STUDY OF HYDROGEN-INDUCED PLASTIC DEFORMATION IN BULK METALLIC GLASS

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ABSTRACT

Two kinds of bulk metallic glasses $Zr_{57}Cu_{15.4}Ni_{12.6}Al_{10}Nb_5$ and $Zr_{41.2}Ti_{13.8}Ni_{10}Cu_{12.5}Be_{22.5}$ were used to study the hydrogen-induced plastic deformation in this work. Results show that hydrogen blistering could form in the former containing niobium during hydrogen charging when current density is large enough. But it could occur more easily accompanying with microcracks in the later containing beryllium. For $Zr_{41.2}Ti_{13.8}Ni_{10}Cu_{12.5}Be_{22.5}$ bulk metallic glass, when the current density of hydrogen charging is smaller than 20 mA/cm^2, hydrogen-induced delayed fracture (HIDF) can occur during charging at sustained load in and the threshold stress intensity factor of HIDF, K_{IH}, is 0.63 times of the notched toughness, K_Q; when the current density is equal to or larger than 20 mA/cm^2, blistering or blistering plus microcrack appears during charging without loading, and the threshold stress intensity factor of HIDF, K_{IH}, is 0.26 times of K_Q and independent upon the current density of hydrogen charging.

1 INTRODUCTION

Atomic hydrogen will concentrate at defects and compose into molecule hydrogen H_2 when the hydrogen concentration is high in metallic materials [1-4]. The molecule hydrogen brings inner pressure in material, and the inner pressure increases with increasing in the concentration of hydrogen. When the pressure reaches up to the yield strength, the plastic deformation occurs. If there are some defects such as impurities in the inner of the material at which hydrogen preferentially gather together, that means the sample surface would bulge and the hydrogen blistering form. When the hydrogen pressure reaches high to the fracture strength, the material will crack. The susceptibilities of hydrogen blistering and hydrogen-induced microcracks are different from each other for different material.

For Zr-based bulk metallic glasses, in situ tensile tests in scanning electron microscope (SEM) showed that formation and growth of shear hands gradually during loading, and a mode II shear crack (or cracks) initiated and grew along the main shear bands when the plastic flow developed into certain degree [5]. During further extending, the mode II shear crack opened into mode I crack, and propagated fast along the shear plane into a through crack, then the specimen fractured by rapidly propagating of the through crack. Therefore, the shear bands play an important role in deformation and fracture of bulk metallic glasses [5].

For steel, hydrogen blistering and flaking could appear during charging with high hydrogen fugacity [6]. For bulk metallic glass, whether hydrogen can enhance localized plastic flow of bulk metallic glasses is still a question. Some workers indicated that it could. By now, there is less report on the direct observation of the hydrogen blistering. This is the objective of this work. The second objective is to recognize whether hydrogen induced delayed fracture (HIDF) in the bulk metallic glass can occur when hydrogen concentration is below the critical value necessary for hydrogen blistering formation.

2 EXPERIMENTAL

Both bulk metallic glasses of $Zr_{57}Cu_{15.4}Ni_{12.6}Al_{10}Nb_5$ and $Zr_{41.2}Ti_{13.8}Ni_{10}Cu_{12.5}Be_{22.5}$ (nominal composition in atomic percent) were chosen in this work. Samples were produced by arc melting the pure elements together under a purified argon atmosphere into ingots of the desired composition; each ingot was then remelted twice to ensure a homogeneous composition. Then bulks of metallic glass with size of 2×20×40 mm^3 were made by suction casting the molten alloy into a copper mold. The bulks were confirmed to be non-crystalline by a conventional X-ray diffraction.

