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Thermodynamic properties of liquid, undercooled liquid and amorphous Al–Cu–Zr and Al–Cu–Ni–Zr alloys

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Abstract

The heat capacity, $C_p(T)$, of undercooled liquid, amorphous and crystalline $Al_{7.5}Cu_{27.5}Zr_{65}$, the crystallization enthalpy of the amorphous state and the enthalpy of melting of crystalline $Al_{7.5}Cu_{27.5}Zr_{65}$ were measured using differential scanning calorimetry. An adiabatic calorimeter was used to measure the heat capacity of liquid $Al_{7.5}Cu_{27.5}Zr_{65}$. The association model was applied to calculate the thermodynamic functions of liquid and undercooled liquid Al–Cu–Zr, Cu–Ni–Zr and Al–Cu–Ni–Zr alloys. The measured $C_p(T)$ of liquid $Al_{7.5}Cu_{27.5}Zr_{65}$ and $Al_{7.5}Cu_{17.5}Ni_{10}Zr_{65}$ at the liquidus temperature is larger than that of the undercooled liquid state above the glass transition temperature. The calculated $C_p(T)$ curves exhibit a maximum for the undercooled liquid state.

Keywords: Enthalpy of formation; Heat capacity; Undercooled liquid alloys; Amorphous Al–Cu–Zr, Al–Cu–Ni–Zr

1. Introduction

Amorphous alloys are produced at cooling rates greater than 10^4 K s^{-1} to avoid nucleation and crystal growth between liquidus and glass transition temperatures, and thus, their shape is limited to thin ribbons with thicknesses less than 50 μm [1]. In recent years, new alloy compositions were found which enable the production of bulk amorphous alloys at cooling rates less than 10^2 K s^{-1} [2]. Liquid Al–Cu–Zr and Al–Cu–Ni–Zr alloys exhibit this easy glass formation [3,4] which is directly correlated to their thermodynamic properties in the liquid and undercooled liquid state. In order to calculate their thermodynamic properties, it is necessary to have reliable thermodynamic data for their constituent binaries and ternaries first. We have already performed an extensive series of investigations of the composition dependence of the enthalpy of mixing, ΔH, of liquid alloys such as Al–Cu [5], Al–Ni [5], Cu–Ni [5], Cu–Zr [7,10] Al–Zr [11] Ni–Zr [12], Al–Cu–Ni [6], Al–Cu–Zr [11], Cu–Ni–Zr [12], Al–Ni–Zr [13] and Al–Cu–Ni–Zr [13]. In this work, the heat capacity in the amorphous, crystalline and undercooled liquid state and the crystallization enthalpy of $Al_{7.5}Cu_{27.5}Zr_{65}$ were measured by differential scanning calorimetry (DSC). The heat capacity of liquid $Al_{7.5}Cu_{27.5}Zr_{65}$ was measured by an adiabatic calorimeter. Previously, we have described the thermodynamic properties of liquid and undercooled liquid Al–Cu [5], Al–Ni [5], Cu–Ni [5], Al–Zr [18], Ni–Zr [18], Al–Cu–Ni [6] and Al–Ni–Zr [18] using the association model. The ternary data of the liquid Al–Cu–Zr, Cu–Ni–Zr alloy will be described in Section 4 using the association model. On the basis of the model parameters of the constituent binary and ternary systems,

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the thermodynamic properties of Al–Cu–Ni–Zr will be calculated.

2. Experimental

The alloy samples for the measurements were prepared from Al (purity 99.9%), Cu (purity 99.99%), Ni (purity 99.95) and Zr (purity 99.95%). The studied amorphous alloy ribbons were produced using the melt-spinning apparatus at the Max-Planck-Institut für Metallforschung. Ribbon production was carried out in a low pressure (1.3×10^4 Pa He atmosphere) chamber; the gap between the chilling copper wheel and the silica glass crucible with a planar slot was 3 mm. The surface velocity of the copper wheel was about 20 m s^{-1}. More details about the spinning procedure have been described previously in [14]. The heat capacity of the relaxed amorphous and the crystalline $Al_{7.5}Cu_{27.5}Zr_{65}$ alloys were measured by DSC using the stepwise heating method [15].

