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The influence of Pd on tension–tension fatigue behavior of Zr-based bulk-metallic glasses

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A B S T R A C T

Zr-based bulk-metallic glasses (BMGs) are being studied widely because Zr-based BMGs exhibit good glass-forming abilities and excellent properties, such as material strengths. In the current paper, the fatigue behaviors of $Zr_{50}Cu_{40-x}Al_{10}Pd_x$ [x: 0–7 atomic percent (at.%)] BMGs were investigated. The uniaxial tension–tension fatigue experiments were performed on the button-head rod fatigue specimens. The test environment was air at room temperature. The fatigue limit of $Zr_{50}Cu_{37}Al_{10}Pd_3$ was found to be the highest with a value of 945 MPa among the BMGs studied. A mechanistic understanding of the fatigue behavior of these Zr-based BMGs is suggested. The effect of the Pd content on the fatigue behavior was analyzed. A possible relationship between the fatigue limit (or the fatigue ratio) and the volume change, which probably corresponds to excessive free volume, was developed.

1. Introduction

As excellent candidates for structural materials, bulk-metallic glasses (BMGs) are being studied extensively [1.2]. Because the fatigue behavior is a very important characteristic for the application of structural materials, the fatigue investigation of BMGs attracts attention [3–20]. However, the understanding of the fatigue behavior of BMGs is still limited. Gilbert et al. [3,4] were the first to report the fatigue results of BMGs. They performed four-point-bend fatigue experiments on Vitreloy 1 [$Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ (in atomic percent, at.%)] beam specimens and claimed that the fatigue limits, based on the stress range, were approximately 8% of the ultimate tensile strength. Menzel and Dauskardt also obtained similar fatigue results [5]. These values are very low compared to conventional crystalline alloys, such as high-strength steels, copper, and aluminum alloys, whose fatigue limits are typically 30–40% of the ultimate tensile strength.

On the other hand, tension–tension fatigue results of taper notched LM001 BMG samples that have the same composition as Vitreloy 1 revealed that the fatigue limits, based on the stress range, were 31% of the ultimate tensile strengths [6]. In addition, Peter et al. [7,8] and Wang et al. [9–13] performed tension–tension fatigue tests on notched Zr-based BMG samples, and Yokoyama et al. [14] did rotating-beam fatigue experiments on Zr-based BMGs. They found fatigue limits as high as 40–50% of the ultimate tensile strength. Recently, Nakai et al. conducted fatigue tests on smooth Zr-based BMGs specimens under fully reversed cyclic loading and reported that the fatigue limit, based on the stress amplitude, is 26% of the ultimate tensile strength [15].

According to these fatigue studies of Zr-based BMGs, it was found that Zr-based BMGs with various compositions exhibited very different fatigue lives. What caused such a large difference among these fatigue results of BMGs? Many factors could be involved, such as the material quality, mean stress, specimen geometry, chemical environment, temperature, cyclic frequency, residual stress, and surface condition. In fact, any processing that changes the static mechanical properties or microstructure will probably also affect the fatigue behavior of materials. However, some of factors mentioned above must play an important role in affecting the fatigue behavior of BMGs. The formation of shear bands is still unclear during the cyclic deformation of BMGs. How the fatigue crack initiates and propagates in metallic glasses needs to be solved. Thus, it is essential to perform the fundamental research on the fatigue behavior of BMGs.

$Zr_{50}Cu_{40}Al_{10}$ shows good mechanical behavior, and the fatigue behavior can be improved. In order to strengthen the fatigue behavior of $Zr_{50}Cu_{40}Al_{10}$ BMGs, in general, some small additive elements like Ni and Pd were added into this alloy system [14]. In the current paper, uniaxial tension–tension fatigue experiments on the $Zr_{50}Cu_{40-x}Al_{10}Pd_x$ [x: 0–7 atomic percent (at.%)] were performed. The applied stress versus fatigue cycle (S–N) curves of these BMGs is presented. The fracture surfaces were observed and analyzed using scanning-electron microscopy (SEM). In addition, the factors

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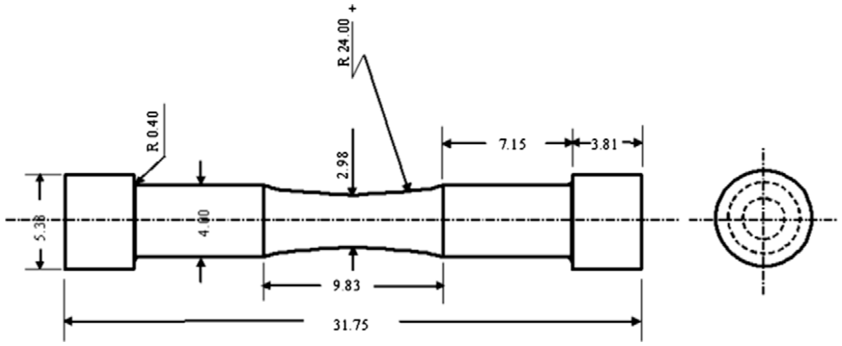

Fig. 1. Specimen geometry for tension–tension fatigue experiments (unit: mm).

which influence the fatigue limit were discussed. Thus, the effect of the Pd content on the fatigue behavior of BMGs was clarified.

