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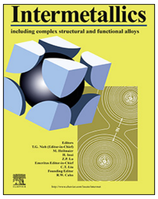

Mechanisms for the free volume tuning the mechanical properties of metallic glass through ion irradiation

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ABSTRACT

The irradiation response of metallic glass $Ni_{50}Nb_{10}Zr_{15}Ti_{15}Pt_{7.5}Cu_{2.5}$ under 3 MeV Au ion irradiation was studied. Significant hardness decrease was observed under low dose irradiation. However, the hardness restores to the level of unirradiated sample under higher dose irradiation. Positron annihilation Doppler broadening results indicate that ion bombardment would destroy the short range order (SRO) in metallic glass and introduce excessive free volume under low dose irradiation. While the formation of local ordered structure would consume the free volume due to enhanced atom mobility under higher dose irradiation. Our results help to understand the mechanism of the irradiation effect in metallic glass, and moderate ion radiation can be an efficient way to improve the mechanical property of metallic glass by introducing free volume in metallic glass.

1. Introduction

Due to its amorphous nature of atomic structure, metallic glass often exhibits excellent mechanical properties like high strength [1], high toughness [2] and good corrosion resistance [3]. But the strain localization induced by shear band formation [4] usually results in brittle failure at room temperature, which limits its practical application. The main challenge in this field is to promote the ductility of metallic glass at room temperature.

Ion irradiation is an effective way to change the microstructure and mechanical properties of materials. For crystalline metallic materials, the formation of irradiation defects would commonly result in the degradation of their mechanical properties [5,6]. However, irradiation effects in metallic glass are quite diverse, some even opposite. For example, ion irradiation induced hardening accompanying with the formation of nanocrystals [7,39], and ion irradiation induced softening [8] were both observed in metallic glass. Meanwhile, phenomena like ion irradiation induced viscous flow [9] and structure rejuvenation [10] were also observed under different radiation conditions in various metallic glass. Recently, some experimental [11,12] and simulation studies [13,14] showed that mechanical properties like strength and tensile ductility of metallic glass can be promoted by ion irradiation under certain circumstance. The underlying mechanisms of these radiation responses in metallic glass are not well understood. Furthermore, there are few direct experimental evidences for the corresponding atomic scale structural changes induced by ion irradiation.

Although metallic glass is long range disordered, short range order in metallic glass, which cannot be detected by conventional diffraction based technique such as XRD, was recently verified by several experimental and simulation works [15,16]. The densely packed cluster-like entities consisting of ten of atoms, were found to be possible building blocks for metallic glass. The free volume (FV), which is the atomic scale open spaces (loosely packed region) distributed throughout the metallic glass, is thought to be the main structural defect that controls the plastic flow of metallic glass [17], when there are no nanocrystal particles in the metallic glass matrix. Simulation studies [18,19] showed that the plastic deformation in metallic glass involves the collective rearrangement of a few atom clusters, called shear transformation zone (STZ), and the activation of STZ is closely related with free volume. Meanwhile, some experimental studies showed that the reduction of free volume content caused by low temperature annealing would make metallic glass more fragile [20,21]. Others showed that the increase in free volume leads to a decrease of yield strength, accompanying with a larger plasticity as the formation of multiple shear bands is promoted [22]. These results indicate that the mechanical behavior of metallic glass is closely related with the free volume content.

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However, due to the amorphous atomic structure of metallic glass, direct characterization of such radiation induced structural defects in metallic glass is still lacking, which hampers the investigation of irradiation effect in metallic glass. Furthermore, the mechanisms of the correlations between the mechanical properties and free volume induced by ion irradiation in metallic glass are not fully understood.

It's well known that positron annihilation is a powerful tool to characterize the vacancy-like defect [23] in crystalline materials. When a monochromatic positron beam penetrates into the material, the positrons would annihilate with surrounding electrons at a certain depth from the surface, and γ signals with small energy shift are emitted. This energy shift is determined by the momentum of the annihilated electrons in material. Several studies showed that positron annihilation is also an effective way to probe the atomic-scale open-volume regions (i.e. free volume) in metallic glass [24,25]. By analyzing the Doppler broadening energy spectrum of the emitted γ photon, we can obtain a qualitative results of the content of free volume in metallic glass [24], and by adjusting the positron energy, the free volume content in different depths can be obtained. It should be noted that an understanding of free volume evolution is not only essential for controlling and optimizing the mechanical properties of metallic glass by ion irradiation, it can also help us to design and exploit new type metallic glass for structural nuclear material under radiation environment.

In this study, Au ion irradiation experiments with different ion doses were performed to investigate the irradiation response of metallic glass $Ni_{50}Nb_{10}Zr_{15}Ti_{15}Pt_{7.5}Cu_{2.5}$. Nanoindentation test was applied to characterize the hardness change of metallic glass samples. X-ray diffraction and positron annihilation Doppler broadening (DB) measurement were then performed to examine the corresponding structural change in metallic glass. The free volume content in irradiated metallic glass samples under different Au ion doses was measured, and the correlation between the hardness and free volume induced by ion irradiation was unambiguously discussed. These results provide some details about the microstructure evolution of metallic glass under ion irradiation.