The heat capacity of the liquid was measured using an adiabatic calorimeter. Details concerning the calorimeter set-up and the measurement procedure have been published previously [16]. The measurements were performed in the isothermal mode. The sample and the boron nitride (BN) container were heated for a short time (about 2–4 s) and the associated small temperature increase ΔT (about 1–1.5 K) is measured within 10–20 s. From the electrical energy ΔQ supplied to an inner heater of the sample container, the product of specific heat capacity of container, heater and sample $c_p^{c,s}$ and their mass $m^{c,s}$ is given by

$$c_p^{c,s}\left(T+\frac{\Delta T}{2}\right)m^{c,s}=\frac{\Delta Q}{\Delta T} \quad (1)$$

The heat capacity C_p^l of the liquid alloy can be obtained from

$$C_p^l=\frac{m^{c,s}c_p^{c,s}-m(\mathrm{BN})c_p(\mathrm{BN})}{M} \quad (2)$$

The product of the specific heat capacity of container material and heater c_p(BN) and their mass m(BN) is measured using a massive BN block with the dimensions of the sample container. M is the number of moles of the alloy. With this adiabatic calorimeter, C_p^l of liquid alloys can be determined without any calibration procedure [16].

3. Results

Amorphous $Al_{7.5}Cu_{27.5}Zr_{65}$ exhibit a glass transition temperature at T_g = 666 K followed by a wide undercooled liquid region with a temperature interval ΔT = 74 K and the onset of crystallization at T_c = 740 K (see Fig. 1) using a heating rate of 0.67 K s^{-1}. The measured crystallization and melting enthalpy of relaxed amorphous $Al_{7.5}Cu_{27.5}Zr_{65}$ and $Al_{7.5}Cu_{17.5}Ni_{10}Zr_{65}$ amounted to 4.5 ± 1, 7.2 ± 1 and

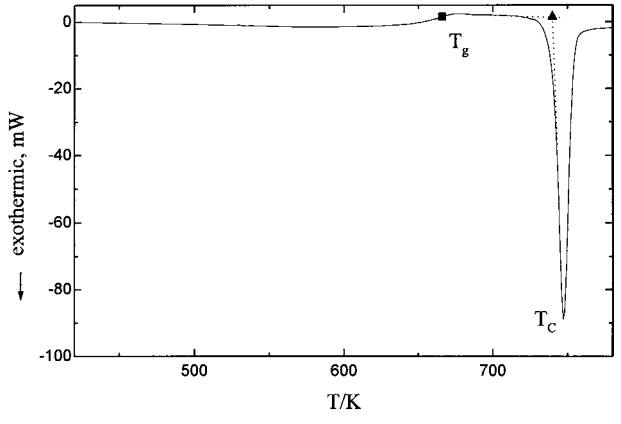

Fig. 1. DSC curve of amorphous $Al_{7.5}Cu_{27.5}Zr_{65}$ at a heating rate of 0.67 K s^{-1}. T_g and T_c represent the glass temperature and the crystallization temperature, respectively.

Table 1
Temperature dependence of the heat capacity of $Al_{7.5}Cu_{27.5}Zr_{65}$

C_p^s (T)	$(21.52 \pm 0.2) + (8.5 \pm 0.2)\times10^{-3}$ T (300 K < T < 750 K)
C_p^g (T)	$(23.19 \pm 0.2) + (8.5 \pm 0.2)\times10^{-3}$ T (300 K < T < 627 K)
C_p^l (T)	42 ± 2 (669 K < T < 677 K)

Table 2
Heat capacity of liquid $Al_{7.5}Cu_{27.5}Zr_{65}$

Temperature (K)	C_p (J mol^{-1} K^{-1})	Temperature (K)	C_p (J mol^{-1} K^{-1})
$Al_{7.5}Cu_{27.5}Zr_{65}$			
1175	43.4	1217	42.1
1180	42.6	1220	43.1
1185	44.9	1225	42.7
1190	42.7	1227	42.1
1195	43.0	1230	40.9
1200	43.4	1235	40.1
1205	44.8	1238	40.4
1207	44.4	1244	40.7
1210	43.2	1249	42.2
1212	42.8	1254	40.8
1215	42.9	1259	39.7

12.8 ± 1.5 and 10.3 ± 1.5 kJ mol^{-1}, respectively. The heat capacities obtained from the stepwise heating method of the relaxed amorphous and crystalline $Al_{7.5}Cu_{27.5}Zr_{65}$ exhibit a linear temperature dependence (see Table 1 and Fig. 8).