After electropolishing in methanol solution containing 33 percent volume fraction of HNO_3 and charging with various current densities for 48 h，the blistering was observed in optical microscopy and SEM microscopy; and the blistering density (blistering area per unit surface area) was measured. Three-point bend specimen with dimensions of 2×4×15 mm^3 containing a notch of 1.2 mm depth in the middle of length along the width direction was prepared by electric spark wire cutting. An additive cutting on the top of the notch was made to produce an additive notch of about 0.1 mm depth and 0.1 mm root radius by a saw blade to remove possible crystalline layer induced by local heating. The stress intensity factor is given by

$$K_I = \frac{PS}{4BW\sqrt{W}} f(a/W) \qquad (1)$$

where B=2 mm, W=4 mm, S=3W, a=1.3 mm is the depth of the notch, P is load and $f(a/W)$=6.39 corresponding to a/W=0.325 . Substituting fracture load P_C into Eq. (1), the notched toughness K_Q can be obtained. A set of specimens with different K_I were dynamic charged under sustained load in a 0.5 mol/l H_2SO_4+0.25 g/l As_2O_3 solution with various current densities, and the time to fracture was recorded. The threshold stress intensity factor of hydrogen-induced delayed fracture is obtained on the basis of following equations [7]

$$K_{IH} = (K_{Iy} + K_{In})/2 \qquad (2)$$

$$K_{Iy} - K_{In} < 0.05(K_{Iy} + K_{In}) \qquad (3)$$

where K_{Iy} is the minimum K_I at which delayed fracture occurred and K_{In} is the maximum K_I at which delayed fracture would not occur within the fixed time, e.g. 100 h. To ensure the error of measured K_{IH} is less than 5 percent, Eq. (3) must be satisfied, otherwise, an additive specimen is loaded to $(K_{Iy}+K_{In})/2$.

3 RESULTS

3.1 Hydrogen blistering

For $Zr_{57}Cu_{15.4}Ni_{12.6}Al_{10}Nb_5$ bulk metallic glass, when the sample was charged with current density of equal to or smaller than 100 mA/cm^2 for 48h, no hydrogen blistering was observed on the sample surface in optical microscopy, as shown in Fig.1(a). When the current density is larger than 300 mA/cm^2, blistering appears and the blistering density increases with increasing current density, as shown in Fig. 1(b). The blistering density is listed in Table 1. The specimen later was observed in SEM. Fig. 2 shows blistering with average size of a couple of micrometers formed during hydrogen charging with current density of 900 mA/cm^2. In Fig. 2(a), blistering A was unbroken, B was broken. And in Fig. 2(b) there was a coalescence of several broken blisterings with microcracks such as a, b, c and d. Fig. 2 shows that the blistering with size of several micrometers formed through hydrogen charging and then broke when growing large enough.

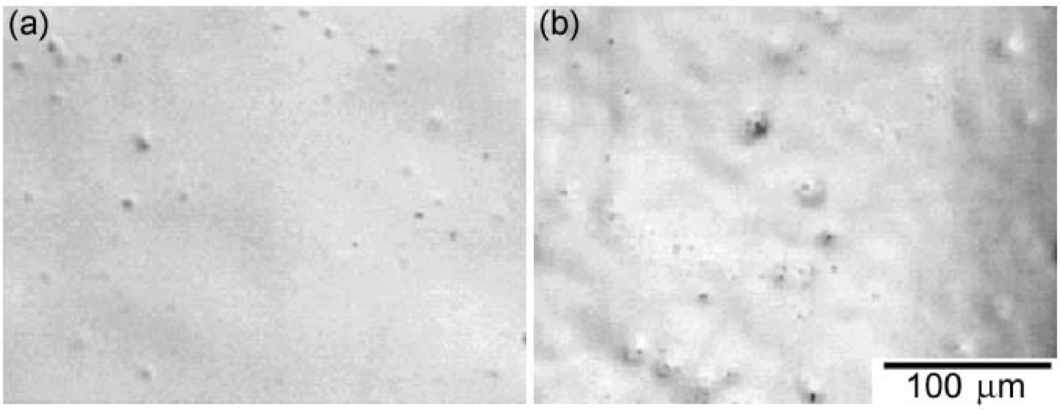

Fig. 1 Optical microscopy of hydrogen blistering in $Zr_{57}Cu_{15.4}Ni_{12.6}Al_{10}Nb_5$ formed under current density of (a) 300mA/cm^2 and (b) 900mA/cm^2.

