Quantification of free volume differences in a $Zr_{44}Ti_{11}Ni_{10}Cu_{10}Be_{25}$ bulk amorphous alloy

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Deformation of metallic glasses requires the existence of free volume to allow atomic movement under mechanical loading. Accordingly, quantification of the free volume state of the alloy is crucial to understand its mechanical behavior. By annealing below the glass transition temperature, the free volume of a $Zr_{44}Ti_{11}Ni_{10}Cu_{10}Be_{25}$ bulk metallic glass was varied via structural relaxation. Differential scanning calorimetry was used to quantify enthalpy differences between the relaxed and as-cast materials, which were then quantitatively related to average free volume differences. These results can be used to characterize the average free volume in this alloy for future mechanical property studies. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2766659]

Although metallic glasses do not have a traditional microstructure, structural differences can exist which affect the mechanical properties. This is because the deformation of metallic glasses requires extra "free" volume relative to a fully dense glass that is frozen into the atomic structure and allows physical space for atomic movement under mechanical loading.[1,2] Accordingly, the amount of free volume affects the mechanical properties of bulk metallic glasses.[3–8] Free volume differences may exist in nominally identical metallic glasses in the as-processed state due to differences in their processing conditions,[9] and it may be altered by annealing below the glass transition temperature T_g. Such annealing has long been known to decrease the ductility of conventional metallic glasses;[10] however, understanding the role of free volume is sometimes complicated by the formation of brittle crystalline phases or phase separation.[6,11]

Despite its importance, the role of free volume has often been ignored in the mechanical behavior literature (e.g., as in Refs. 12–18). For example, free volume has only recently been considered as a factor affecting the fatigue properties in the absence of hydrogen embrittlement.[9] Although free volume may locally vary throughout a metallic glass, the globally averaged macroscopic free volume differences between glasses may be quantitatively characterized using various methods based on differential scanning calorimetry (DSC).[9,19–23] Accordingly, the present work quantitatively examines the macroscopic, or average, free volume changes associated with structural relaxation for a $Zr_{44}Ti_{11}Ni_{10}Cu_{10}Be_{25}$ (Vitreloy 1b) alloy. These results will allow precise characterization of free volume differences caused by different processing conditions or subsequent annealing heat treatments. Such results will be vital to future studies on the mechanical behavior of this alloy.

Fully amorphous bulk metallic glass with a composition $Zr_{44}Ti_{11}Ni_{10}Cu_{10}Be_{25}$ was produced and supplied by Liquidmetal© Technologies. This alloy was chosen because it does not show phase separation in the supercooled liquid state,[24] thus helping to suppress the formation of nanocrystals. DSC experiments were performed with heating rates of 0.1, 0.25, 1, 2, and 3 K/s in argon atmosphere (Perkin Elmer Diamond DSC).

The magnitude of structural relaxation can be calorimetrically observed in the temperature interval ΔT_g, which is defined as the temperature range between the onset and the end of the endothermic glass transition event. At a constant heating rate, the average relaxation time τ can be described as

$$\tau = \Delta T_g / R, \tag{1}$$

where R is the heating rate. The onset value of T_g at each heating rate is the temperature that corresponds to each τ value in the Vogel-Fulcher-Tamman (VFT) relation,

$$\tau = \tau_0 \exp\left(\frac{D^* T_0}{T - T_0}\right), \tag{2}$$

where D^* is the fragility parameter and T_0 is the VFT temperature, defined as the temperature at which $\tau \to \infty$. τ_0 is the value of the relaxation time in the limit as $1/T \to 0$ and is very similar for all Zr-based bulk metallic glasses, $\sim 2.5 \times 10^{-13}$ s.[25] To determine D^* and T_0 for $Zr_{44}Ti_{11}Ni_{10}Cu_{10}Be_{25}$, the relaxation time was determined for each heating rate. These data were fitted with Eq. (2) as shown in Fig. 1, D^* and T_0 were found to be 31.6 and 321 K, respectively.