The experimental results of the heat capacity measurement of liquid $Al_{7.5}Cu_{27.5}Zr_{65}$ are given in Table 2 and shown in Fig. 8. The standard deviation of the obtained values is about ±5%. The liquidus temperature, T_L = 1180 K, of $Al_{7.5}Cu_{27.5}Zr_{65}$ was determined from the C_p measurements using the fact that the crystallization of a solid phase at $T < T_L$ causes a reduction of the total heat capacity of the sample.

4. Discussion

The large negative ΔH values of liquid Cu–Ni–Zr [12] and Al–Cu–Zr [13] alloys show a strong compound forming tendency which result in chemical short range order (CSRO). The CSRO depends on composition and temperature. The association model [17] describes a relation between CSRO and the thermodynamic mixing functions. This model assumes the existence of associates, each with fixed stoichiometry but undefined life time and free atoms in dynamic equilibrium with them. This equilibrium is governed by the law of mass action. For liquid alloys, the following relations are derived for the enthalpy and entropy of mixing:

$$\Delta H = \frac{1}{\sum_{j=1}^{k} n_j} \times \left(\frac{1}{2} \sum_{k=1}^{k'} \sum_{l=1}^{k'} C_{k,l}^{\mathrm{reg}} \frac{n'_k n'_l}{\sum_{i=1}^{k'} n'_i} + \sum_{i=1}^{k'} n'_i \Delta H_i^0 \right) \tag{3}$$

$$\Delta S = \frac{1}{\sum_{j=1}^{k} n_j} \left(\sum_{i=1}^{k'} (-R n'_i \ln z_i + n'_i \Delta S_i^0) \right) \tag{4}$$

where k is the number of components, n the number of moles of the components, k' the number of species (monomer, associates), n'_i the number of moles and z_i the composition of the species, respectively. ΔH_i^0 and ΔS_i^0 are the enthalpy and entropy of formation of the associates with $\Delta G_i^0 = \Delta H_i^0 - T\Delta S_i^0 < 0$. The monomers (say A) are described as associates of the type A_1, B_0, C_0,... and the Gibbs energy of formation $\Delta G^0_{A_1B_0C_0} = 0$. The interaction parameters between the species k and l are represented by $C_{k,l}^{\mathrm{reg}}$ and it is assumed that $C_{k,k}^{\mathrm{reg}} = 0$. The equilibrium values of n'_i are determined by the law of mass action:

$$\exp\left[-\frac{\Delta H_i^0 - T\Delta S_i^0}{RT} \right] = \frac{z_i \gamma'_i}{\prod_{j=1}^{k} (z_j \gamma'_j)^{e_{i,j}}} \tag{5}$$

γ' is the activity coefficient of the respective species k'. $e_{i,j}$ is the stoichiometric factor of component j in associate i. The parameters ΔH_i^0, ΔS_i^0 and the interaction parameters are determined by solving Eqs. (3)–(5) iteratively by fitting the experimental data. These parameters are determined for liquid Al–Zr [18], Al–Cu [5] and Ni–Zr [18] alloys assuming the existence of Al_2Zr_1, Al_1Cu_3 and Ni_2Zr_1 associates, respectively. Stoichiometry of associate and the parameters of liquid Cu–Zr were determined from the experimental results [7,8–10] and are given in Table 3. The Cu–Ni alloys can be described using the regular solution model [5]. For the calculation of the thermodynamic properties of the ternary liquid Al–Cu–Zr and Cu–Ni–

Table 3
Association model parameters of the limiting binary and ternary systems of Al–Cu–Ni–Zr (in kJ mol^{-1})

