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SPECIFIC HEAT MEASUREMENTS OF ZrAlNiCuCo ALLOY①

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ABSTRACT Specific heats of undercooled liquid, crystal, and glass states for the ZrAlNiCuCo alloy are measured by a calorimeter. Different heating rates are used to enlarge the measuring temperature range of specific heat for an undercooled liquid. The specific heat data of the glass with a zero heating rate are obtained by extrapolating the measured specific heat data of the glass with different heating rates. And specific heat functions of undercooled liquid, crystal and glass are obtained too.

Key words ZrAlNiCuCo alloy specific heat amorphous alloy

1 INTRODUCTION

To examine the thermodynamics and dynamics of glass transition of amorphous alloy, it is necessary to measure specific heat of the alloy including undercooled liquid (c_p^l), glass (c_p^g) and the crystal (c_p^c). Because an undercooled liquid only exists within a limited time due to its metastable nature, c_p^l($T < T_m$) values (T_m is melting temperature) can only be measured near T_m and near T_g(glass transition temperature). Structures and energetic states of a glass depend on its relaxation processes. The more relaxed the glass is, the smaller the energetic state as well c_p^g(T) values is. The as-quenched glass with a frozen-in structure of the liquid at T_g has the highest energetic state of the glass and the largest c_p^g values. When the as quenched glass is relaxed by annealing at T_r($T_r < T_g$), its energetic state and c_p^g values are lowered. The relaxed glass has a frozen-in energetic state of T_r because the subsequent cooling of the glass is quicker than that for equilibrium. A further structural relaxation of the relaxed glass takes place when the relaxed glass is aged at T_a[1]. The same phenomenon is present during heating the glass where the ageing temperature continuously changes. A smaller q (heating rate) corresponds to a longer ageing time and lower c_p^g values. c_p^c data are obtained by measuring the as-cast crystalline specimen. When c_p^c values are measured after the crystallization of glass the corresponding c_p^c values are that of the nanostructured crystals(c_p^n)[2-5].

2 EXPERIMENTAL

To measure c_p^l near T_g, the $Zr_{65}Al_{7.5}Ni_{10}Cu_{15}Co_{2.5}$ (mole fraction, %) alloy is selected because its $T_x - T_g = 126$ K[6,7](T_x is crystalline temperature of glass). The cast alloy ingot of $Zr_{65}Al_{7.5}Ni_{10}Cu_{15}Co_{2.5}$ in mass of 5 g was obtained by melting starting metals of Zr, Al, Ni, Cu, Co with 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). The specimen used for DSC runs was a piece of ribbon in size of 4 mm × 4 mm × 0.03 mm. This design of the shape improves the measuring accuracy. The reasons are as follows: (1) the movement of the specimen itself in the pan of DSC during the measurement is avoided because the size of the specimen diagonal and the diameter of

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pan are similar[8,9]; (2) a uniform temperature in the specimen at a large q(400 K· min^{-1}) is guaranteed due to a thin thickness and a small mass of 3 ~ 4 mg of specimen; (3) the measuring error for one piece of specimen (±1 %) is only one half of that of a specimen consisting of many small pieces of ribbons (±2 %)[9].

The basic temperature calibrations for the DSC were carried out within 0.1 K by T_m of In and Zn. The heat flow was calibrated within 0.01 J · g^{-1} by melt enthalpy of In (q = 2 K· min^{-1}). Because the specimen mass is only 3 ~ 4 mg, the effect of the specimen mass on the temperature is negligible. The effect of q on apparent temperature of DSC was calibrated by a T_m of In (429.7 K) with Al pan and a T_m of Zn (692.6 K) with Al_2O_3 pan, respectively. The calibrated differences between the apparent temperature and the real temperature of DSC (ΔT) by different q and pans are shown in Table 1.

Table 1 Dependence of ΔT on q

q/(K· min^{-1})	ΔT(Al pan)/K	ΔT(Al_2O_3 pan)/K
0.2	-0.2	-0.5
0.5	-0.2	-0.3
1	-0.1	0.2
2	0.0	0.8
5	0.6	1.2
10	1.4	1.8
20	3.4	4.1
40	6.9	8.7
80	12.8	17.1
160	24.6	35.1
320	40.5	59.8
500	55.3	91.2

Before each measurement the pan was carefully positioned at the center of the furnace, two cover holes of the furnace were remained in the same direction at each measurement. For the c_p measurements a base-line obtained by measurement without a specimen was firstly made. The measured c_p values were calibrated by sapphire in a similar mass of specimens. c_p values in J·g^{-1}·K^{-1} were changed to molar unit by timing a molar mass of 78.19 g· mol^{-1}. If $T < 800$ K, Al pan was used to improve the measuring accuracy. Otherwise, when $T > 800$ K, Al_2O_3 pan was utilized to avoid any chemical reaction between the specimen and the pan.

