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Relaxation of Ni-free $Ti_{40}Zr_{10}Cu_{36}Pd_{14}$ bulk metallic glass under mechanical stress

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ABSTRACT

Dynamic mechanical behavior of $Ti_{40}Zr_{10}Cu_{36}Pd_{14}$ bulk metallic glass was investigated by mechanical spectroscopy. The mechanical spectra of $Ti_{40}Zr_{10}Cu_{36}Pd_{14}$ bulk metallic glass show the main α relaxation while the slow β relaxation is not evident. The isothermal relaxation process of the loss factor tanδ can be well described by the Kohlrausch-Williams-Watts (KWW) stretched exponential relaxation function. In the current study, the stretched exponential relaxation parameter β_{age} remains constant below the glass transition temperature T_g, while the value increases when the temperature approaches T_g. In addition, atomic mobility of the $Ti_{40}Zr_{10}Cu_{36}Pd_{14}$ bulk metallic glass decreases during the physical aging.

1. Introduction

Compared with other metallic implant materials, titanium alloys have received much attention for medical applications (i.e. orthopedic and osteosynthesis) due to specific mechanical, physical properties and excellent biocompatibility [1]. In general, the conventional titanium alloys show high fracture strength and poor corrosion properties [2]. However, the mismatch of the Young's modulus between the bone of human body and the titanium bio-implant (i.e. Ti–6Al–4V titanium alloy) limits its application as a biomaterial [1,2].

In the past decades, metallic glasses have received wide attention due to their unique mechanical, physical and chemical properties [3–7]. Unlike their crystalline counterparts, Ti-based metallic glass exhibits high specific strength, lower Young's moduli, excellent corrosion resistance, wear resistance as well as low density [8–11]. Therefore, it is a potential candidate for biomaterials [2]. Some Ti-based metallic glasses show excellent plasticity at ambient temperature [12,13]. It should be noted that some Ti-based metallic glasses include the toxic or allergic elements, i.e. Be, Ni and Co [7]. These elements are harmful to the human body, which limits the applications as biomaterials. Recently, it has been reported that $Ti_{40}Zr_{10}Cu_{36}Pd_{14}$ metallic glass without toxic elements shows an excellent glass forming ability, which could be an ideal medical material [14,15].

Dynamic mechanical analysis (DMA) is an effective technique to probe the atomic or molecular mobility in glassy materials and metallic glass matrix composites [16,17]. It is well documented that the main α relaxation and secondary β relaxation processes are strongly associate with the glass transition phenomenon, diffusion, crystallization behavior and mechanical properties in metallic glasses [18]. For the glassy solids (amorphous polymers, oxide glasses, colloidal gels as well as other non-crystalline solids), the main α relaxation process can be described by the VFT (Vogel-Fulcher-Tamman)-type equation while the β relaxation (i.e. fast β and slow β relaxation) obeys the Arrhenius function [19]. In order to understand better the physical and mechanical properties of $Ti_{40}Zr_{10}Cu_{36}Pd_{14}$ metallic glass, it is essential to investigate its mechanical relaxation behaviors.

2. Experimental procedure

The $Ti_{40}Zr_{10}Cu_{36}Pd_{14}$ metallic glass (at.%) was chosen as representative alloy in the current study due to its high glass forming ability [20], good corrosion resistance [21] and excellent biocompatibility [21]. The $Ti_{40}Zr_{10}Cu_{36}Pd_{14}$ metallic glass was prepared by copper mold casting method in a Ti-gettered high purified argon atmosphere. The ingots were re-melted at least 5 times before suction process to guarantee the chemical homogeneity of the master alloy.