Associate	ΔH^0_{ass}	ΔS^0_{ass}	$C^{reg}_{A,B}$	$C^{reg}_{A,ass}$	$C^{reg}_{B,ass}$	$C^{reg}_{A,ass}$	$C^{reg}_{B,ass}$	$C^{reg}_{C,ass}$	Reference
Cu_2Zr_1	−55.94	−0.02214 K^{-1}	−55.33	−25.88	−48.77				This work
Al_1Cu_3	−82.95	−0.0348 K^{-1}	−38.57	−74.78	−11.37				[5]
Al_2Zr_1	−155.14	−0.045 K^{-1}	−75.85	−28.87	−125.06				[18]
Ni_2Zr_1	$-124.1–10^{-2} \times (T - 2360) + 2.25 \times 10^{-5} \times (T^2 - 2360^2) - 3.53 \times 10^{-9} \times (T^3 - 2360^3)$	$-0.0405–10^{-2} \times \ln(T/2360) + 4.5 \times 10^{-5} \times (T - 2360) - 5.3 \times 10^{-9} \times (T^2 - 2360^2)$ K^{-1}	−113.46	−113.04	−115.17				[18]
Al_1Ni_1	−127.0	−0.029 K^{-1}	−68.9	−23.0	−32.7				[5]
Cu–Ni	–	–	13.2	–	–				[5]
$Al_1Cu_1Zr_1$	$-160.4–0.091 \times (T - 1650) + 1.07 \times 10^{-3} \times (T^2 - 1650^2) - 3.7 \times 10^{-7} \times (T^3 - 1650^3)$	$-0.024–0.091 \ln(T/1650) + 2.14 \times 10^{-3} \times (T - 1650) - 5.5 \times 10^{-7} \times (T^2 - 1650^2)$ K^{-1}				−65.80	−80.04	−58.60	This work
$Al_2Ni_2Zr_1$	$-329.6 + 8 \times 10^{-2} \times (T - 1400) - 2.75 \times 10^{-4} \times (T^2 - 1400^2) + 1 \times 10^{-7} \times (T^3 - 1400^3)$	$-0.014 + 0.08 \times \ln(T/1400) - 5.5 \times 10^{-4} \times (T - 1400) + 1.5 \times 10^{-7} \times (T^2 - 1400^2)$ K^{-1}				–81.24	−89.32	−85.65	[18]

Zr alloys, one has to consider three monomers and three binary associates, respectively. Interaction between the associates themselves is not assumed. The equilibrium values of the mole numbers of the different species n'_i are determined according to Eq. (5) with the model parameters listed in Table 3. The $\Delta H(x)$ of liquid and undercooled liquid Cu–Ni–Zr alloys calculated using the association model of their constituent binaries for different section at 1565 K correspond reasonably to the experimental results [12] (see Fig. 2). The $\Delta H(x)$ values of liquid and undercooled liquid Al–Cu–Zr alloys at 1568 K calculated on the basis of their binary model parameter are less negative than the experimental values given in [11]. The difference between experimental as well as the extrapolated experimental values and calculated values shows systematic deviations due to additional large ternary interactions. The deviations of about -16.5 kJ mol^{-1} center around the composition $Al_{33}Cu_{33}Zr_{34}$ (see Fig. 3). The influence of these ternary interactions, which produce additional composition and temperature dependent CSRO, is described in a further evaluation by an additional ternary association reaction with an $Al_1Cu_1Zr_1$ stoichiometry. It is assumed that this ternary associate interacts only with the monomers. The consideration of additional interactions between associates divides only the influence of the interactions and increases the number of model parameters.

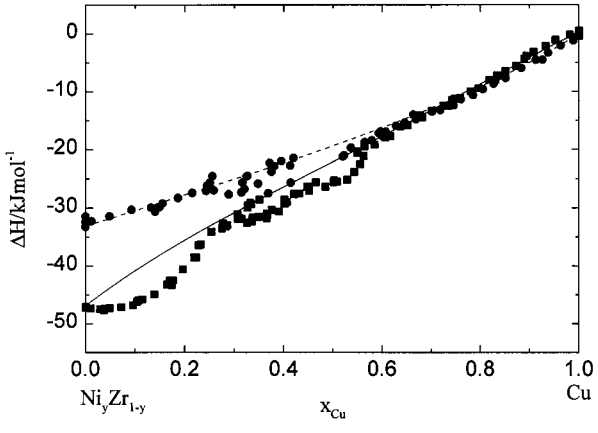

Fig. 2. Integral enthalpy of mixing of the liquid and undercooled liquid Cu–Ni–Zr alloys calculated using the association model with model parameters of the limiting binary systems given in Table 3 for $y = 0.64$, — and $y = 0.36$, - - - at 1556 K; ■, $y = 0.64$; ●, $y = 0.36$ experimental values [12]. Standard states: Cu(l), Ni(l) and Zr(l).

