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Structural relaxation of Ti-based bulk metallic glasses

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The enthalpy relaxation behavior of $\text{Ti}_{41.5}\text{Cu}_{37.5}\text{Ni}_{7.5}\text{Zr}_{2.5}\text{Hf}_5\text{Sn}_5\text{Si}_1$ bulk metallic glass (BMG) was investigated in this study. It is found that relaxation behavior follows the general characteristics for amorphous materials: the annealing time dependence of recovery enthalpy follows a stretched exponential function with the mean relaxation time obeying an Arrhenius law. In addition, the equilibrium recovery enthalpy ΔH_T^{eq} , mean relaxation time τ and stretching exponent β are annealing temperature dependent, and the higher the annealing temperature, the lower the values of ΔH_T^{eq} , τ and higher of β . The activation energy for enthalpy relaxation is calculated to be 3.06 eV, suggesting that the governing mechanism for the enthalpy relaxation process of this alloy is the rearrangement involving the collective hopping mechanism for the small and medium size atoms. Two parameters, β_g and τ_g , representing the stretching exponent and the mean structural relaxation time at the calorimetric glass transition temperature, respectively, have been introduced to construct the correlation with glass forming ability and thermal stability. The high value of β_g for $\text{Ti}_{41.5}\text{Cu}_{37.5}\text{Ni}_{7.5}\text{Zr}_{2.5}\text{Hf}_5\text{Sn}_5\text{Si}_1$ BMG that is higher than 0.84 however lower than that of typical BMGs which approaches unity reveals its relatively good, however worse glass forming ability compared with typical BMGs; in addition, its high value of τ_g indicates its comparable good thermal stability with typical BMGs.

Keywords: Bulk metallic glass; Titanium alloy; Structural relaxation; Glass forming ability; Thermal stability

1. Introduction

Since a glass can be described as an undercooled melt, such glassy structure is thermodynamically metastable compared with the ideal glassy state and tends to undergo structural rearrangement to reach the ideal glassy state (structural relaxation) [1,2] or transform to an equilibrium crystalline structure through a series of continuous transformations (crystallization) once the external energies are supplied either thermally by heat treatments or mechanically by application of external stresses, leading to continuous changes in physical, chemical and mechanical properties of amorphous materials. Ti-based bulk metallic glasses (BMGs) have attracted more attention as potential structural materials due to their excellent properties (low density, high strength and high specific strength) [3-9]. $\text{Ti}_{41.5}\text{Cu}_{37.5}\text{Ni}_{7.5}\text{Zr}_{2.5}\text{Hf}_5\text{Sn}_5\text{Si}_1$ BMG, as a typical Be-free Ti-based BMG, has been found to exhibit good glass forming ability (GFA), thermal stability as well as room-temperature mechanical properties [10]. In addition, our recent investigations have shown that its mechanical property changes were caused by structural transformations [11], and the crystallization behavior of this alloy has been presented in a previous report [12]. The aim of this study is thus to clarify the structural relaxation behavior of $\text{Ti}_{41.5}\text{Cu}_{37.5}\text{Ni}_{7.5}\text{Zr}_{2.5}\text{Hf}_5\text{Sn}_5\text{Si}_1$ BMG for further understanding the GFA and thermal stability of this alloy in addition to the mechanical response induced by structural relaxation.

2. Experiment

The ingots of master alloy with nominal composition of $\text{Ti}_{41.5}\text{Cu}_{37.5}\text{Ni}_{7.5}\text{Zr}_{2.5}\text{Hf}_5\text{Sn}_5\text{Si}_1$ were prepared according to the process described in ref. [11]. Cylindrical samples (2 mm in diameter, 40 mm in length) were prepared for these experiments. The glass transition temperature (T_g) and the onset crystallization temperature (T_{x1}) were determined to be 432 and 485°C, respectively, by differential scanning calorimetry (DSC).

