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Experimental analysis to the structural relaxation of $Ti_{48}Zr_{20}V_{12}Cu_5Be_{15}$ metallic glass matrix composite

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ABSTRACT

The mechanical relaxation characteristics of *in-situ* $Ti_{48}Zr_{20}V_{12}Cu_5Be_{15}$ metallic glass matrix composite with dendrites reinforced are investigated by using mechanical spectroscopy. An abnormal internal friction behavior below the glass transition temperature is detected. Considering the irreversible feature and based on the transmission electron microscopy analysis, the abnormal internal friction behavior is mainly induced by the precipitation of nanocrystals in the dendritic phase. In order to understand better the dynamic mechanical properties of the $Ti_{48}Zr_{20}V_{12}Cu_5Be_{15}$ metallic glass matrix composite, the kinetic characteristics of glass transition are analyzed in the framework of quasi-point defects theory. In addition, an isothermal annealing conducted at lower than the glass transition temperature induces a significant change on both modulus and loss factor, the kinetics of relaxation under annealing can be well described by the stretched exponential relaxation equation.

1. Introduction

Amorphous materials are ubiquitous in nature, such as oxide glasses, polymers, and organic liquids [1,2]. In the past decades, bulk metallic glasses (BMGs) emerged as a new class of the amorphous materials, which have many specific mechanical and physical properties due to their unique disordered structure [3,4]. Metallic glasses show high yield strength and hardness, large elastic limit, superior wear resistance and good formability in the supercooled region [2–7]. However, the lacking of plasticity at room temperature due to the rapid propagation of shear band seriously hinders their application as engineering structural materials. To improve the plasticity of metallic glasses, one effective strategy is to introduce the secondary crystalline phases as the reinforcing medium. The secondary phase can be *ex-situ* (like Ta, WC particles or fiber) or *in-situ* (like dendrite reinforced or B2 phase) introduced into the glassy matrix as the reinforcement [8–15].

Metallic glasses are known as intermediate materials between strong glasses (such as oxide glasses) and fragile glasses (such as polymers), their relatively simple atomic packing structure benefits to the experimental research and theoretical analysis [2,16,17]. Metals have a strong tendency to crystallization, which suggests that high cooling rate is required to avoid the crystallization and freezing in a glassy structure. Since amorphous materials are in thermodynamically metastable state, the relaxation behaviors are one of the most fundamental and intriguing topics in this research field, which refers to the process of atoms gradually approach towards their equilibrate state [18,19]. In general, there are two relaxation modes in amorphous materials: the main relaxation, also called α relaxation, which is responsible for the large-scale rearrangements of atoms or molecules. The other relaxation is named Johari-Goldstein relaxation, also called β relaxation, which is a fast process corresponding to localized events of atomic or molecular movements [1,20–22]. The relaxation behaviors in amorphous materials can be studied by dielectric spectroscopy [23], mechanical spectroscopy [24] and other experimental methods [17]. Among these methods, dynamic mechanical analysis (DMA) is commonly adopted due to its broad applicability and high sensitivity to detect rearrangements of atoms in amorphous

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materials [1,17,25].

Many efforts have been devoted to clarify the origin of the mechanical relaxation of metallic glasses, but the nature of relaxation and the mechanical mechanism of metallic glasses are still elusive. Profiting from the lower density and excellent mechanical properties, the Ti-based metallic glass matrix composite (MGMC) reported by Johnson and Hofmann et al. [9,26] with highly improved plasticity at room temperature is a promising candidate of the next-generation engineering materials. In the current work, an in-situ dendrites reinforced Ti-based MGMC is chosen with the composition of $Ti_{48}Zr_{20}V_{12}Cu_5Be_{15}$ from Ref. [9] as the target composition, which shows good combination of high strength and ductility. The structural relaxation properties of the Ti-based MGMC are investigated by using DMA, showing different characteristics from that of typical monolithic BMGs. The experimental results are analyzed to understand the structural relaxation behaviors of the Ti-based MGMC.

2. Experimental methods

Ingots of $Ti_{48}Zr_{20}V_{12}Cu_5Be_{15}$ were prepared by arc melting pure metals (the purities of mixing raw elements Ti, Zr, V and Cu are above 99.9%, whereas the purity of Be is higher than 99.5%) under a Ti-gettered argon atmosphere. Each ingot was remelted six times to ensure the compositional homogeneity. The cylinders with dimension of 3 mm × 3 mm × 85 mm (length) and 3 mm (diameter) × 85 mm (length) were fabricated by water-cooled copper mold suction casting, which were used to prepare the samples for the compression and dynamic mechanical experiments. The natural structure of as-cast rods was detected by X-ray diffraction (XRD, X'Pert PRO) with monochromatic Cu-Kα radiation and differential scanning calorimetry (DSC, PerkinElmer DSC 8500) at a fixed heating rate of 5 K/min. The microstructure of the MGMC was observed by scanning electron microscope (SEM, Hitachi TM3030) and high resolution transmission electron microscopy (HRTEM, Tecnai F30 and FEI Titan G2 60-300), the transmission electron microscopy (TEM) samples were ground to the thickness of approximately 50 μm, then were made transparent to electrons by firing ions using ion milling machine. The samples with a diameter of 3 mm and 5 mm in height were prepared for the compression tests with both ends polished, the compression tests were carried out in an Instron 5969 with a constant nominal strain rate of 1×10^{-3} s^{-1}. Dynamic mechanical analysis (DMA, TA DMA-Q800) experiments were performed in a single cantilever mode, the samples with a dimension of 30 mm (length) × 2 mm (width) × 1 mm (thickness) were prepared. In the DMA experiments, the storage modulus E' and loss modulus E'' as a function of temperature were recorded.