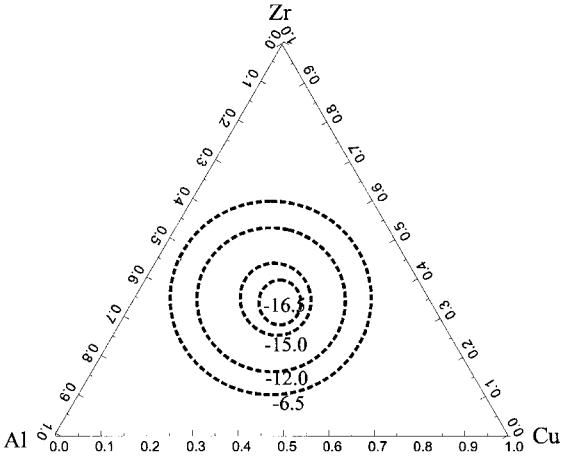

Fig. 3. Difference between the experimental [12] and the calculated enthalpy of mixing of liquid and undercooled liquid Al–Cu–Zr alloys at 1568 K in kJ mol^{-1} using model parameters of the limiting binary systems given in Table 3. Standard states: Al(l), Cu(l) and Zr(l).

The temperature dependence of ΔH of liquid Al–Cu–Zr alloys could be described assuming a temperature dependent enthalpy and entropy of formation of $Al_1Cu_1Zr_1$. A temperature dependence of the interaction parameters is not assumed. The temperature dependent $\Delta H^0_{Al_1Cu_1Zr_1}(T)$ and $\Delta S^0_{Al_1Cu_1Zr_1}(T)$ are calculated using the excess heat capacity ΔC^l_p which can be calculated from the experimental C^l_p in Table 3 and the C^l_p of the mechanical mixture of the pure liquid and undercooled liquid components. ΔC^l_p is directly connected to $\Delta H(x,T)$:

$$\Delta C^l_p\left(x_1, T_1+\frac{T_1-T_2}{2}\right)=\frac{\Delta H(x_1,T_1)-\Delta H(x_1,T_2)}{T_1-T_2} \tag{6}$$

$\Delta H^0_{Al_1Cu_1Zr_1}(T_0)$ and $\Delta S^0_{Al_1Cu_1Zr_1}(T_0)$ were fixed at 1650 K where the extrapolated ΔC^l_p tended to zero and the following relationships for $T < 1650$ K were used:

$$\Delta H^0_{ass}(T) = \Delta H^0_{ass}(T_0) + A(T-T_0) + \frac{B}{2}(T^2-T_0^2) + \frac{C}{3}(T^3-T_0^3) \tag{7}$$

$$\Delta S^0_{ass}(T) = \Delta S^0_{ass}(T_0) + A\ln\left(\frac{T}{T_0}\right) + B(T-T_0) + \frac{C}{2}(T^2-T_0^2) \quad (8)$$

The resulting model parameters are given in Table 3. The calculated C_p^l of $Al_{7.5}Cu_{27.5}Zr_{65}$ and $\Delta H(x,1568\,K)$ show a good agreement with the experimental results (see Figs. 4, 5, 6 and 8). Fig. 7 shows the projection of the calculated isoenthalpic lines on the Gibbs triangle of liquid and undercooled liquid Al–Cu–Zr alloys at 1568 K. The strongest interactions in these ternary alloys show up in the binary Al–Zr system. The calculated C_p^l (T) of liquid and undercooled liquid $Al_{7.5}Cu_{27.5}Zr_{65}$ exhibits a maximum in the undercooled liquid state and corre-

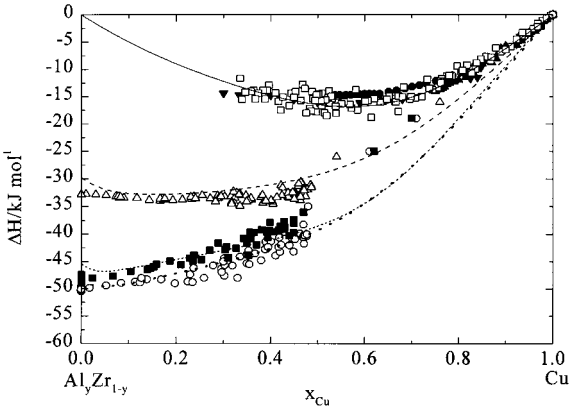

Fig. 4. Integral enthalpy of mixing of the liquid and undercooled liquid Al_yZr_{1-y}–Cu alloys calculated using the association model with model parameters given in Table 3 for $y = 0$, —; $y = 0.4$, ...; $y = 0.62$, · · ·and $y = 0.8$, - - - at 1568 K; □ [7], ▼ [8], ● [9] ▲ [10], $y = 0$; ■, $y = 0.4$; ○, $y = 0.62$ and △, $y = 0.8$ [11] experimental values. Standard states: Al(l), Cu(l) and Zr(l).