2. Experiment methods

The metallic glass ribbon of $Ni_{50}Nb_{10}Zr_{15}Ti_{15}Pt_{7.5}Cu_{2.5}$ was fabricated by rapid solidification method. This metallic glass was selected for study because of its wide supercooled region [26,40], which means that it owns good stabilization against crystallization. Meanwhile, the Ni-based metallic glass exhibits excellent mechanical properties, and we studied its irradiation effect to exploit new structural nuclear material. Three groups of samples with 10 mm × 3 mm size were prepared. The 3 MeV Au^{2+} ion irradiation experiments were performed by NEC 1.7 MV tandem accelerator, with ion fluence of $1 \times 10^{14}\ cm^{-2}$, $1 \times 10^{15}\ cm^{-2}$, and $1 \times 10^{16}\ cm^{-2}$, respectively. By using the Monte Carlo based program Stopping and Range of Ions in Matter (SRIM), we found that the average radiation damage is about 0.49 dpa, 4.9 dpa, and 49 dpa, respectively. The maximum Au penetration depth is evaluated to be about 630 nm under 3 MeV Au ion irradiation. The beam flux was about 200 nA, and the temperature was kept at room temperature during the ion irradiation experiments. Base pressure in the chamber was less than 5×10^{-4} Pa.

After ion irradiation, the mechanical properties of the metallic glass samples were characterized by nanoindentation on Agilent Nano Indenter G200w. Continuous stiffness mode (CSM) was used to extract the hardness profile along with the increase of indentation depth. For each sample, ten indentation points were selected to eliminate accidental errors. Berkovich indenter was used, and the constant strain rate of 0.05/s was set for all tested samples.

The microstructure of the unirradiated and ion-irradiated metallic glass samples was characterized by X-Ray diffraction (XRD) and positron annihilation DB measurement. The PANalytical X-Pert3 Powder diffractometer with Cu $K\alpha_1$ ($\lambda = 1.54056$ Å) radiation was used, and the scanning speed was 8.57°/min. Positron annihilation DB measurement was performed using a slow positron beam facility in the Institute of High Energy Physics, with the positron beam energy ranging from 0.03 to 20 keV. By adjusting the beam energy, the detective depth can be controlled. The relationship between the detective depth and the incident energy can be expressed by the empirical equation [27]:

$$R = \left(\frac{40}{\rho}\right)E^{1.6} \tag{1}$$

where R is the detective depth of positron beam in unit of nm, ρ is the density of metallic glass, expressed in g/cm^3 and E is the incident energy of the slow positron beam, which is in unit of keV. The DB measurement is sensitive to the vacancy-like defect, i.e. free volume in metallic glass. The S parameter is defined as the ratio of the counts in central low momentum area (510.2–511.8 keV) to the total counts, and W parameter is the ratio of the counts in two flanks high momentum areas (514.83–518.66 keV and 503.34–507.17 keV) to the total counts. More details about positron annihilation spectroscopy can be found elsewhere [25,28].

3. Results and discussion

3.1. Hardness characterization

The hardness measurement is based on Oliver-Pharr method, and the hardness is defined by:

$$H = \frac{P}{A} \tag{2}$$

where P is the load, and A is the projected contact area of the indenter. To avoid the error induced by tip blunting of the indenter, the hardness data from depth over 100 nm is considered. In order to evaluate the hardness change, we defined the average number of hardness values from 100 nm to 600 nm to be the average hardness for each sample. As shown in Fig. 1, the average hardness of unirradiated sample is 10.42 GPa. For ion-irradiated samples, it is found that the hardness of all the samples drops with different extents. Comparing with the unirradiated sample, the average hardness of irradiated sample with dose of $1 \times 10^{14} cm^{-2}$ largely decreases about 37% to 6.58 GPa. When the ion dose increases to $1 \times 10^{15} cm^{-2}$ (4.9 dpa) and $1 \times 10^{16} cm^{-2}$ (49 dpa), the average hardness of the irradiated sample restores to 7.41 GPa and 9.70 GPa, respectively. Such radiation induced softening in metallic glass is very different from crystalline metallic material. For crystalline alloy, ion radiation would cause a substantial amount of hardening as the radiation induced defects would act as obstacles for dislocation slip [29]. For metallic glass, the mechanical properties are closely related to the free volume content, and further microstructure characterization is needed to understand such ion induced softening in metallic glass.

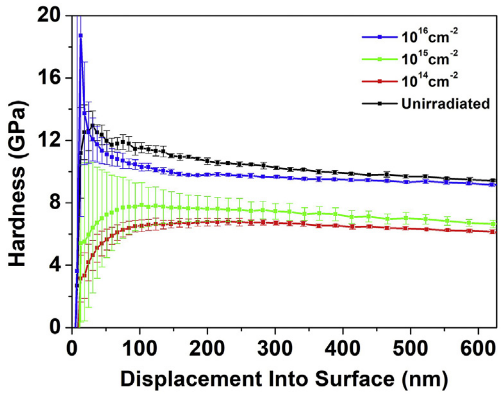

Fig. 1. The depth profiles of hardness for unirradiated sample and ion-irradiated samples with different ion doses.