Structural relaxation was investigated through measuring the relaxation of the frozen-in enthalpy towards the equilibrium state as a function of time at a certain temperature by using DSC. The enthalpy reduction during an isothermal relaxation below the calorimetric glass transition is recovered as an “overshoot” in the glass transition region during a subsequent continuous heating DSC run. The detailed experimental program can be summarized as followed: to erase the thermal history of metallic glasses, each sample is heated from room temperature to the desired temperature (about 20 °C above T_g) at a heating rate of 20 K/min, then immediately cooled down to room temperature at a cooling rate of 50 K/min, and then reheated to the isothermal annealing temperature T (387, 397, 412 and 422 °C) at a heating rate of 30 K/min to be annealed for various time t (5 min-10 h); after each isothermal annealing, the sample was heated up to high temperature to complete the crystallization (700 °C) at a heating rate of 20 K/min for the following calculation of recovery enthalpy; finally, this heating process was

repeated for the baseline correction.

3. Results

The enthalpy relaxation of $\text{Ti}_{41.5}\text{Cu}_{37.5}\text{Ni}_{7.5}\text{Zr}_{2.5}\text{Hf}_5\text{Sn}_5\text{Si}_1$ BMG was investigated according to the process described above. Fig. 1 shows the typical continuous heating DSC curves of the $\text{Ti}_{41.5}\text{Cu}_{37.5}\text{Ni}_{7.5}\text{Zr}_{2.5}\text{Hf}_5\text{Sn}_5\text{Si}_1$ sample isothermally annealed (relaxed) at 387 °C as well as the as-cast (unrelaxed) sample. The enthalpy of a glass at a certain temperature T (below T_g) may deviate from its equilibrium value H_T^{eq} , since some additional enthalpy can be trapped when the glass forms. Long-time annealing of the glass at that temperature will result in the loss of this additional enthalpy and the glass gradually relaxes into the equilibrium supercooled liquid state. The enthalpy of the glass that is lost during the isothermal annealing can be recovered by a subsequent DSC scan of the annealed sample ($\Delta H_T(t)$), resulting in an overshoot in the DSC curve with respect to the unrelaxed sample, as it can be observed from Fig. 1 where an overshoot is located at the vicinity of glass transition region (marked with dashed rectangle) and the area of the overshoot increases with annealing time t . The reduction of the enthalpy during relaxation can be understood as the result of local rearrangements of the atoms causing the reduction of the free volume that has been frozen-in during cooling throughout the glass transition.

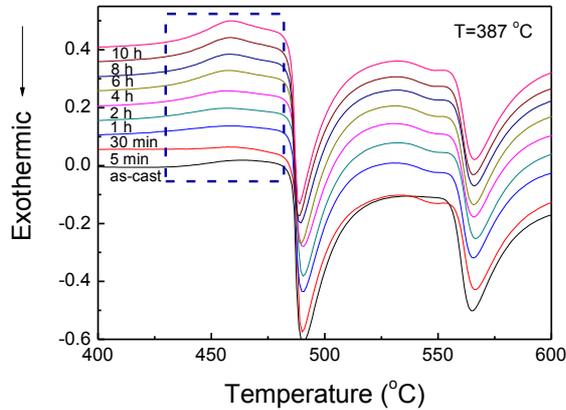


Figure 1. Typical enthalpy recovery DSC curves of the $\text{Ti}_{41.5}\text{Cu}_{37.5}\text{Ni}_{7.5}\text{Zr}_{2.5}\text{Hf}_5\text{Sn}_5\text{Si}_1$ samples after isothermal relaxation at 387 °C for different times as well as the DSC curve for an unrelaxed sample.

