

# Specific volumes of the $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ alloy in the liquid, glass, and crystalline states

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The specific volumes of the  $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$  alloy as a function of temperature,  $T$ , are determined by employing an image digitizing technique and numerical calculation methods applied to the electrostatically levitated spherical alloy. The linear fitting of the volumes of the alloy in the liquid,  $V_l$ , glass,  $V_g$ , and crystalline  $V_c$ , states in the temperature ranges shown in parentheses are  $V_l(T) = 0.1583 + 8.877 \times 10^{-6}T$  ( $cm^3/g$ ) (700–1300 K);  $V_g(T) = 0.1603 + 5.528 \times 10^{-6}T$  (400–550 K);  $V_c(T) = 0.1583 + 6.211 \times 10^{-6}T$  (400–850 K). The average volume thermal expansion coefficients within the temperature ranges are determined to be 5.32, 3.39, and  $3.83 \times 10^{-5}$  (1/K) for the liquid, glass, and crystalline states, respectively. © 1997 American Institute of Physics. [S0003-6951(97)03906-5]

A family of the Zr–Ti–Cu–Ni–Be alloys which exhibit an exceptional glass formability has provided a rare opportunity to study the thermophysical properties and phase transition kinetics of glass forming metallic alloys in a deeply undercooled liquid state and the glass transition region. The critical cooling rate of the alloys for glass formation is of the order of  $-10$  K/s or less,<sup>1</sup> which is sufficiently slower than experimental time scales of some measurements. The reported thermodynamic studies include the measurements of the specific heat,<sup>2</sup> hemispherical total emissivity,<sup>3</sup> viscosity,<sup>4</sup> and atomic diffusion coefficient.<sup>5</sup> The kinetic studies include the evaluations of the time-temperature-transformation (TTT) curve<sup>6</sup> and the Gibbs free energy change on crystallization.<sup>2</sup> In this letter, we report the results of specific volume measurements of the  $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$  alloy in the liquid, glass, and crystalline states, and the associated analyses. The specific volume is a fundamental property and it is indispensable to study the nature of phase transitions, specifically the glass transition for the present alloy.

Samples of typically 40 mg (approximately 2.2 mm in diameter) were separated from a bulk molten alloy whose nominal composition was  $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$  in at. %, and were formed to make spheres in an arc melter. The samples were then weighed and placed individually in a high temperature electrostatic levitator<sup>7</sup> which was operated in a high vacuum. Once a sample was levitated, it was heated above the liquidus temperature,  $T_L = 993$  K<sup>1</sup>, with a high intensity xenon arc lamp. Cooling of the sample was achieved by natural radiative heat loss to the surroundings. During the experiment, the sample temperature was monitored by a single color pyrometer with a preset emissivity. Also, the images of the levitated sample were stored on videotape. The specific volumes were determined from these images by employing an image digitizing technique and numerical calculation methods. The detailed description of the

volume measurement technique has been reported elsewhere.<sup>8</sup>

Figure 1 shows a typical thermogram of a sample on cooling when the xenon lamp is completely shut off. The temperature,  $T(t)$ , smoothly decreases at the rate which is basically proportional to the fourth power of  $T(t)$  except a small hump around 780 K. The cooling rate,  $dT(t)/dt$ , of the sample as a function of temperature was calculated by taking the derivative of  $T(t)$  with respect to time. As seen, the cooling rate varies from  $dT(t)/dt = -17$  K/s at 1200 K to  $dT(t)/dt = -0.2$  K/s at 500 K during the cooling process.

Figure 2 shows the results of the specific volumes of the alloy in the liquid,  $V_l$ , glass  $V_g$ , and crystalline,  $V_c$ , states as a function of decreasing temperature. The volume of the liquid linearly decreases as the sample temperature decreases until it is transformed into the glass. A small hump indicating volume increase is observed around 780 K (also seen in the temperature–time curve in Fig. 1). It is attributed to decomposition (phase separation) in the undercooled liquid<sup>3,9</sup> which may accompany the volume expansion of the sample