3. Results and discussion

3.1. Structural and thermal properties of the as-cast $Ti_{48}Zr_{20}V_{12}Cu_5Be_{15}$ MGMC

Fig. 1 (a) shows the XRD pattern of $Ti_{48}Zr_{20}V_{12}Cu_5Be_{15}$ MGMC, the sharp peaks overlapping at the broad diffraction peak are confirmed as the β-Ti phase, which indicates that the $Ti_{48}Zr_{20}V_{12}Cu_5Be_{15}$ MGMC is composed of amorphous phase and the β-Ti crystalline phase. Thermal analysis was carried out by differential scanning calorimetry (DSC). The glass transition temperature T_g and the onset temperature of crystallization T_x are measured to be 611 K and 656 K, respectively. It is worth noting that a weak exothermic peak appears around 500 K on the DSC curve.

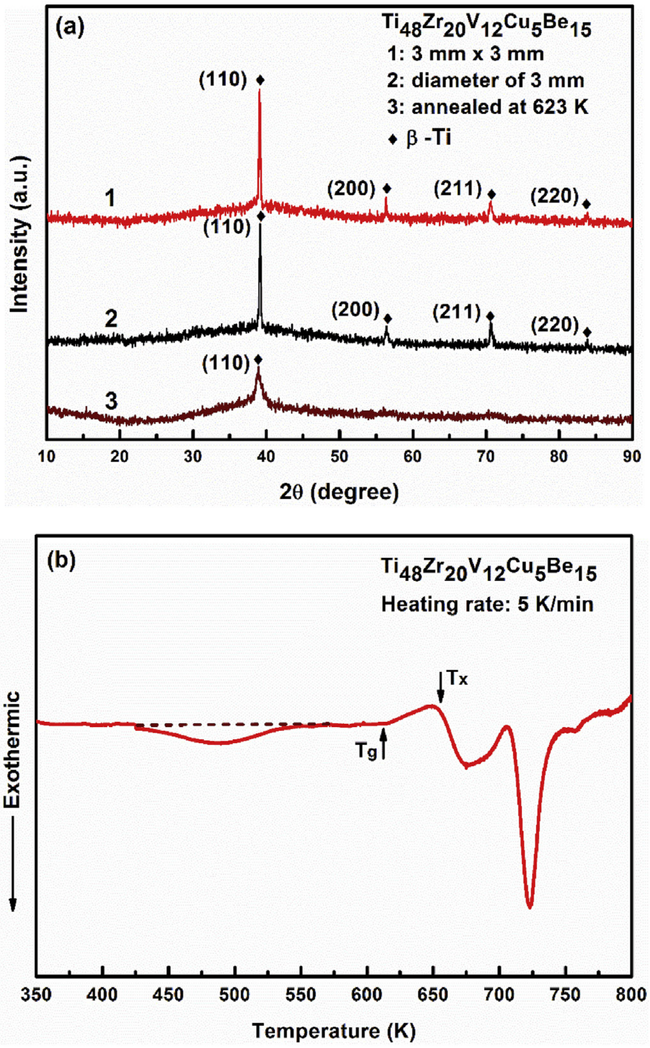

Fig. 1. (a) XRD patterns of as-cast samples and the DMA sample annealed at 623 K for 7 h with monochromatic Cu-Kα radiation. (b) DSC curve of as-cast $Ti_{48}Zr_{20}V_{12}Cu_5Be_{15}$ MGMC with a heating rate of 5 K/min.

The microstructure image of as-cast $Ti_{48}Zr_{20}V_{12}Cu_5Be_{15}$ MGMC is shown in Fig. 2 (a), which depicts that the dendrites are distributed uniformly in the glassy matrix. The microstructure of $Ti_{48}Zr_{20}V_{12}Cu_5Be_{15}$ MGMC was investigated further by high-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED). As shown in Fig. 2 (b), the dendrites are embedded in a continuous amorphous matrix. HRTEM image of the interface between the dendrite and the amorphous phase in the blue dotted circle area are shown in Fig. 2 (c). The inset figure at the lower right corner of Fig. 2 (c) was captured from the area 2 marked with blue dotted circle in Fig. 2 (b), illustrating a typical SAED pattern of the amorphous structure. Fig. 2 (d) shows the SAED pattern of the crystalline structure taken from the area 1 in Fig. 2 (b), indicating that the left side is the BCC-Ti crystalline phase with an ordered arrangement of atoms, while the right side exhibits a disordered atomic arrangement as shown in Fig. 2 (c). An evident interface between the two phases is located in the area between two blue dotted lines, which denotes that the glassy matrix and the dendrites are tightly bound together. From Fig. 2 (e) to (j), the glassy matrix is enriched in the elements of Zr and Cu, while the crystalline phase is enriched in the elements of Ti and V, which suggests that there is an elemental separation in the MGMC during cooling.