The measured recovery enthalpies $\Delta H_T(t)$ as a function of annealing time t at various annealing temperatures T of 387, 397, 412 and 422 °C for $\text{Ti}_{41.5}\text{Cu}_{37.5}\text{Ni}_{7.5}\text{Zr}_{2.5}\text{Hf}_5\text{Sn}_5\text{Si}_1$ BMG are shown in Fig. 2. It is clearly seen that the relaxation process is time and temperature dependent. The value of $\Delta H_T(t)$ increases rapidly with increase in t at the

initial stage of relaxation, then changes to increase gradually, finally tends to saturate, indicating that the amorphous materials relax towards lower enthalpic state with increase in annealing time t and eventually approach to the equilibrium state after a long-time annealing. Further investigation reveals that the $\Delta H_T(t)$ - t relation does not follow a simple exponential relaxation function, which could be due to the microstructure heterogeneities of the sample, and suggests that the enthalpy relaxation of the $\text{Ti}_{41.5}\text{Cu}_{37.5}\text{Ni}_{7.5}\text{Zr}_{2.5}\text{Hf}_5\text{Sn}_5\text{Si}_1$ liquid does not involve a single Debye relaxation event, in accordance with the previously reported amorphous materials.

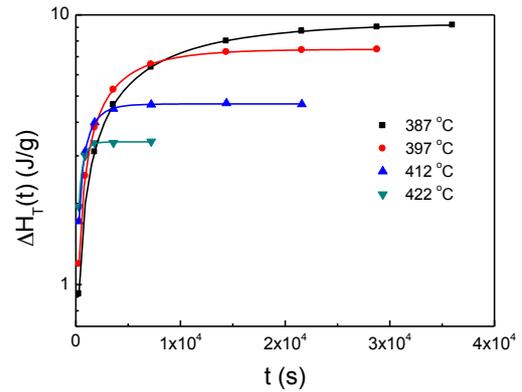


Figure 2. Experimental relaxation recovery enthalpy $\Delta H_T(t)$ as a function of annealing time t at various temperatures of 387-422 °C for $\text{Ti}_{41.5}\text{Cu}_{37.5}\text{Ni}_{7.5}\text{Zr}_{2.5}\text{Hf}_5\text{Sn}_5\text{Si}_1$ BMG, and fitted with stretched exponential function.

The time dependence of $\Delta H_T(t)$ at a given temperature of amorphous materials can be generally fitted by a stretched exponential relaxation function [13-15]:

$$\Delta H_T(t) = \Delta H_T^{eq} \left\{ 1 - \exp\left[-\left(\frac{t}{\tau}\right)^\beta\right] \right\} \quad (1)$$

where τ is the mean structural relaxation time, ΔH_T^{eq} is the equilibrium value of $\Delta H_T(t)$ for $t \rightarrow \infty$ at the annealing temperature T , β is the stretching exponent whose value is $0 < \beta \leq 1$, reflecting the width of relaxation time distribution spectrum originating from the inhomogeneity of the supercooled liquid. The value of $\beta=1$ corresponds to a single relaxation time with exponential behavior. The smaller the value of β , the more the distribution of atomic motions deviates from a single exponential behavior. So, if the relaxation time distribution becomes broader, the value of β will be reduced, and the enthalpy recovery curve will be spread out over a wider temperature range. Obviously, the experimental $\Delta H_T(t)$ - t relation for $\text{Ti}_{41.5}\text{Cu}_{37.5}\text{Ni}_{7.5}\text{Zr}_{2.5}\text{Hf}_5\text{Sn}_5\text{Si}_1$ BMG can be well fitted with stretched exponential relaxation function. The obtained ΔH_T^{eq} , τ and β , at various annealing temperatures are summarized in Table 1.

Table 1. The values of ΔH_T^{eq} , τ and β at various temperatures for $\text{Ti}_{41.5}\text{Cu}_{37.5}\text{Ni}_{7.5}\text{Zr}_{2.5}\text{Hf}_5\text{Sn}_5\text{Si}_1$ BMG determined from the $\Delta H_T(t)$ vs. t curves fitted with the stretched exponential relaxation function.