2. Experimental procedures

$Zr_{50}Cu_{40-x}Al_{10}Pd_x$ (x: 0–7 at.%) BMGs were the ternary and quaternary alloys used in the present experiments. The ladle-hearth type arc-melt tilt-casting technique was employed to manufacture these BMGs. The master-alloy ingots were prepared by arc-melting mixtures of pure Zr, Cu, Al, and Pd metals in an argon atmosphere. A special Zr-crystal rod [<0.05 at.% oxygen] was employed in order to maintain the low-oxygen concentration of the alloys [21,22]. The tilt-casting technique has an advantage to control the molten alloy flow to restrict the formation of cold shuts, which probably induces early fatigue–crack initiation and propagation behavior [21,22]. Rod BMG ingots were produced with a length of 60 mm and a diameter of 8 mm. One taper notched specimen (Fig. 1) was machined from each ingot. The fatigue samples were, then, polished to minimize surface effects. The thermal properties of these BMG samples were measured in a Perkin–Elmer Diamond differential scanning calorimeter (DSC) at a heating rate of 20 K/min. The weight of samples used for DSC was in the range of 30–50 mg.

The previous research result revealed a decrease in the free volume by annealing a BMG [23]. The free-volume changes could result in the variation of the BMG volume. Therefore, the volume change due to the structural relaxation at the glass-transition temperature (T_g) could be a convenient method to evaluate the free-volume difference in the glass structure.

The volume change is defined as the volume change ratio of BMGs from the as-cast state to the annealed state at T_g. The following equation is used to determine the value of the volume change [24]:

$$\Delta V = \frac{\rho_0^{-1} - \rho_{Tg}^{-1}}{\rho_0^{-1}}$$

where ΔV is the volume change, ρ_0 is the density of the as-cast alloy, and ρ_{Tg} is the density of the alloy after annealing at T_g for 90 min.

A computer-controlled Material Test System (MTS) servohydraulic testing machine was employed for fatigue studies. The machine was aligned prior to use, and as required. Samples were tested at various stress ranges with a R ratio ($R = \sigma_{min}/\sigma_{max}$, where σ_{min} and σ_{max} are the applied minimum and maximum stresses, respectively) of 0.1 under a load-control mode, using a sinusoidal waveform at a frequency of 10 Hz. Upon failures or 10^7 cycles, samples were removed and stored for later examinations by SEM. The fracture surfaces of selected specimens were examined, using a Leo 1526 SEM machine with the energy-dispersive spectroscopy (EDS) to provide fatigue and fracture mechanisms.

3. Results and discussion

Fig. 2 shows the DSC thermograms obtained from the as-cast fatigue samples during continuous heating at a heating rate of 20 K/min. An endothermic reaction, corresponding to the transition from a glassy state to a supercooled liquid state, and the following exothermic reaction, corresponding to crystallization are clearly observed. These parameters are labeled as the glass-transition temperature, T_g, and crystallization temperature, T_x, respectively. The characteristic temperatures, as well as heats of crystallization (ΔH_x), are given in Table 1. In addition, the supercooled liquid region $\Delta T_x = T_x - T_g$) was also calculated, as shown in Table 1. ΔT_x may indicate that the larger the accessible supercooled liquid region is, the greater the glass-forming ability is [25]. The value of T_g increases with increasing the Pd content in these BMGs. However, the value of T_x and ΔH_x exhibit slight decreases when the Pd content increases from 0% to 7% in these glassy alloys. The increase of Pd resulted in a slight decrease of the supercooled liquid region ΔT_x), which may indicate that Pd has the negative effect on

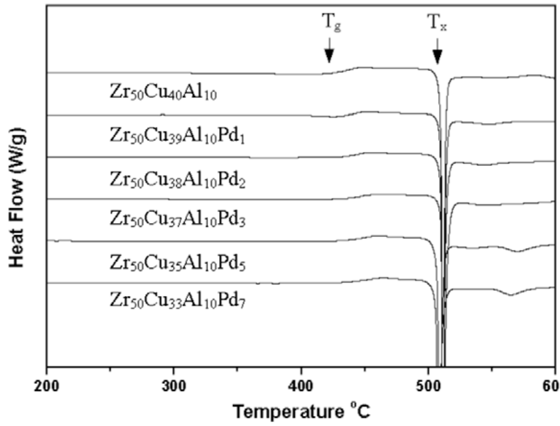

Fig. 2. DSC thermograms of the $Zr_{50}Cu_{40-x}Al_{10}Pd_x$ (x: 0–7 at.%) glassy alloys. The heating rate was 20 K/min. Locations of the characteristic temperatures (T_g and T_x) are indicated by arrows.

Table 1
Glass-transition temperature (T_g), crystallization temperature (T_x), and heat of crystallization (ΔH_x), as well as a supercooled liquid region ($\Delta T_x = T_x - T_g$) for the $Zr_{50}Cu_{40-x}Al_{10}Pd_x$ (x: 0–7 at.%) alloys, as obtained from DSC at a heating rate of 20 K/min.

Materials	T_g (°C)	T_x (°C)	ΔH_x (J/g)	ΔT_x (°C)
$Zr_{50}Cu_{40}Al_{10}$	417	507	43	90
$Zr_{50}Cu_{39}Al_{10}Pd_1$	428	507	43	79
$Zr_{50}Cu_{38}Al_{10}Pd_2$	431	507	39	76
$Zr_{50}Cu_{37}Al_{10}Pd_3$	431	507	40	76
$Zr_{50}Cu_{35}Al_{10}Pd_5$	434	503	34	69
$Zr_{50}Cu_{33}Al_{10}Pd_7$	435	504	33	69