

GLASS TRANSITION AND THERMODYNAMIC FUNCTION OF ZrAlNiCuCo ALLOY^①

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ABSTRACT The thermodynamic functions of ZrAlNiCuCo alloy in different states are calculated. By comparing the calculated thermodynamic function of the liquid with that of the glass, it is found that the glass transition with a small transition activation energy could be considered as a thermodynamic transition. Kauzmann temperature is determined by either an isentropic condition or Vogel-Fulcher law.

Key words ZrAlNiCuCo alloy glass transition thermodynamic function Kauzmann temperature

1 INTRODUCTION

The glass transition as a polymorphous one (requiring equality of composition in all phases) needs a very small E (activation energy) without a long distance atom diffusion^[1, 2]. Klose and Fecht^[1] indicate that E for AuPbSb alloy is 0.02 eV in comparison with 1.5 eV for crystallization of the undercooled liquid. Thus, the shift of T_g required by the molecular relaxation time (τ) is small. However, a shift of T_g more than 40 K for glassy PdNiPSi alloy^[2] is observed when q (heating rate) varies 5 000 times, which is contradictory with the above consideration. In addition, although an organic glass, such as polyvinyl acetate, has a more complicated structure and a longer τ than a metallic glass has, it changes T_g only 8 K when q changes 5 000 times^[3]. Therefore, as q changes, a large change of T_g for a metallic glass can not be simply considered as a kinetic reason. To examine this issue, it is necessary to calculate thermodynamic functions. This paper measured C_p of the ZrAlNiCuCo alloy and calculated the thermodynamic functions in different states.

2 EXPERIMENTAL AND CALCULATING METHOD OF THERMODYNAMIC FUNCTION

The cast alloy ingot of Zr₆₅Al_{7.5}Ni₁₀Cu₁₅Co_{2.5} (mole fraction, %) in mass of 5 g was obtained by melting metals of Zr, Al, Ni, Cu and Co with a purity of 99.9 % to 99.99 % in a vacuum arc furnace. The glass ribbons prepared by melt spinning are 4.0 mm in width and 0.03 mm in thickness. The specific heat measurements were carried out by a differential scanning calorimeter (DSC-7, Perkin Elmer) and T_m , ΔH_m (melting enthalpy) and ΔS_m (melting entropy) of the alloy were measured by a differential thermal analyzer (DTA-7, Perkin Elmer). The details are shown in Ref.[4].

With the measured thermodynamic data, the enthalpies of crystal (H^c) and liquid (H^l) as well S^c and S^l (S^l and S^c are the entropies of the liquid and the crystal) are obtained by

$$H^c(T) = \int_{298}^T C_p^c(T) dT \quad (1)$$

$$S^c(T) = \int_{298}^T C_p^c(T)/T dT \quad (2)$$

$$H^l(T) = \Delta H_m + H^c(T_m) +$$

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$$\int_{T_m}^T C_p^l(T) dT \quad (3)$$

$$S^l(T) = \Delta S_m + S^c(T_m) + \int_{T_m}^T C_p^l(T)/T dT \quad (4)$$

In Eqs.(1) and (2) H^c (298) and S^c (298) are assigned as zero.

Let $S^l(T_g) = S^g(T_g)$ (entropy of the glass), T_g is obtained. To determine S^g and H^g (enthalpy of the glass), we assume that there exists a temperature T_c , where $C_p^g(T_c) = C_p^c(T_c)$. When $T < T_c$, $C_p^g = C_p^c$. In addition, let $S^g(T_c) = S^c(298)$ and $S^g(298) - S^c(298) < 0.2\Delta S_m$. These assumptions are based on the fact that $S^g(T)$ is a little larger than $S^c(T)$ when $T < 300\text{ K}$ ^[3]. Thus,

$$S^g(T) = S^g(T_c) + \int_{T_c}^T C_p^g(T)/T dT \quad (5)$$

$$H^g(T) = H^l(T_g) + \int_{T_g}^T C_p^g(T) dT \quad (6)$$

$$(H^g(T_g) = H^l(T_g))$$

With Eqs. (1) to (6), the Gibbs free enthalpy functions of liquid (G^l), glass (G^g) and crystals (G^c) are obtained by $G = H - TS$.

