Calorimetric glass transition in bulk metallic glass forming Zr-Ti-Cu-Ni-Be alloys as a free-volume-related kinetic phenomenon

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The change of the calorimetric glass transition in $Zr_{46.25}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ (vit4) bulk metallic glass during differential scanning calorimetry experiments was simulated with the free-volume theory. With the kinetics of the free-volume annihilation and production, calculations carried out on this basis are in good agreement with available experiment data in vit4 alloy both on structural relaxation and the glass transition. The change of the glass transition process is dependent upon the reduced free volume remained in the specimens. The structural relaxation occurring during annealing below the calorimetric glass transition temperature for different times is relative to the annihilation of the excess free volume. The results support that the calorimetric glass transition is a mainly kinetic process.

Glass is well known to be formed from falling out of equilibrium of undercooled melt.[1] Undercooling (supercooling) of a liquid is associated with a large increase of the viscosity. When the viscosity reaches a value of the orders of $10^{13.5}$ P, structural arrest occurs on the time scale of the cooling process.[2,3] The kinetic glass transition involves a sudden change of the specific-heat capacity ΔC_p. The most difficult question is whether there exists at sufficiently slow cooling an underlying phase transition from the liquid to the ideal glassy state or whether the thermal glass transition simply reflects the crossover of intrinsic relaxation times with typical time constraint of experimental technique used.[4–8] The temperature dependence of molecular cooperativity observed by means of heat-capacity spectroscopy indicated a general behavior: A cooperativity onset in the crossover region and strong increases at low temperature.[9] In the free-volume theory, the structural change is described intuitively as a gradual reduction of the free volume.[10] The calorimetric glass transition process has been simulated based on the free-volume theory in conventional metallic glasses.[11,12]

Recently, new families of bulk metallic glass forming alloys such as La-Al-Ni,[13] Zr-Ni-Al-Cu,[14] and Zr-Ti-Cu-Ni-Be (Refs. 15 and 16) have been found. The bulk metallic glasses (BMG's) have been expected to be ideal glassy system for studying the glass transition, since they are comparable well to a hard-sphere system and higher thermal stability.[17] In this paper, we exhibit that the calculations based on the free-volume theory are in good agreement with available experimental data for $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10.0}Be_{27.5}$ BMG. It is found that the calorimetric glass transition is accompanied with the production of the free volume. Structural relaxation occurring during isothermal annealing corresponds to the annihilation of the excess free volume. The results exhibit that the calorimetric glass transition is an important characteristic of glassy state, and very sensitive to the excess free volume remained in the system.

The $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10.0}Be_{27.5}$ BMG was prepared by sucking the melt into copper module with a rate ≈ 100 K/s. The amorphous nature as well as the homogeneity of the BMG was ascertained by x-ray diffraction and differential scanning calorimetry (DSC). The sample annealing at 568 K was performed in a furnace with a vacuum of 2.0 $\times 10^{-3}$ Pa. The stability of the temperature is controlled within ± 1 K. The scope of the annealing time is from 4.32 $\times 10^4$ to 2.0×10^5 s. The DSC measurements were carried out under a purified argon atmosphere in a Perkin-Elmer DSC7.

In order to investigate the effects of the formation process on the glass transition, the annealing of the as-cast sample is performed in Perkin-Elmer DSC7. The process involved the heating up to 683 K at a heating rate of 0.667 K/s and the cooling down to room temperature at a cooling rate of 2 K/s. Figure 1 shows the DSC curves of two samples at a heating rate of 0.667 K/s. The solid line is the curve of the as-cast sample. The dash line is the curve of the annealed sample. An obvious difference between the two curves is found at the glass transition. The glass transition process in the annealed sample shifts to a lower temperature, at the same time the height of the glass transition peak is increased. The main difference of the two samples is the different formation con-
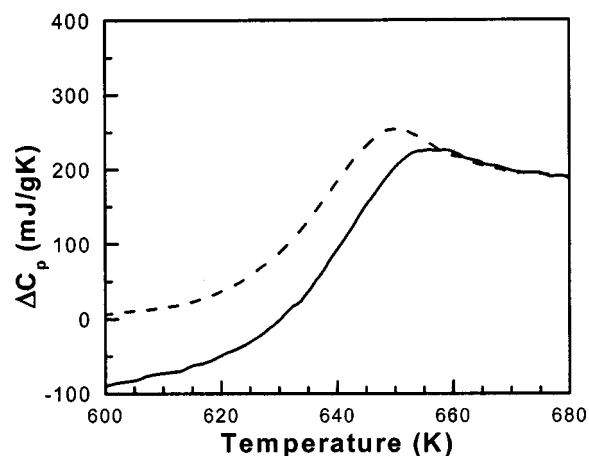

FIG. 1. The curves of the DSC at the heating rate of 40 K/min. The solid line is obtained from the as-cast sample; the dash line is obtained from the sample cooled from 683 K at the cooling rate of 80 K/min.