The as-quenched glass was relaxed by preheating the specimen to 623 K with q = 40 K· min^{-1} and was cooled with q = 200 K· min^{-1}. c_p^g values were measured with different q among 25 ~ 400 K· min^{-1} from 250 K to a finishing temperature for the glass transition. c_p^c and c_p^n values were determined by measuring the as-cast specimen and the crystallized glass with q = 40 K· min^{-1}, respectively. c_p^l values were measured by heating the glass over T_g with different q. When q was double, T_g increased 5 ~ 6 K, c_p^l was still measured in the temperature range of T_g + 35 K. Thus, the total measuring range of c_p^l values reaches 70 K.

If the scattering data after the repetition of runs on DSC are fitted to some algebraic functions, e.g. $c_p^c = B_0 + B_1 T$, the mean deviation (θ) is ±0.15 % for Au in the temperature range of 350 ~ 650 K[8]. To reach this θ value in this experiment, the used c_p values have to be averaged values of 40 measured points ($\pm 0.15\ \% = 40^{-1/2} \times \pm 1\ \%$)[10]. Hence, ten c_p values were averaged in a single run. Together four independent c_p runs were carried out and were averaged again. In the extended temperature range of c_p^l (T) function, the corresponding θ reaches ±3 %, which is also a θ value of calculated thermodynamic functions. The calculated T_g is in an error range of ±15 K.

T_m, ΔH_m(melt enthalpy) and ΔS_m(melt entropy) of the alloy were measured by a differential thermal analyzer (DTA - 7, Perkin Elmer) with q = 40 K· min^{-1} within a measuring error of ± 1 %. The specimen had the same shape as above stated and was sealed in a pan to avoid oxidation.

3 RESULTS AND DISCUSSION

The as-quenched glass is measured by q = 100 K· min^{-1} for three times in-situ. The c_p^g(T) values of the as-quenched glass (the first run) and of the relaxed glass (the second and the third runs) are presented in Fig. 1. Between 285 and 340 K, c_p^g values of the as quenched glass (about 42 J·mol^{-1}·K^{-1}) are much larger than that of the relaxed glass (about 27 J·mol^{-1}·K^{-1}). The fitted c_p^g is 40.92 + 0.005 21 T. When $T > 345$ K, a relaxation characterized by a decrease of apparent c_p^g values occurs. c_p^g values between the 2nd and the 3rd runs are the same in the error range. Thus, when q and T_r are fixed, the relaxed glass has a fixed energetic state. When $T < 365$ K, c_p^g values of the relaxed glass are constant. The relaxed glass has also a frozen-in energetic state although it is lower than that of the as-quenched glass.

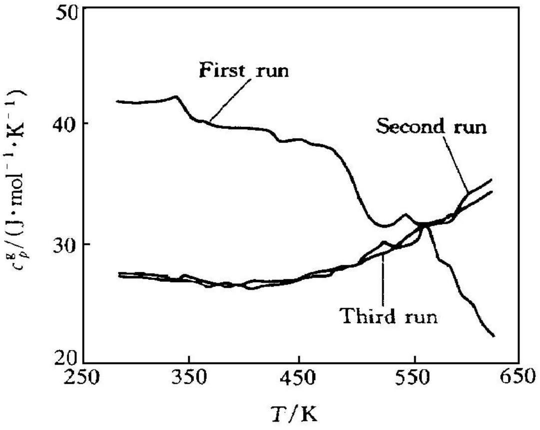

Fig.1 Three successive $c_p^g(T)$ runs for as-quenched and relaxed glass in-situ

c_p^g data of relaxed glasses with different q are plotted in Fig. 2. A larger q leads to larger $c_p^g(T)$ values and a higher T_g. The fitted $c_p^g(T)$ functions are:

At $q = 25$ K·min^{-1}, $c_p^g(T) = 20.24 + 0.0205\,T$ $(370\ \mathrm{K} < T < 461\ \mathrm{K})$ (1)

At $q = 50$ K·min^{-1}, $c_p^g(T) = 20.01 + 0.021\,4\,T$ $(370\ \mathrm{K} < T < 487\ \mathrm{K})$ (2)

At $q = 100$ K·min^{-1}, $c_p^g(T) = 19.83 + 0.0221\,T$ $(370\ \mathrm{K} < T < 530\ \mathrm{K})$ (3)

At $q = 200$ K·min^{-1}, $c_p^g(T) = 19.63 + 0.0229\,T$ $(370\ \mathrm{K} < T < 557\ \mathrm{K})$ (4)

At $q = 400$ K·min^{-1}, $c_p^g(T) = 19.45 + 0.023\,6\,T (370 < T < 574\ \mathrm{K})$ (5)

Through regressing the coefficients of c_p^g functions with different q, an extrapolated c_p^g function with $q = 0$ is $c_p^g = 21.28 + 0.0159\,T$.

The relaxation enthalpy of the as-quenched glass (H_r) is measured by $q = 500$ K·min^{-1}. $H_r = 1.832$ kJ·mol^{-1}. The as-quenched glass of this alloy relaxes even at ambient temperature. After the as-quenched glass has been manufactured about 1 year, measured H_r is zero.

The measured $T_m = 1\,149 \pm 2$ K is similar to $T_m = 1\,116$ K for $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ alloy[6, 7]. $\Delta H_m = 14.81$ kJ·mol^{-1}. $\Delta S_m = \Delta H_m / T_m = 12.89$ J·mol^{-1}·K^{-1}. The determined ΔH_m is smaller than 16.4 kJ·mol^{-1} for $Zr_{76}Ni_{24}$[11].

c_p^l values obtained by 20 independent measurements with five different q are presented in Fig.3. The measuring temperature range of c_p^l data is 70 K (675 ~ 745 K). The largest c_p^l value measured by the slowest q (25 K·min^{-1}) is 54.5 J·mol^{-1}·K^{-1}, which is larger than $c_p^l \approx 50$ J·mol^{-1}·K^{-1} for $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ glassy alloy at $q = 40$ K·min^{-1}[7]. The c_p^l values measured at different q is equal at the same temperature, which indicates that an equilibrium state of liquid is realized in the experimental time scale. The fitted function of $c_p^l(T) = 133.28 - 0.164\,T + 0.000\,069\,9\,T^2$ is extended to T_m. When $T < T_m$, the $c_p^l(T)$ curve has a negative slope induced by the chemical short range order in the liquid[12]. The estimated $c_p^l(T_m)$ is 37.1 J·mol^{-1}·K^{-1}. A positive $c_p^l(T_m) - c_p^c(T_m) = 6.0$ J·mol^{-1}·K^{-1} is present as expected.

The c_p^c, c_p^n and c_p^g ($q = 25$ K·min^{-1}) data are also shown in Fig.3. The measured c_p^c data above 568 K have been eliminated due to the oxidation (increase height of sample is over 3%, when $T > 568$ the slop of curve mesured have evidently changed). However, the nanocrystal does not oxidize up to 793 K. The oxidation resistance of the nanocrystals is much better than that of the crystals. The $c_p^c(T)$ function fitted is $c_p^c(T) = 24.20 + 0.005\,99\,T$ between 293 and 568 K, which is comparable with those of $Zr_{61}Ni_{39}$ alloy ($c_p^c = 25.0 + 0.003\,58\,T$)[13] and

$Zr_{76}Ni_{24}$ alloy ($c_p^c = 24.3 + 0.00659\ T$)[11].

The fitted $c_p^n(T)$ function between 368 and 658 K is $c_p^n(T) = 18.08 + 0.0257\ T$, which has the largest temperature coefficient and $c_p^n(T)$ values among all states of the alloy showing a contribution of the interface energy of nanocrystals on the specific heat.