A continuous temperature transformation diagram (CTT diagram) describes the kinetic transition conditions of the glass transition and the crystallization. The crystallization curve in a CTT diagram is mathematically expressed by Eq.(7) based on the heterogeneous nucleation theory^[5]:

$$\ln \tau_1 = (\alpha + \beta / (\Delta G_V^2 T)) \quad (7)$$

In Eq.(7) α is related to viscosity of the liquid, β is determined by the interfacial energy. $\tau_1 = (T_x - T_k)/q$ is a crystallization time in second (T_x is a crystallization temperature of the glass and T_k is Kauzmann temperature^[6]). ΔG_V is the volume Gibbs free enthalpy difference between the liquid and the crystal in $\text{J}\cdot\text{cm}^{-3}$.

The glass transition curve in the CTT diagram can be calculated by Vogel-Fulcher law^[1,2,7]:

$$\ln \tau_2 = \ln \tau_0 + E/(T_g - T_k) \quad (8)$$

where $\tau_2 = (T_g - T_k)/q$ in second, τ_0 is a constant in second, E is in K (to transform E to

a usual molar quantity of $\text{J}\cdot\text{mol}^{-1}$, the value of E must be multiplied by $R_0 = 8.314\text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$). With Eqs.(7) and (8), CTT diagram is obtained.

3 RESULTS AND DISCUSSION

By measurement and calculation the specific heat C_p and function of C_p in different states were obtained^[4] as follows.

C_p^g data of relaxed glasses with different heating rates q are:

$$\text{At } q = 25\text{ K}\cdot\text{min}^{-1}, C_p^g(T) = 20.24 + 0.0205T \quad (370\text{ K} < T < 461\text{ K}) \quad (9a)$$

$$\text{At } q = 50\text{ K}\cdot\text{min}^{-1}, C_p^g(T) = 20.01 + 0.0214T \quad (370\text{ K} < T < 487\text{ K}) \quad (9b)$$

$$\text{At } q = 100\text{ K}\cdot\text{min}^{-1}, C_p^g(T) = 19.83 + 0.0221T \quad (370\text{ K} < T < 530\text{ K}) \quad (9c)$$

$$\text{At } q = 200\text{ K}\cdot\text{min}^{-1}, C_p^g(T) = 19.63 + 0.0229T \quad (370\text{ K} < T < 557\text{ K}) \quad (9d)$$

$$\text{At } q = 400\text{ K}\cdot\text{min}^{-1}, C_p^g(T) = 19.45 + 0.0236T \quad (370\text{ K} < T < 574\text{ K}) \quad (9e)$$

Through regressing the coefficients of C_p^g functions with different q , an extrapolated C_p^g function with $q = 0\text{ K}\cdot\text{min}^{-1}$ is obtained: $C_p^g = 21.28 + 0.0159T$.

$C_p^l(T) = 133.28 - 0.164T + 0.0000699T^2$ is extended to T_m .

$$C_p^c(T) = 24.20 + 0.00599T \quad (293\text{ K} < T < 568\text{ K})$$

$$C_p^n(T) = 18.08 + 0.0257T \quad (368\text{ K} < T < 658\text{ K})$$

Based on the condition of $C_p^c(T_c) = C_p^g(T_c)$, the calculated T_c are 295, 273, 272, 271, 270, 270 K for $q = 0, 25, 50, 100, 200, 400\text{ K}\cdot\text{min}^{-1}$, respectively.

The measured $T_m = 1149 \pm 2\text{ K}$ is similar to $T_m = 1116\text{ K}$ for $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ alloy^[8], $\Delta H_m = 14.81\text{ kJ}\cdot\text{mol}^{-1}$, $\Delta S_m = \Delta H_m/T_m = 12.89\text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. The determined ΔH_m is smaller than $16.4\text{ kJ}\cdot\text{mol}^{-1}$ for $\text{Zr}_{76}\text{Ni}_{24}$ alloy^[9].