T (°C)	ΔH_T^{eq} (J/g)	τ (s)	β
387	9.4	5988	0.7537
397	7.4	2753	0.7870
412	4.7	800	0.7953
422	3.4	361	0.8762

It is found that the values of ΔH_T^{eq} , τ and β are annealing temperature dependent, and the higher the annealing temperature, the lower the values of ΔH_T^{eq} , τ and higher of β , indicating that the enthalpy recovery is determined by the annealing temperatures. The increase in equilibrium recovery enthalpy ΔH_T^{eq} as well as the prolongation of mean relaxation time τ with decrease in annealing temperature is attributed to the slowdown of the relaxation kinetics. The annealing temperature dependence of ΔH_T^{eq} , τ and β is mainly ascribed to the degree of the amorphous phase deviating from its equilibrium state at each annealing temperature. It should be pointed out that for $\text{Ti}_{41.5}\text{Cu}_{37.5}\text{Ni}_{7.5}\text{Zr}_{2.5}\text{Hf}_5\text{Sn}_5\text{Si}_1$ BMG, the stretching exponent β is not constant but slightly increases with annealing temperature. Such annealing temperature dependence of stretching exponent β has been found in some BMGs, for example, $\text{Pd}_{43}\text{Cu}_{27}\text{Ni}_{10}\text{P}_{20}$ [15] $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ [16], and $\text{Zr}_{58.5}\text{Cu}_{15.6}\text{Ni}_{12.8}\text{Al}_{10.3}\text{Nb}_{2.8}$ [17] BMGs, implying a complex structural relaxation behavior of BMGs.

It is also found that the experimental annealing temperature dependence of the mean relaxation time τ for $\text{Ti}_{41.5}\text{Cu}_{37.5}\text{Ni}_{7.5}\text{Zr}_{2.5}\text{Hf}_5\text{Sn}_5\text{Si}_1$ BMG can be well fitted with an Arrhenius plot, and yields a τ_0' of 2.96×10^{-20} s and an E_a of 294 kJ/mol (3.06 eV), similar to Zr-based BMGs [17]. It should be pointed out that such Arrhenius behavior couldn't hold over a wide temperature range since that actually T_0 is not equal to 0 and approximately several tens of Kelvins below T_g for glasses. However, the T_0 item in VFT equation can be ignored when considering the temperature dependence of τ in the experimental annealing temperature range.

The mechanism of enthalpy relaxation is believed to be associated with the atomic rearrangement. It is known that the activation energies for diffusion of the small size atoms such as Ni, Cu are about 2 eV, whereas the medium size atoms such as Ti have activation energies of about 3 eV, however, the activation energies for diffusion of the large size atoms such as Zr are much larger with respect to the small and medium size atoms. In the case of $\text{Ti}_{41.5}\text{Cu}_{37.5}\text{Ni}_{7.5}\text{Zr}_{2.5}\text{Hf}_5\text{Sn}_5\text{Si}_1$ alloy whose activation

energy for enthalpy relaxation is 3.06 eV, although the rearrangements of the medium size atoms Ti as well as the small size atoms Cu, Ni and Si are sufficient to cause complete relaxation into the enthalpic state of the supercooled liquid without involving the motion of the large size atoms (Zr, Hf, Sn). The complete rearrangement of the backbone of the structure is necessary because that the medium size atoms Ti are considered to occupy the backbone position of the amorphous structure, so the rearrangement involving the collective hopping mechanism for the small and medium size atoms is the governing mechanism for the enthalpy relaxation process of $\text{Ti}_{41.5}\text{Cu}_{37.5}\text{Ni}_{7.5}\text{Zr}_{2.5}\text{Hf}_5\text{Sn}_5\text{Si}_1$ alloy, as is in agreement with the case of $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ alloy [18].

4. Discussion

The characteristic parameters, stretching exponent β and mean structural relaxation τ derived from the stretched exponential relaxation function, are essential for the analysis of enthalpy relaxation behavior, which are believed to be correlated with GFA and thermal stability of amorphous materials. However, their characteristic of temperature dependence brings about difficulties for constructing the correlations with GFA and thermal stability.