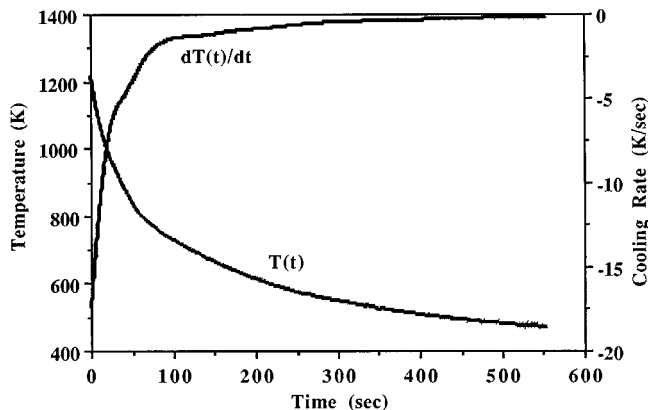


FIG. 1. A typical thermogram of a sample upon cooling. The cooling rate is calculated by taking the derivative of temperature with respect to time.

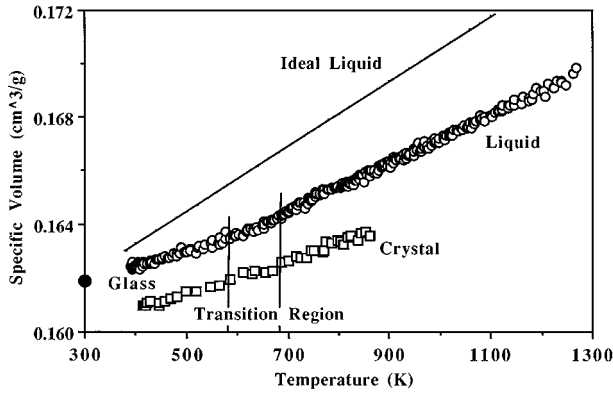


FIG. 2. The specific volumes of the  $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$  alloy in the liquid, glass, and crystalline states. The specific volume of the ideal liquid is the sum of the volume of each constituent element multiplied by the atomic fraction.

as long as the free energy decreases. This decomposition results in the spatial variation of the Zr and Be concentrations in the glass.<sup>10</sup> As expected, the specific volume of the alloy does not show discontinuity on the glass transition. This is because the transition is a kinetic relaxation process rather than a thermodynamic process of the first order. The beginning and ending of the glass transition are approximately 680 and 580 K, respectively. A relatively wide glass transition region (100 K) may indicate that the onset temperature of the transition varies depending on the local concentrations of Zr and Be. Below the transition region, the volume of the glass linearly decreases. The specific volume of the glass at room temperature (shown as the full circle in the figure) was determined by measuring the diameter of the sample using a micrometer after the levitation experiment. The specific volume of the ideally mixed liquid as a function of temperature is also shown in the figure. It is the sum of the specific volume of each constituent element<sup>11</sup> multiplied by the atomic fraction. In addition, the specific volume of a crystalline phase as a function of temperature is also shown as a reference. The crystalline sample was produced by heating up the glass sample to a temperature where it crystallized rapidly, and by holding it at the temperature until crystallization is complete. The linear curve fitting of the volumes are

$$V_l(T) = 0.1583 + 8.877 \times 10^{-6} T \text{ (cm}^3/\text{g)} \quad (700\text{--}1300 \text{ K}), \quad (1)$$

$$V_g(T) = 0.1603 + 5.528 \times 10^{-6} T \quad (400\text{--}550 \text{ K}), \quad (2)$$

$$V_c(T) = 0.1583 + 6.211 \times 10^{-6} T \quad (400\text{--}850 \text{ K}). \quad (3)$$

The temperature ranges at which the curve fitting was performed are given in parentheses. From Eqs. (1)–(3), the average volume thermal expansion coefficients,  $\alpha_l$ ,  $\alpha_g$ , and  $\alpha_c$  are determined to be 5.32, 3.39, and  $3.83 \times 10^{-5}$  (1/K), respectively. The linear thermal expansion coefficient of the glass is measured to be  $1.0 \times 10^{-5}$  (1/K) (373–648 K) by a dilatometric method.<sup>12</sup> This value corresponds to  $\alpha_g = 3.0 \times 10^{-5}$  (1/K).

