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Effect of low-temperature annealing on the structure and mechanical properties of Zr–Cu metallic glasses

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ABSTRACT

The changes in the atomic structure and mechanical properties of Zr–Cu metallic glasses caused by low-temperature annealing were studied by X-ray diffraction synchrotron radiation and nanoindentation. Results show that the nanohardness, wear resistance, and uniformity were improved by low-temperature annealing, which indicated that annealing plays a significant contribution. Diffractions patterns showed that the content of high-strength Zr–Cu pairs was increased whereas those of Zr–Zr and Cu–Cu pairs were decreased after low-temperature annealing. Thus, the process improvement was achieved by increasing the proportion of Zr–Cu pairs.

1. Introduction

Bulk metallic glasses (BMGs) possess isotropic properties, high strength, low coefficient of friction, high wear resistance, and high corrosion resistance, which enable their applications to several specific fields [1–3]. Processing methods such as low-temperature annealing [4], ultrasonic treatment [5], and hydrostatic pressure treatment [6] have been proposed to improve the performance of BMGs. Low-temperature annealing is a relatively economical method, which may play an important role in future development. However, studies in this field are still insufficient and mainly focused on either structure or performance. In this paper, the changes of the structure and mechanical properties of Zr–Cu metallic glasses after low-temperature annealing were studied by X-ray diffraction (XRD) synchrotron radiation and nanoindentation. The Zr–Cu system has a simple atomic structure and is a typical amorphous system [7–9], which is conducive for revealing the internal relations between structure and performance.

2. Experiments

Zr–Cu alloy with a nominal composition of $Zr_{36}Cu_{64}$ (at%) was prepared by arc melting from a mixture of high-purity Zr and Cu. BMG cylindrical ingots were produced by copper mold casting in an argon atmosphere. The sample size was approximately 30 mm long with a diameter of 1 mm. A sample was isothermally annealed at 680 K, below the glass transition temperature ($T_g = \sim 720$ K) for 10 h in a vacuum furnace at a maximum pressure of 3×10^{-5} mbar. The sample was immediately removed from the furnace and allowed to cool at room temperature while inside the vacuum chamber. For comparison, another sample was not annealed and will be, henceforth, denoted as the as-cast specimen. The samples for nanoindentation (Φ 1 mm × 1 mm) were carefully polished to obtain a smooth surface. Indentations were conducted to measure nanohardness, and the friction coefficient was determined through nanoscratching to evaluate wear resistance.

Powder was carefully scraped using a 4Cr13 stainless steel scalpel from the amorphous rods. The amorphous nature of the scraped powder was confirmed by XRD. Powder was collected in a diamond anvil cell. The culet of the diamond anvil was 400 μm in diameter. An amorphous powder sample, together with the pressure-calibrator ruby, was loaded into a 120 μm-diameter hole of a T301 stainless steel gasket, which was pre-indented to a thickness of approximately 40 μm. Silicone oil was utilized as pressure-transmitting media. The position of the diffraction peak of ruby can help confirm the powder under an uncompressed stress state. XRD measurements were carried out in the Beijing Synchrotron Radiation Laboratory. Debye rings were recorded by using an image plate in transmission mode, and XRD patterns were integrated

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from the images using FIT2D software [10]. The size of the X-ray spot was 45 × 26 μm^2. A Li detector was employed to collect diffraction signals.

3. Results and discussion

The experimental results show that the average Vickers hardness of the annealed specimen (914 HV) is higher than that of the as-cast specimen (782 HV), which suggest that low-temperature annealing can indeed play a very important role for strengthening the metallic glasses. To gain a better understanding of the variation in the hardness of $Zr_{36}Cu_{64}$ BMG, contour maps of the spatial distribution of the nanohardness of specimens over a (40 × 40) μm^2 square area before and after low-temperature annealing were obtained, as shown in Fig. 1(a) and (b), respectively. All indentations were programmed to penetrate the same depth of 100 nm, and the spacing between adjacent indentations in both vertical and horizontal directions was 2 μm. The applied loading/unloading rate was 200 μN/s. The average hardness of the material is also evidently increased after low-temperature annealing. To a certain extent, these maps also demonstrated that the amorphous alloy was inhomogeneous at the microscale. The nanohardness of