For longer time scale investigations, specimens were briefly equilibrated above the calorimetric glass transition and cooled at 1 K/s in order to assure the same thermal history for all samples. Isothermal relaxation was performed below T_g by annealing in the DSC. Annealing times were integral numbers of the relaxation time τ, as calculated with Eq. (2) for each annealing temperature. At 10τ, the samples were assumed to be nearly fully relaxed (i.e., in metastable equilibrium).[26] After annealing, enthalpy recovery experi-

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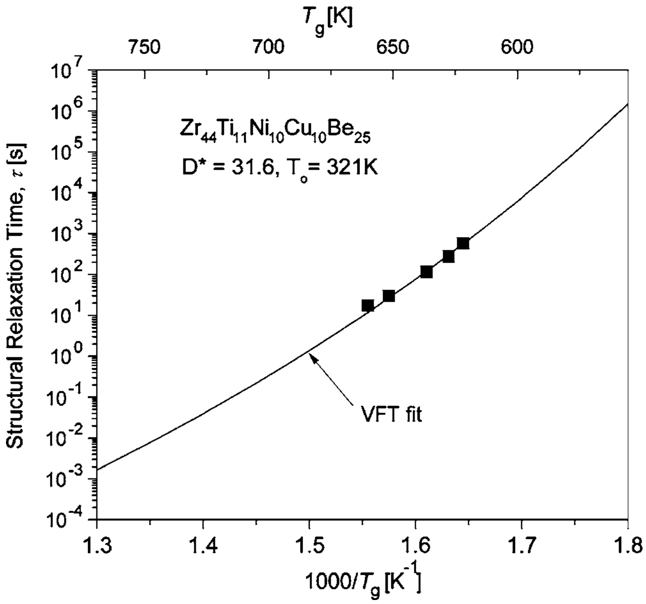

FIG. 1. Fragility plot of the relaxation time at the glass transition onset as a function of inverse temperature for $Zr_{44}Ti_{11}Ni_{10}Cu_{10}Be_{25}$.

ments were performed in the DSC, and Fig. 2(a) shows the ΔT_g interval for specimens annealed for 10τ at three temperatures. Similar experiments were done for samples isothermally relaxed at 595 K for 1τ, 2τ, 5τ, and 10τ [Fig. 2(b)]. Annealed samples show a large endothermic heat recovery in the glass transition region, whereas the "unrelaxed" reference sample does not exhibit this effect. Enthalpy recovery increases with decreasing annealing temperature and/or increasing annealing time. The amount of enthalpy ΔH that was released during the isothermal heat treatment, and recovered during reheating the sample, was determined from the area between the curve of the relaxed sample and the unrelaxed sample (Fig. 2, insets).

To ensure crystallization did not occur during annealing, a sample annealed for 10τ at 595 K was examined by high resolution transmission electron microscopy (HRTEM) using a field emission FEI Tecnai F20. Specimen preparation was done using a Streta DB237 FEI focused ion beam system. A slice of $20\times15\times1$ μm^3 was cut out using Ga+ ion beam of 30 keV. After mounting to a Cu TEM grid, the thickness of the slice was reduced to approximately 100 nm by using lower ion beam current, which was followed by cleaning with Ga+ ion beam of 10 keV to reduce damage. Figure 3 shows a representative HRTEM image and diffraction pattern, indicating that the alloy is still fully amorphous after annealing.

In Fig. 4, the measured recovered heats ΔH are plotted. The enthalpy difference between the supercooled liquid and the crystalline state was estimated from Ref. 27, which used an alloy with very similar composition, $Zr_{41.2}Ti_{13.8}Ni_{12.5}Cu_{10}Be_{22.5}$. It must be emphasized at this point that this change in enthalpy (from Ref. 27) is entirely due to the structural change of the supercooled liquid itself and not due to changes in the crystalline mixture even though the enthalpy is plotted in reference to the crystal. Systematic enthalpy recovery studies as a function of time and temperature have been performed previously for $Zr_{46.75}Ti_{8.25}Ni_{10}Cu_{7.5}Be_{27.5}$,[26] $Pd_{43}Ni_{10}Cu_{27}P_{20}$,[28] and $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$ bulk metallic glasses.[29] For these glasses, the change in the recovered enthalpy with annealing