The overall error involved in the volume measurement with the present technique is  $\pm 0.2\%$ , which excludes the error in the sample temperature determination. If the emis-

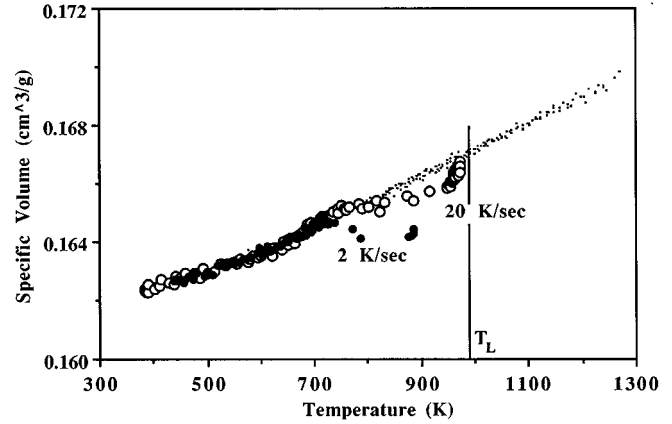


FIG. 3. The specific volume of the alloy determined upon heating the alloy. The heating rates are 2 (full curves) and 20 (open circles) K/s.

sivity of the sample gradually changes as the temperature changes, the temperature measurement generally becomes less accurate at temperatures away from  $T_L$  at which the emissivity is adjusted in the present measurement. The glass transition region determined in the present experiment reasonably agrees with the reported value<sup>2</sup> measured by a differential scanning calorimeter; thus, we believe that the error involved in the temperature measurement is minimal. In other words, the emissivity change is negligible within the present temperature range. This assessment is also supported by the fact that the volume at room temperature (determined independently) is on the line of extrapolation of the volumes at high temperatures. Another error associated with the sample temperature determination may arise from the presence of radial temperature gradient within the sample during cooling. A conservative estimate of the temperature difference between the surface and the center of the sample is less than 5 K at the fastest cooling rate ( $\sim -27$  K/s) in the present measurement. This difference does not significantly change the calculated volumes. The detailed analysis on this matter can be found in Ref. 8.

One may expect that a mixture of elements which leads to dense packing in the liquid state is more resistant to crystallization which requires local compositional fluctuation. The excess volume,  $\Delta V_E$ , over the ideal volume of the alloy is negative (the amount is less than 3% of the specific volume), which implies attractions among the dissimilar elements. The negative  $\Delta V_E$  value is consistent with the fact that the alloy is a compound forming alloy, but does not support the observed decomposition which is normally observed in alloys with positive  $\Delta V_E$ . According to the free volume model of a glass, a liquid becomes the glass when the free volume of the liquid is depleted at low temperatures.<sup>13,14</sup> This idea led to suggest that the glass transition temperature,  $T_g$ , was proportional to  $\alpha_l$  since the free volume was depleted quickly if  $\alpha_l$  was large. In fact, for a number of easy glass forming alloys, the ratio,  $\alpha_l/T_g$  was found to be fairly constant at around  $1.25 \times 10^{-7}$  (1/K<sup>2</sup>).<sup>15</sup> For the present alloy, taking  $T_g = 625$  K,  $\alpha_l/T_g$  is  $0.83 \times 10^{-7}$ . This value is significantly smaller than the above value; thus, the suggested correlation is not held in the present alloy.

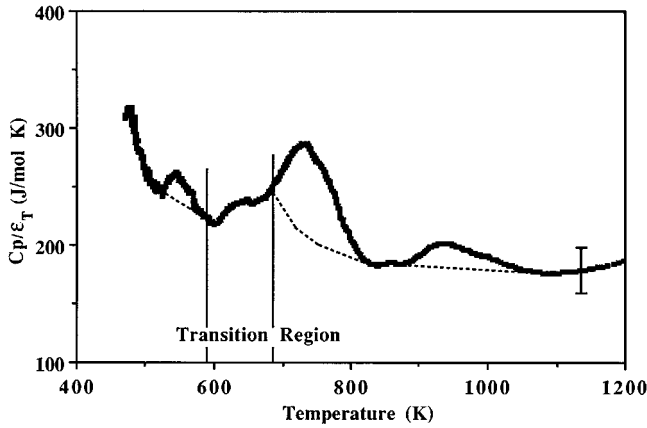


FIG. 4. The  $C_p/\epsilon_T$  curve of the alloy determined from a time-temperature curve upon cooling. If there are no exothermic reactions, the curve is expected to follow the dotted lines.