In this study, two parameters, β_g and τ_g , representing the stretching exponent and the mean structural relaxation time at the calorimetric glass transition temperature T_g , respectively, are proposed to be the indicators of enthalpy relaxation properties. The relation between β_g and GFA of bulk metallic glasses is constructed through fragility index m as a chain, since the stretching exponent β has a correlation with the fragility index m which is an indicator of the fragility of supercooled liquid and a strong liquid (with small fragility index) is generally correlated with a good GFA. It is known that most of the bulk metallic glasses show strong liquid behavior and generally have a fragility index of less than 50 [16,19,20]. In addition, a reduced $m=42/\beta$ relation can be derived from a relation between the fragility index m and stretching exponent β based on the defect diffusion model proposed by Bendler et

al. [21], and this expression has been confirmed to be suitable for describing the m - β relation for polymeric, alcoholic and metallic glasses. Accordingly, the value of stretching exponent β for the bulk metallic glasses who exhibit a good GFA empirically should be larger than 0.84. It is found that the value of β_g for $\text{Ti}_{41.5}\text{Cu}_{37.5}\text{Ni}_{7.5}\text{Zr}_{2.5}\text{Hf}_5\text{Sn}_5\text{Si}_1$ BMG is higher than 0.84, implying its relatively strong liquid behavior and accordingly relatively good GFA; however, the fact that its β_g value is lower than other typical BMGs indicates its worse GFA compared with other typical BMGs.

The relation between τ_g and thermal stability of metallic glasses was constructed on the simple idea that the long structural relaxation time corresponds to a good thermal stability. There exists a linear relationship between the logarithmic relaxation time $\ln\tau$ and the difference between the glass transition temperature and annealing temperature ΔT , namely, $\ln\tau = \ln\tau_g + A\Delta T$. The τ_g value for this alloy is 160 s, much higher than that of other Ti-based BMGs, suggesting that $\text{Ti}_{41.5}\text{Cu}_{37.5}\text{Ni}_{7.5}\text{Zr}_{2.5}\text{Hf}_5\text{Sn}_5\text{Si}_1$ BMG need relatively long relaxation time to reach the internal equilibrium state, and indicating its comparable good thermal stability with other typical BMGs.

5. Conclusions

Structural relaxation behavior of $\text{Ti}_{41.5}\text{Cu}_{37.5}\text{Ni}_{7.5}\text{Zr}_{2.5}\text{Hf}_5\text{Sn}_5\text{Si}_1$ bulk metallic glass was investigated through relaxation enthalpy recovery measurements; the main results are the followings.

- (1) Its enthalpy relaxation behavior follows the general characteristics for amorphous materials. Namely, the annealing time dependence of recovery enthalpy follows a stretched exponential function with the mean relaxation time obeying an Arrhenius law. In addition, the equilibrium recovery enthalpy ΔH_T^{eq} , mean relaxation time τ and stretching exponent β are annealing temperature dependent, and the higher the annealing temperature, the lower the values of ΔH_T^{eq} , τ and higher of β .
- (2) The activation energy for enthalpy relaxation of $\text{Ti}_{41.5}\text{Cu}_{37.5}\text{Ni}_{7.5}\text{Zr}_{2.5}\text{Hf}_5\text{Sn}_5\text{Si}_1$ BMG is calculated to be 3.06 eV, suggesting that the rearrangement involving the collective hopping mechanism for the small and medium size atoms is the governing mechanism for the enthalpy relaxation process of this alloy.
- (3) Two parameters, β_g and τ_g , representing the stretching exponent and the mean structural relaxation time at the calorimetric glass transition temperature, respectively, have been introduced to construct the correlation with GFA and thermal stability, respectively. The high value of β_g for $\text{Ti}_{41.5}\text{Cu}_{37.5}\text{Ni}_{7.5}\text{Zr}_{2.5}\text{Hf}_5\text{Sn}_5\text{Si}_1$ BMG that is higher than 0.84

is however much lower than unity revealing its relatively good glass forming ability. However, presents a worse glass forming ability compared with typical bulk metallic glasses; while its high value of τ_g indicates its comparable good thermal stability with typical bulk metallic glasses.

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