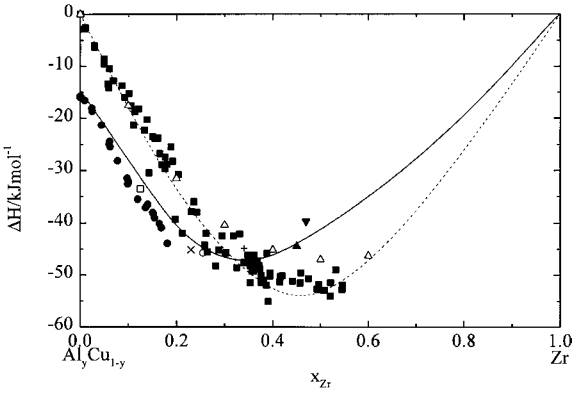

Fig. 5. Integral enthalpy of mixing of the liquid and undercooled liquid Al_yCu_{1-y}–Zr alloys calculated using the association model with model parameters given in Table 3 for $y = 1$, - - - and $y = 0.55$,— at 1568 K; ■ [11], △ [26], $y = 1$; ●, $y = 0.55$ [11] experimental values; □, +, ×, ○ experimental values from different sections [11]. Standard states: Al(l), Cu(l) and Zr(l).

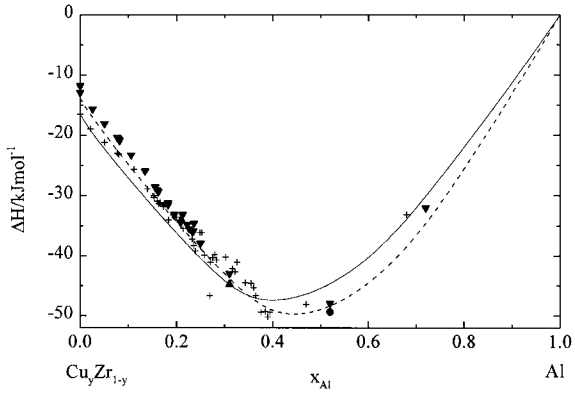

Fig. 6. Integral enthalpy of mixing of the liquid and undercooled liquid Cu_yZr_{1-y}–Al alloys calculated using the association model with model parameters given in Table 3 for $y = 0.33$, - - - and $y = 0.46$, — at 1568 K; ▼, $y = 0.33$; +, $y = 0.46$ experimental values; ●, ▲ experimental values from different sections [11]. Standard states: Al(l), Cu(l) and Zr(l).

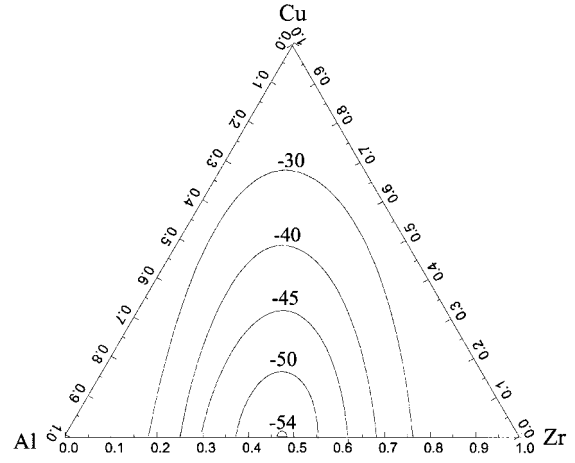

Fig. 7. Integral enthalpy of mixing Al–Cu–Zr liquid alloys at 1568 K in kJ mol^{-1} calculated using the association model. Standard states: Al(l), Cu(l) and Zr(l).

