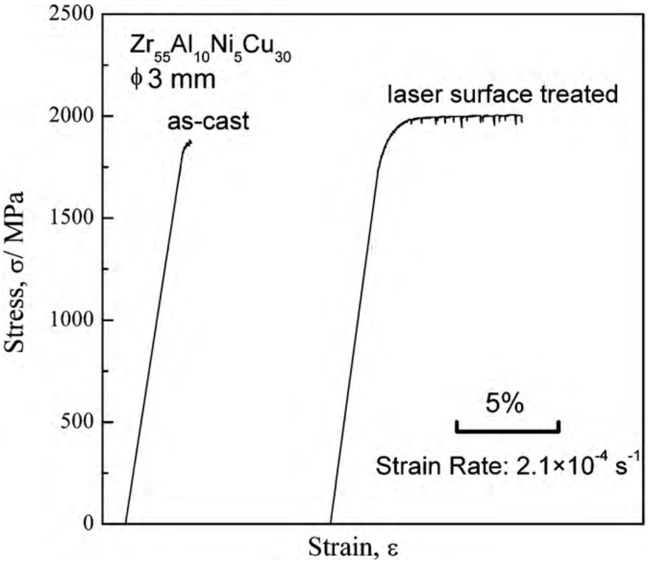

Fig. 3. Compressive stress-strain curves of the as-cast and the LSM treated $Zr_{55}Cu_{30}Al_{10}Ni_5$ glassy rods of 3 mm in diameter.

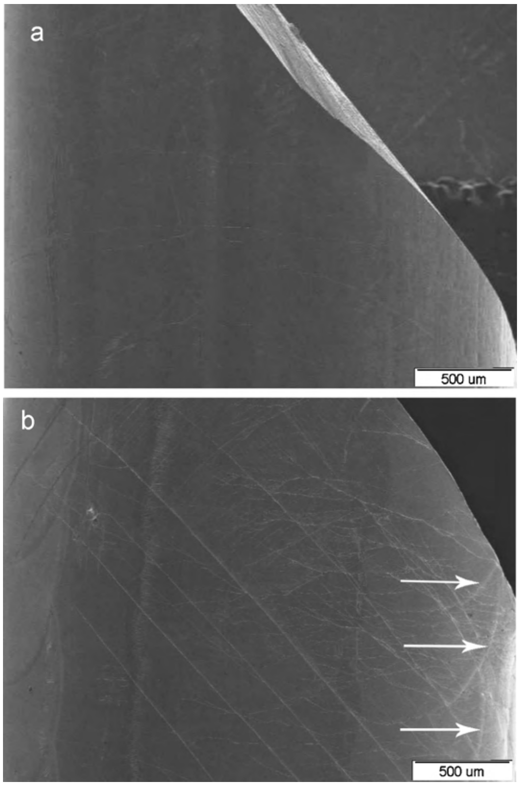

Fig. 4. SEM images showing the side-view appearances of the as-cast (a) and the LSM treated (b) $Zr_{55}Cu_{30}Al_{10}Ni_5$ bulk metallic glasses after the compression tests.

shows a plastic strain of about 0.3% prior to the final fracture at a stress of 1890 MPa. However, it is notable that after yielding, the LSM treated sample did not fracture catastrophically but deformed in a plastic manner with a plastic strain of 5.3%, which is much larger than that of the as-cast sample. The as-cast and the LSM treated samples after the compression tests were observed by SEM. Fig. 4 presents the SEM images showing the side-view appearances of the fractured samples. The tracks of laser surface melting on the treated sample can be seen in the Fig. 4(b) (big circles marked by white arrows). It is indicated that only a few primary shear bands are formed for the as-cast sample. While a number of multiple shear bands, which are beneficial to the plastic deformation of bulk metallic glasses [19], can be observed on the LSM treated sample surface. These observations are in agreement with that the treated sample exhibited larger compressive plastic strain than the as-cast one.

The effect of laser surface melting treatment on improving the compressive plasticity of the metallic glass may mainly come from the residual stress redistributions and the increase in free volume in the surface layer as well as the diminishing of surface defects of the LSM treated glassy alloys. The rapid melting and cooling procedure may introduce complex stresses distribution state in the surface layer [13]. It is considered that, after surface melting by laser, the central pool of melting exhibits a kind of tension stress and the boundaries of each pool show compressive residual stress. The compressive residual stress in samples could lead to extensive shear band formation, resulting in superior compressive plasticity, rather than catastrophic failure on a few dominant shear bands, which have been proven by shot-peening [13]. The present work indicated that the complicate distribution of residual stress induced by laser surface melting also have a positive effect on the multiplication of shear bands, leading to the improvement in the compressive mechanical properties. On the other hand, the Vickers microhardness at the sites of 50 μm from the surface (in the laser-treated surface layer) was ~5.0 GPa, which is much lower than that of the rod center part (~5.5 GPa). It implies that the softer surface region resulted from the laser treatment has more free volume. This result is in agreement with that more free volume may be generated because of the higher cooling rate using laser surface remelting, as discussed above. The multiplication of free volume can act as the nucleation sites of shear bands, which is one of the reasons of enlarged plastic strain [20]. The laser surface melting treatment may also remove some of the defects and flaws caused by rapid solidification during the copper mold casting, e.g. cold shut, which are generally the nucleation site of microcarcks [21,22]. The diminishing of the defects and flaws may also contribute to the plastic deformability, though the effect of defects on plasticity in compression is not as important as that in tension.

4. Conclusions

Laser surface melting has been successfully carried out on $Zr_{55}Cu_{30}Al_{10}Ni_5$ bulk metallic glass for improving the mechanical properties. After the LSM treatment, due to the high cooling rate, the laser-treated sample is still fully amorphous. In comparison to the as-cast Zr-based alloy without distinct plasticity, the LSM treated BMG exhibited enhanced compressive mechanical properties, as evidenced by the plastic strain of 5.3% prior to fracture. The laser surface melting treatment is promising as an effective approach for improving the mechanical properties of bulk metallic glasses.

Acknowledgements

This work was financially supported by the National Basic Research Program of China (2007CB613900), the National Nature Science Foundation of China (Grant Nos. 50631010 and 50771005) and Program for New Century Excellent Talents in University (NCET-07-0041).

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