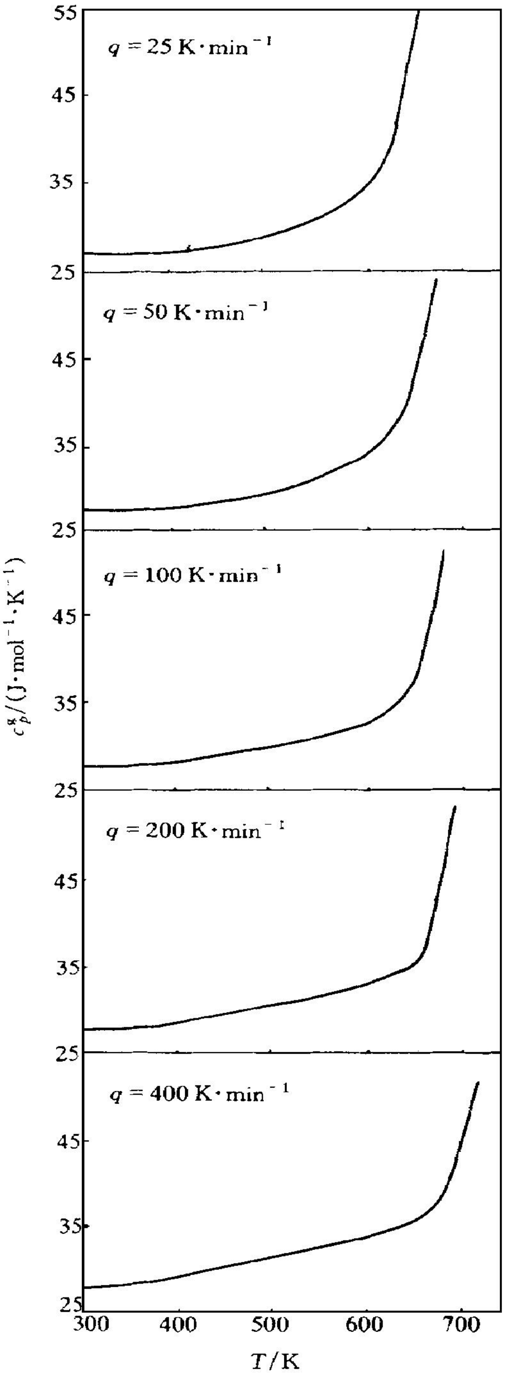

Fig.2 $c_p^g(T)$ measurements with five q

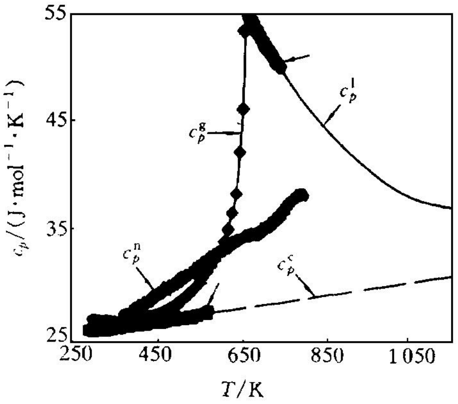

Fig.3 $c_p^l(T)$, $c_p^g(T)$, $c_p^n(T)$ data
(Thick line is measuring scattering data,
thin line is $c_p(T)$ function.)

REFERENCES

1 Altounian Z. Mat Sci Eng, 1988, 97: 461.
2 Lück R, Jiang Q and Predel B. J Non-Cryst Solids, 1990, 117-118: 911.
3 Beeli C, Nissen H U, Jiang Q *et al*. Mat Sci Eng, 1991, A133: 346.
4 Lu K, Wang J T and Wei W D. Scripta Metall Mater, 1991, 25: 619.
5 Lu K, Lück R and Predel B. Acta Metall Mater, 1994, 42: 2303.
6 Inoue A, Zhang T and Masumoto T. J Non-Cryst Solids, 1993, 156-158: 473.
7 Zhang T, Inoue A and Masumoto T. Mater Trans JIM, 1991, 32: 1005.
8 Jiang Q, Lück R and Predel B. Z Metallkd, 1990, 81: 214.
9 Jiang Q, Zhao M and Li J C. Acta Metall Sin (Eng Let), 1995, 8: 23.
10 Jiang Q, Li J C and Tong J. Mat Sci Eng, 1995, A196: 165.
11 Ohsaka K, Trinh E H, Holzer J C *et al*. Appl Phys Lett, 1993, 62: 2319.
12 Bergman C and Komarek K L. Calphad, 1985, 9 (1): 1.
13 Smith J F, Jiang Q, Lück R *et al*. J Phase Equilibria, 1991, 12: 538.

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