Table 1 Density of hydrogen blistering in $Zr_{57}Cu_{15.4}Ni_{12.6}Al_{10}Nb_5$

Current density, i, A/cm^2	100	300	600	900
Area density of blistering, ρ_A	0	0.005	0.022	0.039

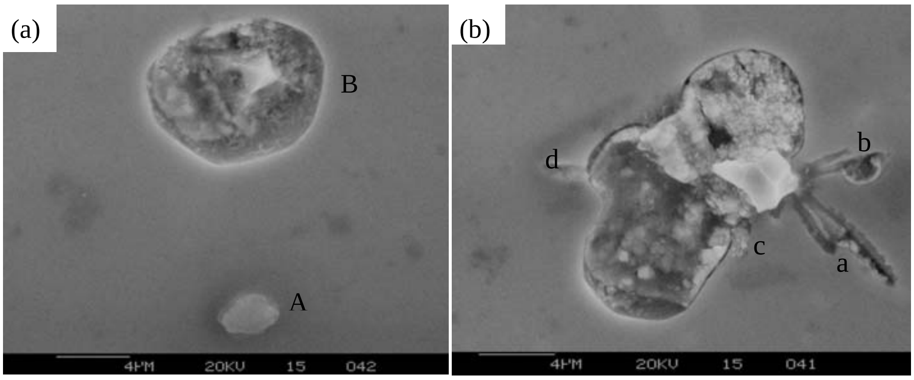

Fig.2 SEM microscopy of hydrogen blistering in $Zr_{57}Cu_{15.4}Ni_{12.6}Al_{10}Nb_5$ formed under current density of $900mA/cm^2$.

3.2 Hydrogen-induced microcracks

For $Zr_{41.2}Ti_{13.8}Ni_{10}Cu_{12.5}Be_{22.5}$, hydrogen blistering formed during hydrogen charging more easily than that in $Zr_{57}Cu_{15.4}Ni_{12.6}Al_{10}$ Nb_5. And furthermore, the blistering grew and propagated fast accompanying with microcracks generating, as shown in Fig.3. The density of hydrogen-induced microcracks is measured as the length per unit area of the sample surface. Table 2 summaries the result. When current density is less than $10mA/cm^2$, no hydrogen-induced microcrack appears on the sample surface. And the density of hydrogen-induced microcracks increases with increasing the current density. The microcracks lengthened and multipled with increasing current density of hydrogen charging, finally resulting in fracture of the sample.

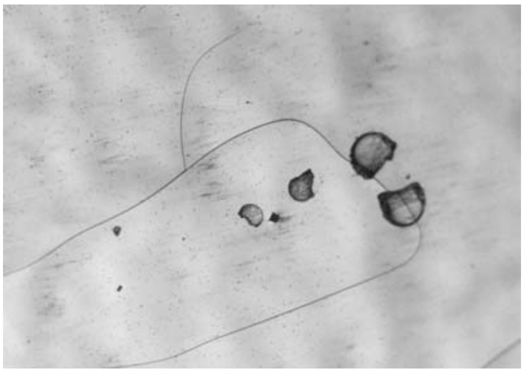

Fig.3 Hydrogen blistering and hydrogen-induced microcracks in $Zr_{41.2}Ti_{13.8}Ni_{10}Cu_{12.5}Be_{22.5}$ formed under current density of $40mA/cm^2$.

Table 2 Density of hydrogen-induced microcracks in $Zr_{57}Cu_{15.4}Ni_{12.6}Al_{10}Nb_5$ versus various current densities of hydrogen charging.

Current density, *i*, mA/cm^2	10	40	50
Densities of microcracks, ρ, $nm/\mu m^2$	0	3.3	5.0

3.3 Hydrogen-induced delayed fracture

The notched toughness of three notched specimens for containing beryllium alloy of $Zr_{41.2}Ti_{13.8}Ni_{10}Cu_{12.5}Be_{22.5}$ is K_Q=60.3, 61.5 and 64.8 MPa·$m^{1/2}$, and the average value is 62.2 MPa·$m^{1/2}$. The blistering density corresponding to various current densities was measured and listed in Table 3. The normalized threshold stress intensity factor of HIDF, K_{IH}/K_Q, can be calculated based on Eq. (2) and are also listed in Table 3. Table 3 shows that if i<20 mA/cm^2, no hydrogen blistering appears during charging without loading, and K_{IH}/K_Q=0.63 during charging at sustained load, but if i≥20 mA/cm^2, blistering appears, K_{IH}/K_Q=0.26 and is independent upon current density. Fig. 4 clearly shows the fracture surface is of brittle style with crack source below the surface, such as point A in Fig. 4(a). It is much different from the fracture surface without hydrogen charging (see Figs. 3 and 7 in Ref. [6]). Fig. 4(b) is local magnified microscopy of the crack source. It can be seen that there are so many hydrogen-induced disconnected microcracks in this region, such as a, b, c.