TABLE I. Values of the parameters to describe the free-volume changes.

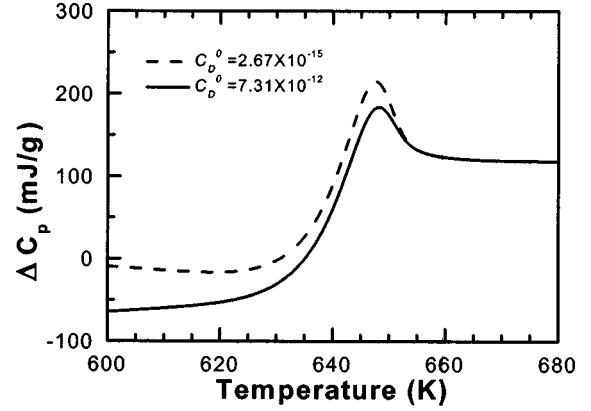| Parameter	Value	Units
k_0	2.4×10^{27}	1/s
E_f	1.75	eV
B	$(9.44 \pm 1.64) \times 10^3$	K
T_0	352	K
β	0.7	eV

FIG. 2. Calculated DSC traces, according to Eq. (1), for the initial defect concentrations indicated. The solid and dash lines are simulated for the DSC curve of the as-cast and annealing samples in Fig. 1, respectively.

dition, in which the cooling rate of the as-cast sample formation (about 100 K/s) is much larger than that of the annealed sample (2 K/s). The difference in the DSC curves is consistent with the view that the glassy phase is formed by falling out of equilibrium of supercooled liquid and the properties of the glass depends on its production.[18] With the free-volume theory, the difference of the glass transition process in the same system is relative to the difference of the excess free volume frozen in Ref. 11.

In order to quantify the glassy states as free volume, the defect concentration c_D was used.[10] According to the free-volume theory, the defect concentration is related to the reduced free volume x by $c_D = \exp(-1/x)$.[10,19] The change in the defect concentration due to structural relaxation during the annealing process is governed by the differential equation[20]

$$\frac{dc_D}{dt} = -k_r c_D (c_D - c_D^{\text{eq}}).\tag{1}$$

In this equation c_D^{eq} [$c_D^{\text{eq}} = \exp(-1/x_{\text{eq}})$] is the defect concentration in metastable equilibrium, t denotes time, and k_r is a temperature-dependent rate factor for structural relaxation. k_r has the form $k_r = k_0 \exp(-E_f/k_B T)$, where E_f is the relaxation activation energy and k_0 is a constant. The reduced free volume in *thermodynamic equilibrium* x_{eq} has the form[20,21] $x_{\text{eq}} = (T - T_0)/B$, where T_0 is the Vogel-Fulcher temperature and B is a constant. As Speapen's view, the rate of the disappearance of the defect concentration is proportional to the product of the concentration of relaxation defects. Equation (1) can be derived from the bimolecular model with the view that the relaxation defect is proportional to the concentration of defects.[20] Equation (1) is much suitable for describing the relaxation in the metallic glasses.[11] The values of B and T_0 (in Table I) for the vit4 are obtained from Ref. 22. The calculated DSC signal is obtained by assuming the observed heat flow, given here as $\Delta C_p = \beta dx/dT$.[11] The fit parameters are E_f, k_0, β, and initial defect concentration c_D^0 [$c_D^0 = \exp(-1/x_0)$, the excess free volume x_0 in glass]. For the same glass system, the parameters E_f, k_0, and β are constant. The changes of the DSC curves are only related to initial c_D^0, which corresponds to x_0. The values of the fit parameters of E_f, k_0, and β used are also listed in Table I.