With measured thermodynamic data, fitted $G(T)$ functions (the superscript of $G^g(T)$ functions in numbers is the corresponding q) are

as follows :

$$G^c(T) = 24.2T + 0.003T^2 - 7478 - T[24.2\ln T + 0.006T - 139.7] \quad (10a)$$

$$G^l(T) = 0.00002T^3 - 0.08T^2 + 133.3T - 41134 - T[0.000035T^2 + 133.3\ln T - 0.16T - 746.2] \quad (10b)$$

$$G^{g,0}(T) = 21.3T + 0.008T^2 - 1641 - T[21.3\ln T + 0.016T - 125.7] \quad (10c)$$

$$G^{g,25}(T) = 20.2T + 0.01T^2 - 167 - T[20.2\ln T + 0.02T - 119.1] \quad (10d)$$

$$G^{g,50}(T) = 20.2T + 0.01T^2 - 126 - T[20.0\ln T + 0.02T - 118.0] \quad (10e)$$

$$G^{g,100}(T) = 19.8T + 0.01T^2 - 54 - T[19.8\ln T + 0.02T - 117.1] \quad (10f)$$

$$G^{g,200}(T) = 19.6T + 0.01T^2 + 167 - T[19.6\ln T + 0.02T - 116.1] \quad (10g)$$

$$G^{g,400}(T) = 19.5T + 0.01T^2 + 205 - T[19.5\ln T + 0.02T - 115.3] \quad (10h)$$

From Eqs. (1) and (3) $H^{c-1}(T) = H^l(T) - H^c(T) = 0.00002T^3 - 0.09T^2 + 109.1T - 33656$. $H^{c-1}(T)$ and $-H_x$ (crystal enthalpy of relaxed glasses with different q) curves are presented in Fig.1. The measured H_x is the averaged values of four independent runs. According to $-H_x = (0.33 \sim 0.36) \Delta H_m$, $-H_x$ is between 4.96 and 5.32 kJ•mol⁻¹ depending on q , which is similar to $-H_x \approx 5$ kJ•mol⁻¹ in NiZr alloy systems^[10]. The enthalpy difference between the liquid and the nanocrystals $[H^{n-1}(T)]$ is calculated by $H^{n-1}(T) = -H_x + \int_{T_x}^T [C_p^l(T) - C_p^n(T)] \cdot dT$, i.e., $H^{n-1}(T) = 0.00002T^3 - 0.095T^2 + 115.2T - 37094$. $H^{n-1}(T)$ function corresponds to $-H_x$ well as shown in Fig. 1. It is observed that $-H_x$ does not evidently increase as T increases due to large C_p^n values. The measured $-H_x$ points are lower than the $H^{c-1}(T)$ curve, their difference is an enthalpy difference between the nanocrystals and the crystals in normal grain size with a quantity of 4 ~ 5 kJ•mol⁻¹ being related to interface energy of the nanocrystals. The details are discussed elsewhere^[11].

Let $S^g = S^l$, calculated $T_g^c(q)$ are equal to the measured $T_g(q)$ in an error range of ± 15 K, which implies that the glass transition is es-

entially a thermodynamic phenomenon. The result is shown in Table 1. The calculated activation energy, E , confirms the above conclusion. Fig.2 shows a diagram of $\ln \tau_2$ versus $1/(T_g - T_k)$. The fitted function in terms of Eq. (8) is $\ln \tau_2 = 6.18 + 1081/(T - 561)$, where $T_k = 561$ K and $E = 1081$ K (9.0 kJ•mol⁻¹). This small E indicates that the kinetic influence on T_g is small. This phenomenon is further identified by