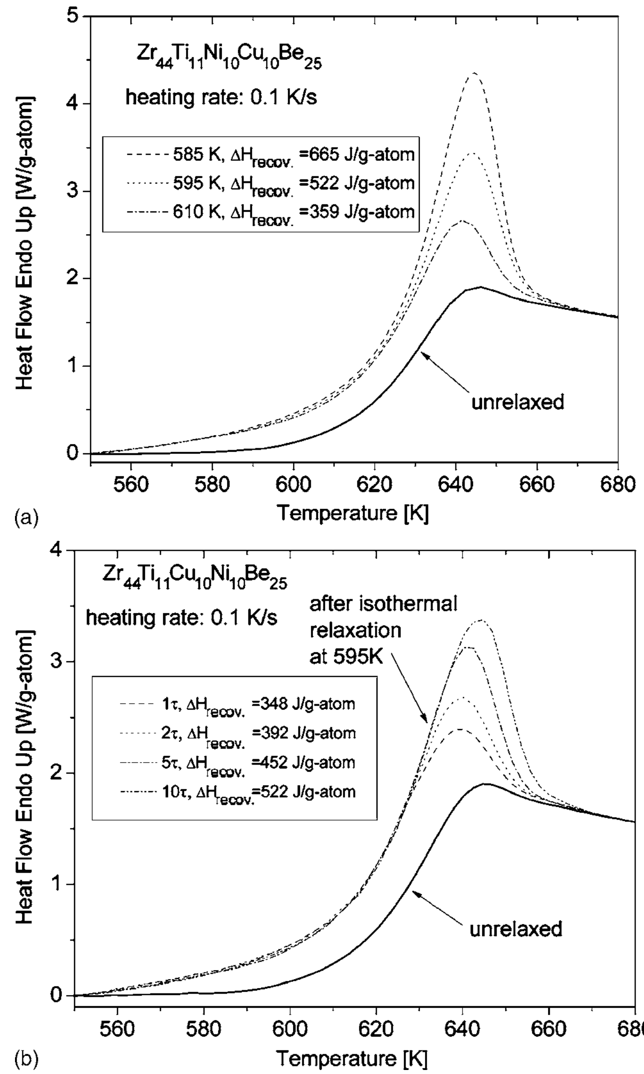

FIG. 2. Enthalpy recovery measurements in the glass transition region after (a) isothermal relaxation for 10τ at three different temperatures; (b) isothermal relaxation from the amorphous state for varying time at 595 K. In addition, the measurement for an unrelaxed "as-received" sample is shown.

temperature has been determined, which is a measure of the difference in specific heat capacity c_p between the glassy state and supercooled liquid state. For all alloys these c_p values, calculated from the enthalpy recovery, are in excellent agreement with c_p measurements of the supercooled liquid at slightly higher temperatures. This indicates that the glass completely relaxes into the supercooled liquid state (on a long time scale) and, most importantly, that the change in enthalpy is entirely due to the structural changes in the amorphous alloy rather than the crystal. We therefore assume that the variation of enthalpy ΔH is proportional to the variation of the average free volume per atom v_f/v_m,[19]

$$v_f/v_m = C\Delta H, \tag{3}$$

where C is a constant, v_f/v_m was determined according to the Cohen and Grest model,[30]

$$v_f = \frac{k}{2s_0}\left(T - T_q + \sqrt{(T-T_q)^2 + \frac{4v_a s_0}{k}T}\right), \tag{4}$$

with the following fit parameters: $bv_m s_0/k = 4933$ K with $b = 0.105$, $4v_a s_0/k = 162$ K, and $T_q = 672$ K.[31] The atomic volume v_m of Vitreloy 1™ has been reported as 1.67