The simulations of the DSC for the as-cast and annealed samples shown in Fig. 1 were performed. The simulated DSC traces are shown in Fig. 2. The solid and dash lines are the traces for the as-cast sample and annealed sample, re-

spectively. It is found that c_D^0 in the as-cast sample (7.31 $\times 10^{-12}$) is three orders of magnitude larger than that in the annealed sample (2.67×10^{-15}). Correspondingly, the excess free volume in the as-cast sample is higher than that in the annealed sample. The resultant calculations affirm that the difference between the curves in Fig. 1 is due to the difference between the excess free volumes in the two samples. Comparing with the defect concentration in Pd-based conventional metallic glass,[12] the defect concentration in vit4 is very low. The lower initial c_D^0 is consistent with the highly dense random packed microstructure, good glass forming ability, and higher thermal stability of vit4.[23] The heating flow in the DSC corresponds to the change of the free volume. Figure 3 shows the temperature dependence of the free volume x in the processes described above. When the as-cast sample is warmed up at a constant heating rate of 40 K/min, the higher excess free volume is found to anneal out and move to the equilibrium line at the temperature higher than
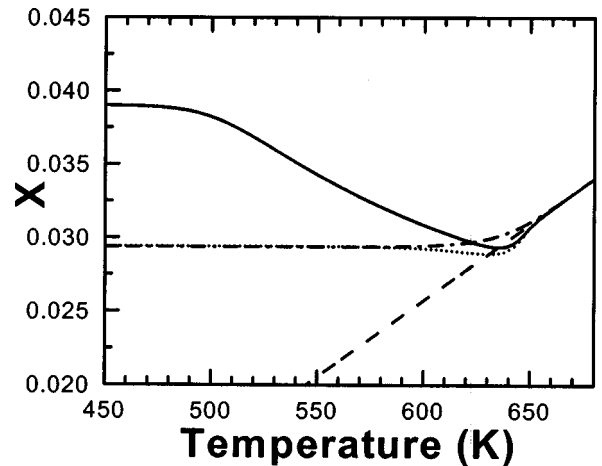

FIG. 3. The temperature dependence of the reduced free volume x. The solid line is simulated for the change of x in the as-cast sample; dash dot line for cooling process; short dot line for the reheating process; dash line for the equilibrium of x.

480 K (see the solid line in Fig. 3). The annihilation of the free volume is an exothermic process, which corresponds to the negative relative heat capacity before the glass transition in the DSC trace in Fig. 2. When x crosses the equilibrium line it becomes smaller than the equilibrium value because the kinetic is too slow to follow the increase of x_{eq} as the continuous heating. The free volume is produced in order to attain the equilibrium only at higher temperature. The production of the free volume is an endothermic process, which corresponds to the glass transition process observed in the DSC trace in Fig. 2. At higher temperature, the production of the free volume is fast enough to keep up with the increase of x_{eq}, which makes the specific capacity constant. When the sample is cooled down from 683 K at the cooling rate of 120 K/min (see the dash dot line in Fig. 3), the decreasing x follows the equilibrium x_{eq} line first. Then, the x deviates from the equilibrium x_{eq} line at about 650 K, which corresponds to the glass transition temperature at the cooling rate of 120 K/min. The deviation means the supercooled liquid falling out of equilibrium. The value of x decreases until 585 K. This implies that the state of the specimen is frozen at 585 K at the cooling rate of 120 K/min. With the simulation, the resultant x is mainly depended upon the cooling rate, rather than the initial defect concentration of the as-cast sample and the onset temperature of the cooling process. The faster the cooling rate is, the more the excess free volume is. The re-heating process is similar to the heating process of the as-cast sample (see short dot line in Fig. 3). But the annihilation process of the excess free volume shifts to higher temperature ($\sim$590 K). The above results indicate that the DSC curves are relative to the change of the free volume with the change of temperature. The calorimetric glass transition is the process accompanying the lower free volume approaching the equilibrium free volume, and is very sensitive to the excess free volume in the system. The excess free volume frozen in the system is depended mainly on the cooling rate of the glass formation and the characteristic of the glass forming liquid. Comparing with the conventional metallic glass, vit4 has very lower excess free volume.