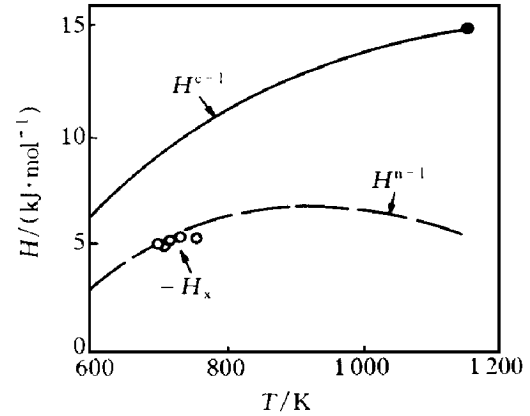


Fig.1 Measured $-H_x$ points and calculated H^{c-1} and H^{n-1} curves

Table 1 Comparison between measured T_g and calculated T_g^c

$q/(K \cdot \min^{-1})$	0	12.5	25	50	100	200	400	500
T_g/K	648	654	660	666	672	678	683	
$(T_g \pm 15)/K$	588		653	663	667	675	679	

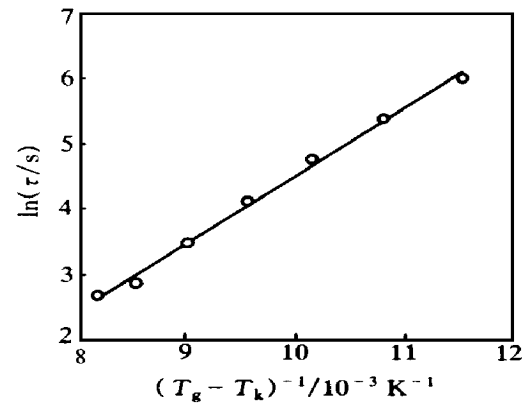


Fig.2 Measured T_g versus $\ln \tau_2$ (shown in open circles) and calculated curve (shown as straight line) by Eq.(8)

analyzing $G^{l-g} = G^g - G^l$ and $G^{c-l} = G^l - G^c$ functions in the measured T_g range. When $648 \text{ K} < T_g < 683 \text{ K}$, $|G^{l-g}| < 0.015 \text{ kJ} \cdot \text{mol}^{-1}$, which is two orders smaller than G^{c-l} ($4.98 \sim 4.81 \text{ kJ} \cdot \text{mol}^{-1}$), where $G^{c-l} = -0.00001165 T^3 + 0.085 T^2 + 715.66 T - 109.08 T \ln T - 33686$. Thus, a small difference of G^g induced by different q changes T_g .

For one-component system, T_k can be expressed as $T_k = \delta T_m^{[12]}$, where δ is a coefficient. T_k in a multi-component system is defined as^[13]

$$T_k = \delta \sum_{i=1}^n x_i T_{mi} \quad (11)$$

where x_i is atomic percentage of the i -th component, T_{mi} is T_m of the i -th component, δ is taken as $0.25 \sim 0.3$ ^[12]. The obtained T_k by Eq. (11) is between 468 and 561 K.

Under the condition of $S^c(T_k) = S^l(T_k)$, $T_k = 569 \pm 15 \text{ K}$. If the obtained T_k by the isentropic condition and by Vogel-Fulcher law are compared, they are the same in the error range ($569 \pm 15 \text{ K}$ and $561 \pm 15 \text{ K}$) showing that T_k can be calculated by Vogel-Fulcher law, namely by measuring T_g with different q . More simply, T_k can be obtained by Eq. (11) without a large error ($468 \sim 561 \text{ K}$).

The coefficients of Eq. (7) are determined by a linear regression between $1/(\Delta G_V^2 T)$ and $\ln \tau_1$ and shown in Fig. 3, where $\Delta G_V = [G^c(T) - G^{g,0}(T)]/11.81 = 0.0004 T^2 - 0.25 T \ln T + 1.43 T - 494.2$ ($11.81 \text{ cm}^3 \text{ mol}^{-1}$ is the molar volume of the alloy). Here τ_1 is calculated by $(T_x - T_k)/q$ and $G^l(T)$ is replaced by $G^{g,0}$ because the experimental data are obtained by heating the glass. The fitted α and β are -67.23 s^{-1} and $0.9429 \times 10^{10} \text{ K} \cdot \text{J}^2 \cdot \text{cm}^{-6}$, respectively. $\ln \tau_1 = -67.23 + 0.94 \times 10^{10}/(\Delta G_V^2 T)$.