Table 3. Hydrogen blistering density, ρ_A, and K_{IH}/K_Q corresponding to various current densities in $Zr_{41.2}Ti_{13.8}Ni_{10}Cu_{12.5}Be_{22.5}$ alloy

i, mA/cm^2	10	15	20	30	50	100
ρ_A	0	0	0.02	0.06	0.25	—
K_{IH}/K_Q	0.63	0.63	0.26	0.26	0.26	0.26

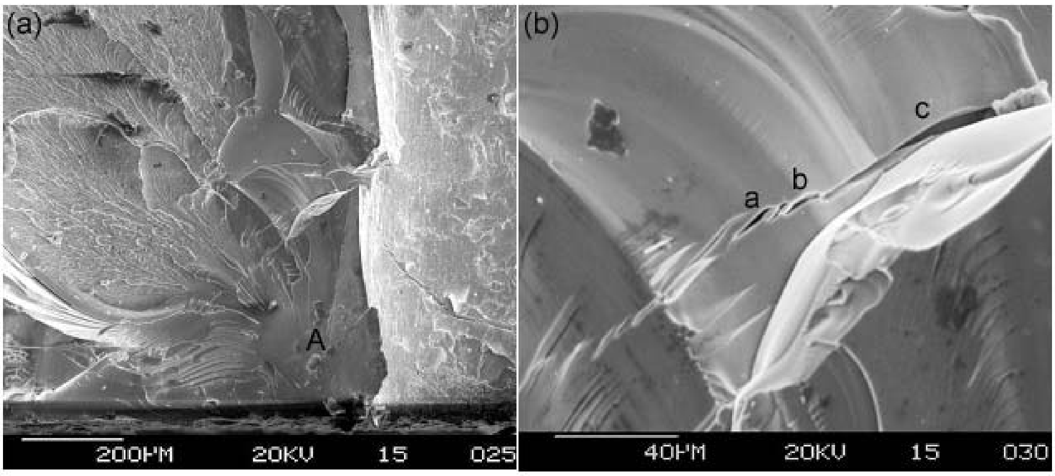

Fig. 4 Fracture surface of hydrogen-induced delayed fracture in $Zr_{41.2}Ti_{13.8}Ni_{10}Cu_{12.5}Be_{22.5}$ alloy under low magnification with crack source (a) and local high magnification (b). The current density is 100mA/cm^2.

4 SUMMARY

Two kinds of bulk metallic glasses were used to study the hydrogen-induced plastic deformation in this work. The main results are as follows:

Hydrogen blistering could form in $Zr_{57}Cu_{15.4}Ni_{12.6}Al_{10}Nb_5$ bulk metallic glass containing niobium during hydrogen charging when current density is large enough. It could occur more easily accompanying with microcracks in $Zr_{41.2}Ti_{13.8}Ni_{10}Cu_{12.5}Be_{22.5}$ bulk metallic glass.

When the current density of hydrogen charging is smaller than 20 mA/cm^2, hydrogen-induced delayed fracture (HIDF) can occur during charging at sustained load in $Zr_{41.2}Ti_{13.8}Ni_{10}Cu_{12.5}Be_{22.5}$ bulk metallic glass and the threshold stress intensity factor of HIDF is $K_{IH}=0.63K_Q$, where K_Q is the notched toughness. When the current density is equal to or larger than 20 mA/cm^2, blisterings or blisterings plus microcracks appear during charging without loading, and the threshold stress intensity factor of HIDF $K_{IH}=0.26K_Q$ and independent upon the current density of hydrogen charging.

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