In order to affirm the nature of the calorimetric glass transition further, the isothermal annealing at 568 K below the calorimetric glass transition was preformed for different times. No crystallization determined by the DSC occurs during the annealing process. Figure 4 show the DSC curves for the sample annealed for 12, 23, 34.5, and 57 h. It is found that the height of peak of the glass transition increases with the increasing time. It is consistent with the other reports.[11,12,24] With the parameters in Table I, the simulation of the DSC for the annealing samples was performed. Figure 5(a) exhibits the calculation results based on the free-volume theory, which is well consistent with the height and position of the glass transition peak in Fig. 4. The values of the initial defect concentration c_D are 0.85×10^{-17}, 1.08×10^{-17}, 1.53×10^{-17}, and 3.97×10^{-17} for 57, 34.5, 23, and 12 h, respectively. The decrease of c_D with increasing annealing time means that the excess free volume in the system decreases with the increasing annealing time. So the increasing height of the glass transition peak is relative to the deceasing excess free volume. The resulting defect concentration as a
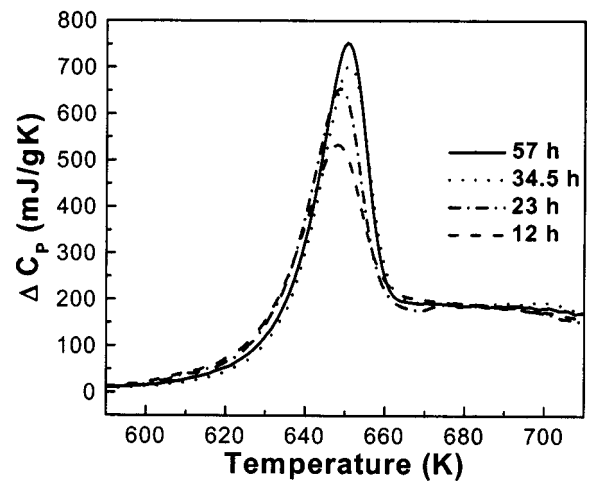

FIG. 4. The curves of the DSC obtained from the samples annealed at 568 K for different annealing times.

function of the annealing time is presented in the inset of Fig. 5(b). The plots are fit well with Eq. (1) using the initial defect concentration of 1.6×10^{-15}, indicating that the annealing makes the excess free volume approach the equilibrium free volume. The value of c_D in equilibrium state at 586 K is 4.249×10^{-20}, which is marked at the position with the dash line in Fig. 5(b). It is found that the time needed to approach the equilibrium at 568 K is so long that the equilibrium cannot be reached in the experimental time scale.

The glass transition, as observed in the DSC experiment, is considered as a phenomenon due to the free volume being out of equilibrium and continuously striving for the attainment of equilibrium. The free volume in thermodynamic equilibrium based on the equilibrium viscosity of supercooled liquid[22] is successfully used, indicating that the nature of the calorimetric glass transition is consistent with the glass transition determined by viscosity measurement.[4,25] So the nature of the calorimetric glass transition is a kinetic process. Though the calorimetric glass transition cannot explain the
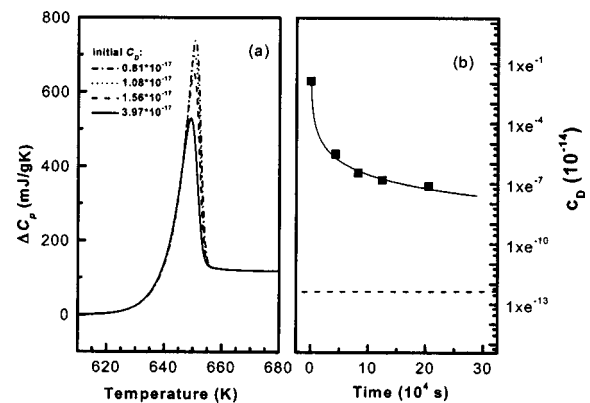

FIG. 5. (a) The resulting DSC line simulated for Fig. 4 by the free-volume theory. (b) The annealing time dependence of the c_D remained in the samples after annealing at 568 K, the line is fit with the equation: $dc_D/dt = -k_r c_D(c_D - c_{eq})$, the dash line is marked for the equilibrium c_D (1.046×10^{-19}) at 568 K.

thermodynamic paradox,[26] the kinetic glass transition is not contrary to the view that an intrinsic glass transition exists since the calorimetric glass transition is not equal to the ideal glass transition.[27]

In summary, the glass transitions observed in vit4 bulk metallic glass during the DSC runs at a constant heating rate are depicted quantitatively in the free-volume theory. The calorimetric glass transition is very sensitive to the excess free volume depended on the glass forming process and the treatment below the calorimetric glass transition temperature.

The annealing below the glass transition makes the excess free volume tend to the equilibrium. To reach the equilibrium is unavailable in experimental time scale. Comparing the conventional metallic glasses, vit4 is much less excess free volume.

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