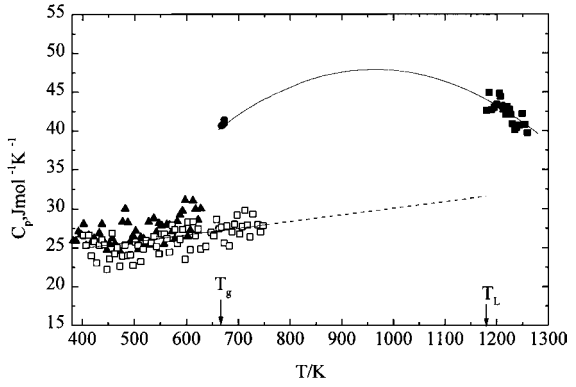

Fig. 8. Heat capacity of liquid (■), undercooled liquid (●), crystalline (□) (- - -) and relaxed amorphous (▲) $Al_{7.5}Cu_{27.5}Zr_{65}$. (—) Calculated using the association model with model parameters given in Table 3. Standard states: Al(l), Cu(l) and Zr(l).

sponds reasonably to the experimental values (see Fig. 8). The temperature dependent CSRO described with the association model produces the maximum of C_p^l (T). The increasing heat capacity of the undercooled liquid as a function of temperature reflects the increasing CSRO. Fig. 9 shows the calculated temperature dependence of the number of moles of the assumed associates of liquid and undercooled liquid $Al_{7.5}Cu_{27.5}Zr_{65}$.The number of moles of Al_2Zr_1 and Al_1Cu_3 are very small. The $C_p(T)$ is determined mainly by the temperature dependence of the number of moles of the ternary associate. $n'_{Al_1Cu_1Zr_1}$ increases

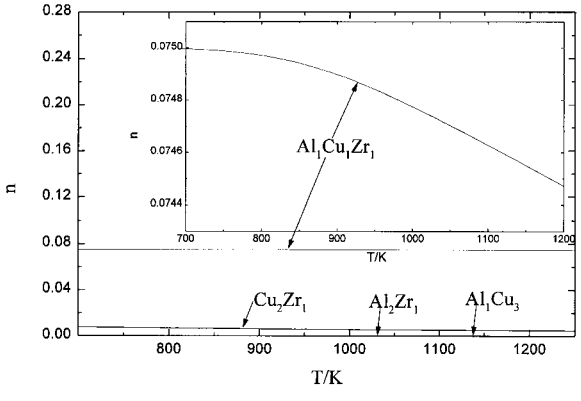

Fig. 9. Temperature dependence of the number of moles of binary Cu_2Zr_1, Al_2Zr_1, Al_1Cu_3 and ternary $Al_1Cu_1Zr_1$ associates.

with decreasing temperature and a change in slope of $n'_{Al_1Cu_1Zr_1}$ causes the maximum in C_p^l (T). A similar C_p^l (T) behavior has been reported recently [18,19–22] for other good glass forming alloys.

The thermodynamic properties of liquid Al–Cu–Ni–Zr alloys were calculated on the basis of the model parameters of the constituent binary and ternary systems. The equilibrium values of the numbers of moles of the different species n'_i are determined according to Eq. (6) with the model parameters listed in Table 3. The calculated $\Delta H(x)$ of liquid and undercooled liquid Al–Cu–Ni–Zr alloys at 1565 K are plotted in Fig. 10. The calculated and the experimental $\Delta H(x)$-values compare reasonably with each other.

The excess heat capacity ΔC_p^l of liquid and undercooled liquid alloys can be obtained from the dependence on temperature and composition of $\Delta H(x,T)$ as given by Eq. (6). C_p^l can be calculated from ΔC_p^l and the C_p^l of the mechanical mixture of the pure liquid and undercooled liquid components. The calculated C_p^l of $Al_{7.5}Cu_{17.5}Ni_{10}Zr_{65}$ also exhibits a maximum in the undercooled liquid state and corresponds reasonably to the experimental values given in [20,23] (see Fig. 11).