With Eqs. (7) and (8), an CTT diagram of the alloy is obtained and shown in Fig. 4, where the measured T_g and T_x with different q (T_x start temperature of glass crystallization is measured for $q = 0.2 \sim 500 \text{ K} \cdot \text{min}^{-1}$) versus $\lg \tau$ are also present. The nose point of the T_x curve lies at 849 K. The critical cooling rate q_c is -54

$\text{K} \cdot \text{s}^{-1}$ with a tangential point on T_x curve at 840 K. The obtained q_c is smaller than the estimated $q_c (= -87 \text{ K} \cdot \text{s}^{-1})$ for LaAlNi alloy^[14]. Thus, ZrAlNiCuCo alloy is a better glass former than LaAlNi alloy^[8]. The intersectional point of q_c on the T_g curve is 691 K, which is the lowest T_g during the cooling of the liquid.

From Eq. (7), the calculated activation energy for nucleation at 840 K, ΔG^* ($\Delta G^* = \beta k_B / \Delta G_V^2$, where k_B is Boltzmann constant) is 5.6

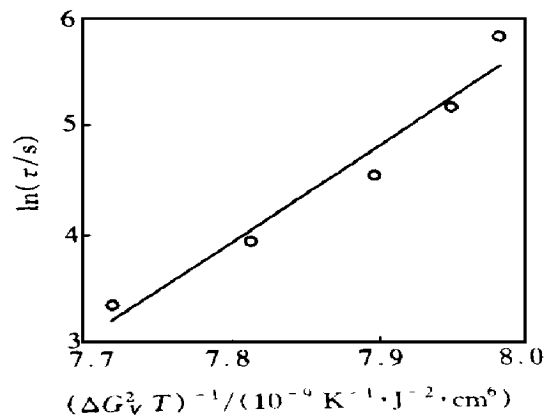


Fig. 3 Dependence between $1/(\Delta G_V^2 T)$ and $\ln \tau$

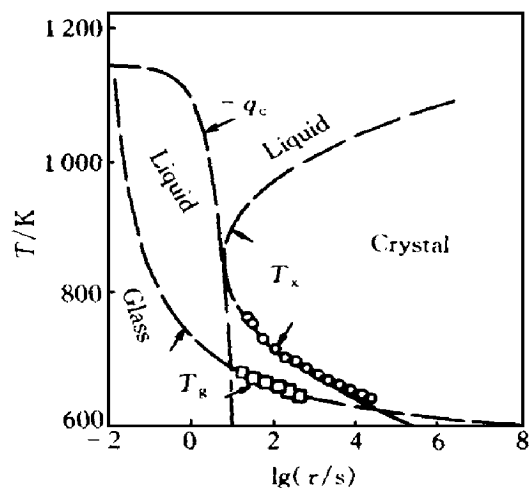


Fig. 4 Measured T_g (\square) and T_x (\circ) versus $\lg \tau$ and fitted curve of T_x and T_g based on Eqs. (7) and (8) (The cooling curve with the $q_c = -54 \text{ K} \cdot \text{s}^{-1}$ is shown in the figure.)

e V/atom ($693.3 \text{ kJ} \cdot \text{mol}^{-1}$) being two order larger than $E = 9.0 \text{ kJ} \cdot \text{mol}^{-1}$. Thus, this alloy is a strong glass former.

4 CONCLUSIONS

The glass transition is a thermodynamic phenomenon with a small E of $9.0 \text{ kJ} \cdot \text{mol}^{-1}$. Because $G^l \approx G^g$ in a broad temperature range, a small change on the energetic state of the glass induced by different q leads to a shift of T_g . $T_k = 561 \pm 15 \text{ K}$ is obtained by an isentropic condition and by the Vogel-Fulcher law. T_k can be approximately estimated by the melting point of the components of the alloy. In the CTT diagram, the calculated q_c is $-54 \text{ K} \cdot \text{s}^{-1}$. The lowest T_g by cooling the liquid is 691 K .

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