Figure 3 shows the specific volumes determined upon heating the sample. The heating rates (2 and 20 K/s) around the glass transition region were achieved by adjusting the intensity of the xenon lamp. The volumes determined upon cooling are shown with the dots. The volumes coincide with those determined upon cooling at low temperatures within the error of the experiment. The deviation above the glass transition region is due to crystallization of the sample. The apparent onset temperature of the crystallization depends on the heating rate because of the incubation time of crystallization. At higher temperatures, the crystalline phases remelt; therefore, the volume returns to that of the value determined upon cooling. It is reported that the specific heat of the alloy exhibits a strong heating rate dependence in the glass transition region.<sup>2</sup> The specific heat change in the glass transition region mainly comes from the change in the configurational entropy whose value is directly related to the specific volume; thus, we initially expected that the volume varied in a similar manner. However, we could not observe the heating rate dependence on the volume. The reason may simply be due to the limited heating rates used in the measurement; thus, further studies using higher heating rates are necessary.

It has been suggested that the time-temperature curves generated upon cooling may be used to study the atomic structure change of the liquid as the temperature changes.<sup>3,16</sup> Since the heat loss during cooling is purely radiative, the cooling rate of a sample is ideally given as

$$\frac{dT}{dt} = -\frac{\sigma\epsilon_T A}{mC_p}(T^4 - T_0^4), \quad (4)$$

where  $m$  is the mass,  $C_p$  is the specific heat,  $\sigma$  is the Stefan-Boltzmann constant,  $\epsilon_T$  is the hemispherical total emissivity,  $A$  is the surface area, and  $T_0$  is the environmental temperature. By rearranging Eq. (4),  $C_p/\epsilon_T$  is given as

$$\frac{C_p}{\epsilon_T} = -\frac{\sigma A}{m}(T^4 - T_0^4)\frac{dt}{dT}. \quad (5)$$

The value of  $dt/dT$  can be obtained from the experimental time-temperature curve by taking a derivative. Figure 4 shows  $C_p/\epsilon_T$  of the alloy as a function of temperature. If either  $C_p$  or  $\epsilon_T$  is independently measured, the other can be

determined from this curve. It should be noted that  $C_p/\epsilon_T$  is very sensitive to  $dt/dT$  which is somewhat difficult to evaluate accurately from the experimental curve; therefore, the errors involved in the curve are relatively large (note the error bar taken from Ref. 3 in Fig. 4). Keep this fact in mind as we further proceed with the analysis of the curve. Three peaks identified in the figure seem to be due to exothermic reactions. Since  $\epsilon_T$  is expected to decrease slowly and monotonously as the temperature decreases, the peaks are created by the increase in the apparent specific heat due to the heat generated by the exothermic reactions. Without these reactions, the curve is expected to follow the dotted lines. The position of the middle peak corresponds to the decomposition detected by the volume measurement. The expected base line (dot line) is drawn to rise toward the upper boundary of the glass transition region. This rise comes from the increase in  $C_p$  due to the rapid loss of the configurational entropy of the liquid.<sup>3</sup> The area between the peak line and the base line is proportional to the heat released during the phase separation. By assuming  $\epsilon_T$  to be 0.18,<sup>3</sup> the released heat is calculated to be roughly 900 J/mol. The decomposition is followed by crystallization if the sample is held at the temperature;<sup>6,9</sup> therefore, one might suspect that the peak is due rather to the heat of partial crystallization. We dismiss this notion for the following reasons: first, the observed volume increase on the reaction does not support crystallization. Second, the released heat is about 16% of the heat of crystallization, 5.5 kJ/mol.<sup>2</sup> Therefore, if it is attributed to the partial crystallization, the volume decrease is approximately 0.3%, which should be detectable with the present method.

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