The results of the association model for the C_p^l of the undercooled liquid forming alloys are examined using the thermodynamic relation

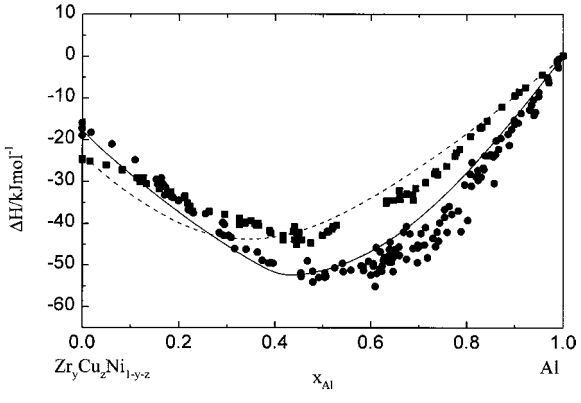

Fig. 10. Integral enthalpy of mixing of the liquid and undercooled liquid Al–Cu–Ni–Zr alloys calculated using the association model with model parameters given in Table 3 for $y = 0.7$, $z = 0.19$, — and $y = 0.35$, $z = 0.41$, - - - at 1565 K; ■, $y = 0.35$, $z = 0.41$ and ●, $y = 0.70$, $z = 0.19$ experimental values [12]. Standard states: Al(l), Cu(l), Ni(l) and Zr(l).

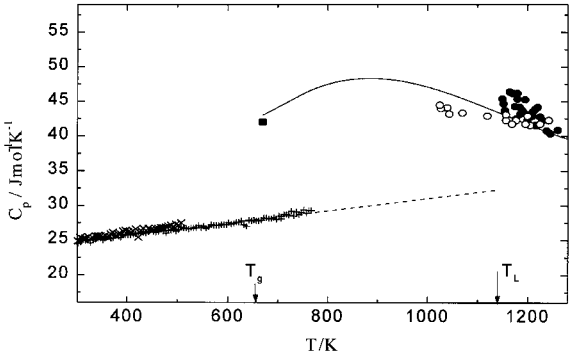

Fig. 11. Heat capacity of liquid (●) [20] (○) [23], undercooled liquid (■) [24], crystalline (+) [24] (- - -) and relaxed amorphous (×) [24] $Al_{7.5}Cu_{17.5}Ni_{10}Zr_{65}$. — Calculated using the association model with model parameters given in Table 3. Standard states: Al(l), Cu(l), Ni(l) and Zr(l).

$$-\Delta H_c(T_c) = \Delta H^m(T_L) + \int_{T_L}^{T_c} [C_p^l(T) - C_p^s(T)]dT \quad (9)$$

The heat capacity C_p^s of crystalline $Al_{7.5}Cu_{27.5}Zr_{65}$ is given in Table 1 and that of $Al_{7.5}Cu_{17.5}Ni_{10}Zr_{65}$ in [24]. The calculated ΔH_c and the ideal glass temperature [25] at $\Delta S^l - \Delta S^s = 0$ of $Al_{7.5}Cu_{27.5}Zr_{65}$ and $Al_{7.5}Cu_{17.5}Ni_{10}Zr_{65}$ are given in Table 4. The calculated ΔH_c corresponds to the measured values. The calculated ideal glass temperature is less than the kinetic glass temperature obtained with a heating rate of 0.67 K s^{-1}.

Table 4
Experimental data for calculating the crystallization enthalpy according to Eq. (9)

Alloys	$Al_{7.5}Cu_{27.5}Zr_{65}$	$Al_{7.5}Cu_{17.5}Ni_{10}Zr_{65}$
T_L (K)	1180	1140
T_c (K)	717	732 [20]
T_g (K)	666	657 [24]
ΔT (K)	51	75
T_g^{id} (K)	609	654
ΔH^m (kJ mol^{-1})	12.8 ± 1.5	10.3 ± 1.5
ΔH_c^{exp} (kJ mol^{-1})	−5.0 ± 1.5	−5.7 ± 1.5
ΔH_c^{cal} (kJ mol^{-1})	−4.5	−7.2

5. Conclusions

The thermodynamic functions of liquid and undercooled liquid Cu–Ni–Zr and Al–Cu–Ni–Zr alloys could be calculated with the association model using the model parameters of the limiting binary and ternary systems, respectively. The calculated C_p^l (T)'s of the undercooled liquid $Al_{7.5}Cu_{27.5}Zr_{65}$ and $Al_{7.5}Cu_{17.5}Ni_{10}Zr_{65}$ exhibit a maximum, which corresponds reasonably to the experimental C_p^l (T). The temperature dependent CSRO described with the association model causes the maximum in the C_p^l (T) curves.

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