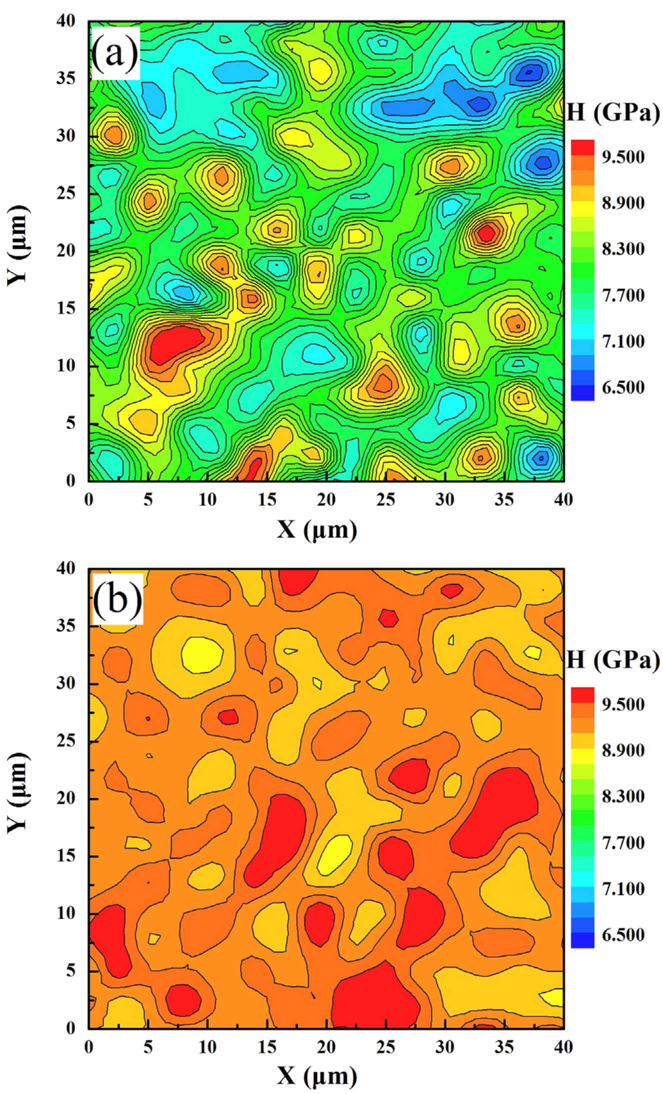

Fig. 1. Contour maps of the spatial distribution of the nanohardness of (a) the as-cast specimen and (b) the annealed specimen.

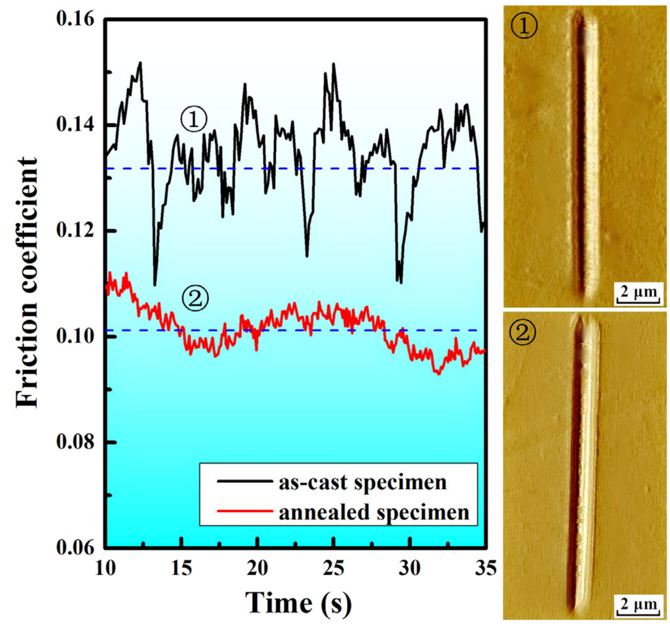

Fig. 2. Friction coefficient as a function of time, and in situ atomic-force microscopy images of nanoscratching taken at different specimens. The scratch direction is from bottom to top at a constant speed of 0.3 μm/s.

the as-cast specimen is arranged from 6.4 GPa to 9.6 GPa, and the nanohardness of the annealed specimen is set from 8.9 GPa to 9.7 GPa. This shows that the maximum value of the nanohardness does not change, and the distribution range reduces significantly after low-temperature annealing, which suggest that the hardness and uniformity of the material is improved.

The same conclusions can be obtained from Fig. 2, which shows the surface friction coefficient of the specimens and in situ atomic-force microscopy images of nanoscratching. The friction coefficient is defined as the ratio between the lateral force P_l and the normal force P_n measured by the force sensors incorporated in the nanoindenter at an ultra-high resolution. During nanoscratching, the load increases from 0 μN to a maximum of 3000 μN in 3 s, remains constant for 40 s at a constant scratch velocity of 0.3 μm/s, and decreases to 0 N in 3 s [11]. The average friction coefficient of the as-cast specimen is found to be approximately 0.132, and the average friction coefficient of the annealed specimen is 0.101. The smaller friction coefficient represents superior wear resistance, which further indicates the reinforcement effect of low-temperature annealing. The fluctuation range of the friction coefficient is also found to be reduced significantly after low-temperature annealing, which implies that the uniformity of the material is improved.

This reinforcement of BMGs is usually attributed to the annihilation of free volume [12–14]. The formation of free volume is due to internal compressive stress and tensile stress in BMGs. The regions suffered by compressive stress have stronger resistance against the invasion of foreign objects and higher hardness. On the contrary, the regions suffered by tensile stress show lower hardness. Along with the annihilation of free volume, the tensile stress and compressive stress balance each other out. Thus, even though the average hardness increased, the maximum nanohardness of local regions should be dropped. The experimental results demonstrate that the maximum nanohardness does not decrease and even increases slightly, which indicate that the annihilation of free volume is not the only cause for reinforcement.

Fig. 3 shows the pair distribution functions of the annealed and as-cast specimens. The whole shape of the first peak is found to clearly change after low-temperature annealing. The amplification