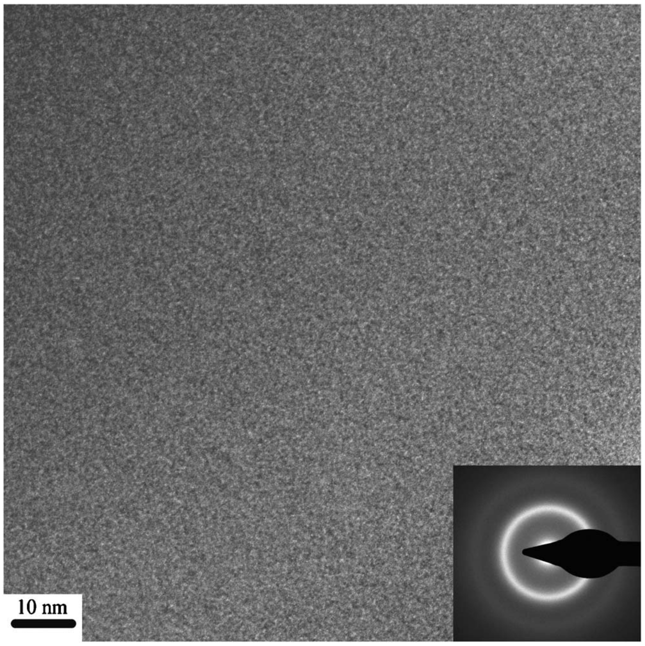

FIG. 3. Representative HRTEM image and diffraction pattern of the sample annealed for 10τ at 595 K. No evidence of nanocrystals was found and the alloy remained fully amorphous.

$\times 10^{-29}$ m^3 near the liquidus.[32] The Cohen and Grest model estimates the average free volume of the supercooled liquid even below that which can be obtained by long time relaxation experiments. Therefore, by matching the curves of the

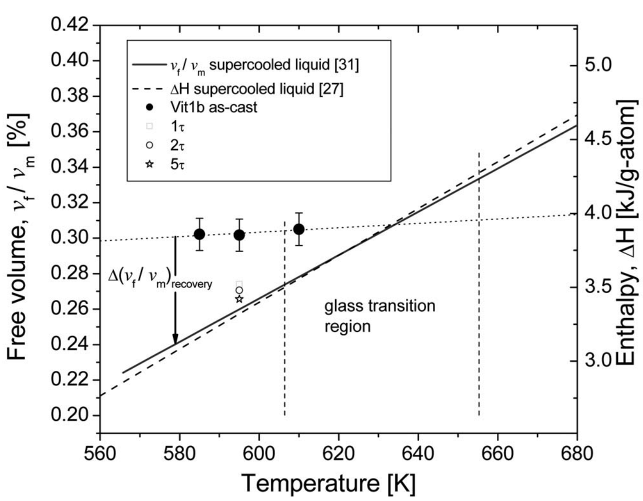

FIG. 4. Enthalpy and free volume difference vs. temperature for different free volume states of the amorphous $Zr_{44}Ti_{11}Ni_{10}Cu_{10}Be_{25}$ alloy. Here the "as-cast" data points at 585, 595, and 610 K were determined by adding the measured values of enthalpy recovery after annealing for a time 10τ [from Fig. 2(a)] to the enthalpy of the supercooled liquid from Ref. 27. At 595 K additional data were collected for intermediate annealing times of 1τ, 2τ, and 5τ [Fig. 2(b)] and those data are also shown here.

average free volume and enthalpy, both for the supercooled liquid as shown in Fig. 4, the proportionality constant C in Eq. (3) was determined as $C=0.080\pm0.001$ kJ/g atom^{-1}. In Eq. (3), ΔH is given in kJ/g atom and v_f/v_m is in %. Figure 4 allows us to map out the average free volume states of the alloy based on DSC results. These results will allow free volume characterization for future studies on the mechanical properties of bulk amorphous $Zr_{44}Ti_{11}Ni_{10}Cu_{10}Be_{25}$.

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