Glass feature of the $Ti_{40}Zr_{10}Cu_{36}Pd_{14}$ metallic glass at ambient temperature was characterized by X-ray diffraction (XRD) with Cu Kα radiation device (Philips PW3830). There are many methods to study the dynamic mechanical behaviours in metallic materials, i.e., quasi-

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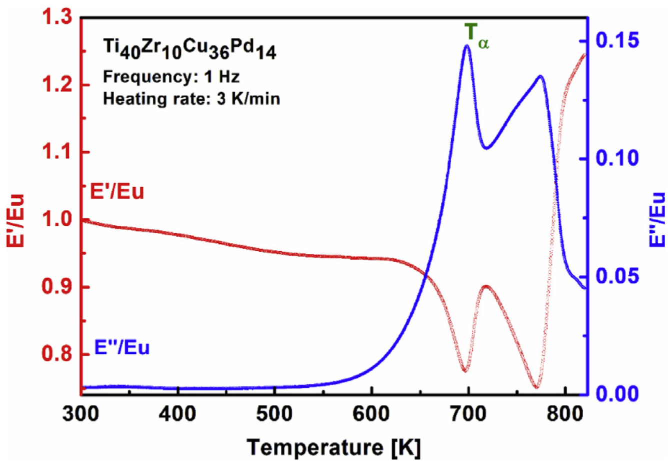

Fig. 1. Normalized storage modulus E'/Eu and loss modulus E''/Eu of $Ti_{40}Zr_{10}Cu_{36}Pd_{14}$ metallic glass as a function of temperature (Heating rate is 3 K/min and driving frequency is 1 Hz). Eu is the non-relaxed modulus corresponds to the value of storage modulus E' at room temperature. T_α is the peak temperature of the primary α relaxation.

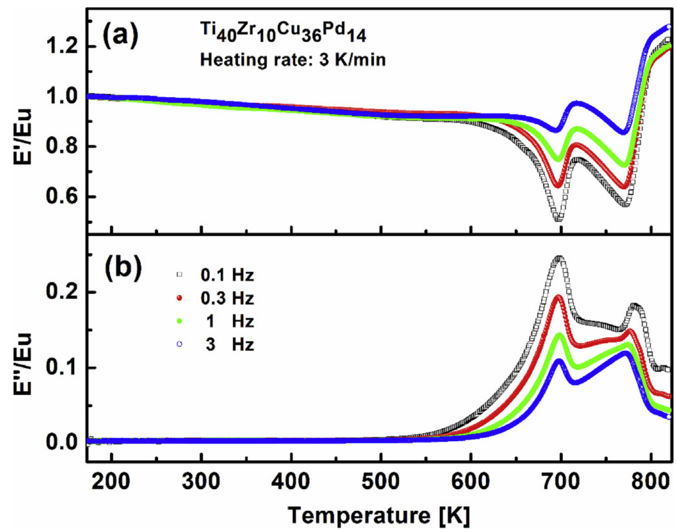

Fig. 2. Evolution of (a) the normalized storage modulus E'/Eu and (b) loss modulus E''/Eu of $Ti_{40}Zr_{10}Cu_{36}Pd_{14}$ metallic glass with temperature at different driving frequencies (Heating rate is 3 K/min). The testing frequency ranges from 0.1 to 3 Hz.

static tests, subresonant experiments, resonant tests and wave-propagation (pulse-echo) methods. Herein, dynamic mechanical relaxation behaviors of the $Ti_{40}Zr_{10}Cu_{36}Pd_{14}$ metallic glasses was studied by using dynamic mechanical analyzer (DMA, TA instruments Q800) at a nitrogen atmosphere. In the framework of the DMA testing, the complex modulus $E^* = E' + iE''$, here E' is the storage modulus and E'' is the loss modulus. The value of E' is related to the storage energy during the elastic deformation, while E'' corresponds to the dissipation of energy during the viscous deformation and the anelastic deformation. Loss factor (also named internal friction) tanδ is defined as E''/E'. In the current study, $Ti_{40}Zr_{10}Cu_{36}Pd_{14}$ metallic glass samples were cut by using electric discharge machining with dimensions of 30 mm (length) × 3 mm (width) × 1 mm (thickness) for the DMA testing.

3. Results and discussion

The evolution of normalized storage modulus, E'/Eu and loss modulus, E''/Eu of the $Ti_{40}Zr_{10}Cu_{36}Pd_{4}$ metallic glass from ambient temperature to 823 K obtained from the DMA measurements are shown in Fig. 1 (the heating rate is 3 K/min and driving frequency is 1 Hz). Similar to other metallic glasses [3,22], the dynamic mechanical relaxation of the $Ti_{40}Zr_{10}Cu_{36}Pd_{4}$ metallic glass shows three typical temperature regimes with respect to the storage modulus and loss modulus:

(i) From room temperature to 550 K, the storage modulus is high and loss modulus is relatively low (i.e., the normalized loss modulus E''/Eu keeps a constant value close to zero). Therefore, it is reasonable to assume that the deformation in this temperature domain is mostly elastic. In parallel, the prominent slow β relaxation cannot be detected in the $Ti_{40}Zr_{10}Cu_{36}Pd_{14}$ metallic glass because the fast β′ relaxation process is always observed at low temperature (i.e. cryogenic temperatures) [19,23].

(ii) In the middle temperature region: From 550 K to 725 K, the storage modulus E′ decreases dramatically while the loss modulus E'' reaches the maximum value (around 700 K). This peak temperature corresponds to the primary α relaxation. It is well accepted that the α relaxation in amorphous materials is connected to the dynamic glass transition phenomenon.

(iii) For temperatures above 725 K, the behavior of the storage modulus E′ and loss modulus E'' with temperature is mainly ascribed to the crystallization kinetics.

The formation of Ti_3Cu_4 phase after the first crystallization process (i.e., when the sample heated to 723 K) should be emphasized. When the $Ti_{40}Zr_{10}Cu_{36}Pd_{14}$ metallic glass was heated to 823 K, the tetragonal Ti_3Cu_4, orthorhombic Ti_2Pd_3 and tetragonal Ti_2Pd have been introduced in the glass matrix [24].

To determine the dynamic mechanical relaxation mechanism of the $Ti_{40}Zr_{10}Cu_{36}Pd_{14}$ metallic glass, evolution of the storage modulus E' and the loss modulus E'' with temperature was measured at various driving frequencies (0.1-0.3-1-3 Hz), as shown in Fig. 2. It can be seen that the storage modulus E' and loss modulus E'' are strongly dependent on the driving frequency. By increasing the frequency, the amplitude of E' of the first crystallization process (formation of Ti_3Cu_4 phase) and the second crystallization process (formation of the tetragonal Ti_3Cu_4, orthorhombic Ti_2Pd_3 and tetragonal Ti_2Pd) decreases, while the intensity of E'' increases. However, in the loss modulus of $Ti_{40}Zr_{10}Cu_{36}Pd_{14}$ metallic glass, it is observed that the peak position of the first crystallization process remains nearly constant. In particular, the peak value of the second crystallization decreases by increasing the frequency.

Fig. 3 shows the normalized storage modulus E'/Eu and loss modulus E''/Eu of $Ti_{40}Zr_{10}Cu_{36}Pd_{14}$ metallic glass as a function of temperature at different heating rates (1-3-5-10 K/min). It should be noted that the α relaxation shifts to higher temperature with increasing of the heating rate. The Flynn-Wall-Ozawa (FWO) equation is adopted to obtain the activation energy of glassy materials in the isochronal mode [25]. The apparent activation energy of the amorphous alloys can be determined by:

$$\ln(R_h) = -1.052\frac{E_a}{RT_p} + C \tag{1}$$

where R_h is the heating rate, E_a represents the activation energy of the crystallization process, R is the gas constant, T_p is the peak value of the loss modulus or loss factor, the parameter C is a material constant. As shown in Fig. 4, the experimental results are in good accordance with the predication of the FWO equation. The activation energies of the first and second crystallization processes in $Ti_{40}Zr_{10}Cu_{36}Pd_{14}$ metallic glass are 272.3 kJ/mol (~2.82 eV) and 297.6 kJ/mol (~3.08 eV), respectively. Physically, the activation energy of the primary α relaxation is around several eV [17,26]. It is well accepted that the α relaxation in glassy materials corresponds to the cooperative motions of atoms or molecules during the thermal activated process.

Fig. 5 shows the evolution of storage modulus E' with temperature at a heating rate 3 K/min and frequency of 1 Hz. It is noted that the