Thermodynamic Modeling of the Undercooled Liquid in the Ni–Zr System

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Using thermodynamic data obtained over a wide range of temperatures, a thermodynamic assessment of the Ni–Zr system was carried out. The associated solution model was applied to describe the short range ordering in the liquid, and the glass transition was treated as a second order transition, using the Hillert–Jarl functions. The driving force of crystallization, and the time–temperature–transformation (TTT) curves were estimated from the optimized parameter set, and compared with experimental data and the results of previous thermodynamic assessments. Taking into account the low temperature thermodynamic data, the calculated driving force was found to have decreased compared to the previous assessments. Consequently, the nose of the TTT curve was shifted to higher times.

Keywords: metallic glasses, crystallization, short range ordering, thermodynamic assessment

1. Introduction

The bulk metallic glasses have been found in various alloy systems.1 It has been investigated intensively in recent years, in order to improve glass-forming ability (GFA) of those glassy alloys and to explore alloys with higher GFA. The GFA has usually been discussed using indicators such as the undercooled liquid range, the reduced glass transition temperature, the critical cooling rate of glass formation and the TTT curves were calculated by using accessed data, and they were compared with the experimental data and the results of the previous assessment.

In the CALPHAD method to estimate the indicators of the GFA of alloys,5–7 enthalpies, activities and phase equilibria are taken into account in the thermodynamic assessments. The short range ordering and heat capacities, however, are usually not included and recognized as the most neglected quantities8,9 of all the thermodynamic quantities in terms of the experimental investigation. When estimating the heat capacity of alloys, in most cases, the Kopp–Neumann rule is assumed. In other words, no short range ordering and random mixing are assumed in the liquid. This is a good assumption for the case where interactions between elements in the liquid are small. For compound-forming systems characterized by large negative interaction energies between elements,10 however, this assumption is not true. In fact, many researchers have reported that the short range ordering exists at low temperatures, in particular, and results in a stable undercooled liquid.11–14 Recently, the authors have shown in the Cu–Zr system15 that these thermodynamic data at low temperatures are required for an accurate estimation of the driving forces and critical cooling rates. Since the Ni–Zr system is a compound-forming system, the low temperature data should be taken into account for the estimation of these indicators of GFA of alloys as well as the Cu–Zr system. In the previous thermodynamic assessment of the Ni–Zr system performed by Ghosh,16 however, only high temperature thermodynamic data were used and low temperature data was not considered.

In the present study, the Gibbs free energy of the liquid phase of the Ni–Zr system was assessed using thermodynamic data obtained over a wide range of temperatures. The driving force of crystallization from the undercooled liquid, the critical cooling rate of glass formation and the TTT curves were calculated by using accessed data, and they were compared with the experimental data and the results of the previous assessment.

2. Method

2.1 Associated solution model

Compared to various thermodynamic models, used to describe the effect of short range ordering in liquids, the Associated Solution Model17,18 is advantageous since it can be applied with ease in the optimization of the CALPHAD assessment. Thus, in the present study the Associated Solution Model was employed for the description of the short range ordering.

In the present assessment, it was assumed that in the liquid there is only a single associate NiZr1 because of the minimum in the mixing enthalpy of the liquid, found in the Ni-rich side.19 In the liquid, it is assumed that nNiZr1 mole of the associate Ni2Zr1 is in equilibrium with nNi and nZr moles of free Ni and Zr atoms, respectively.

The excess Gibbs free energy of mixing, $G_m^{ex}$, is given by

$$
G_m^{ex} = \frac{n_{NiZr1}}{n} G_{NiZr1}^{0} + \frac{n_{Ni}}{n} G_{Ni}^{reg} + \frac{n_{Zr}}{n} G_{Zr}^{reg} + n_{NiZr1} \ln \frac{n_{NiZr1}}{n} + n_{Ni} \ln \frac{n_{Ni}}{n} + n_{Zr} \ln \frac{n_{Zr}}{n} + RT \left( \frac{n_{Ni}}{n} \right) + \Delta G_m^{L-Am} \tag{1}
$$

where $G_{NiZr1}$, $T$, $R$ and $n$ are the change in the Gibbs free energy due to the formation of the associate, temperature, the gas constant and the sum of moles of atoms and associates, given by $n = n_{Ni} + n_{Zr} + n_{NiZr1}$, respectively. $G_{NiZr1}^{reg}$, $G_{Ni}^{reg}$ and $G_{Zr}^{reg}$ are the Gibbs free energies due to the interactions between Ni, Zr, and the associate, given by the Redrich–Kister polynomials as
where $L_{ij}^k$ are interaction parameters between components $i$ and $j$. $\Delta G_{i,j}^{L-Am}$ is the change in the Gibbs free energy for the glass transition. The parameters in eqs. (1) and (2) were fitted to experimental data using the Parrot module in the Thermo-Calc software package.

### 2.2 A thermodynamic model for the glass transition

In this study, the thermodynamic model proposed by Shao\cite{20} was employed because the model has the advantage that the glass transition temperature can be fitted directory to experimental data. In this model the glass transition is treated as a second order transition with the Hillert–Jarl functions.\cite{21}

The Gibbs free energy change due to the glass transition is described by the following equation:

$$ \Delta G^{L-Am}_{m} = -RT_{g} \ln(1 + \alpha) f(\tau), \quad (3) $$

where $\tau$, $\alpha$, and $f(\tau)$ are temperature (normalized by the glass transition temperature $T_{g}$), a factor due to the amorphization, and the Hillert–Jarl function, respectively. $\alpha$ and $T_{g}$ are composition dependent and for the Ni–Zr liquid are given by the following equations:

$$
T_{g} = n_{Ni} T_{Ni}^{N} + n_{Zr} T_{Zr}^{N} + n_{Ni,Zr} T_{Ni,Zr}^{N} + n_{Ni} n_{Zr} \Omega_{0}^{Ni} n_{Ni}^{2} \frac{n_{Ni}^{2} T_{Ni} + 2 n_{Ni} n_{Zr} \Omega_{0}^{Ni,Zr} T_{Ni,Zr}}{n_{Ni} n_{Zr} + n_{Ni}^{2} \Omega_{0}^{Ni} n_{Ni}^{3} + n_{Ni} n_{Zr} \Omega_{0}^{Ni,Zr}}, \quad (4a)
$$

$$
\alpha = \alpha_{Ni} + \alpha_{Zr} + \alpha_{Ni,Zr} + \alpha_{Ni} n_{Zr} + \alpha_{Ni} n_{Zr} \Omega_{0}^{Ni} n_{Ni} n_{Zr}, \quad (4b)
$$

$$
\alpha_i, T_i^{N}, \Omega_i^{N}, \text{and } \Omega_i^{N,j}, \text{are constants and were fitted to experimental data using the PARROT module in the Thermo-Calc software package.}
$$

### 2.3 Experimental data

The mixing enthalpies in the liquid have been studied at 1565 K,\cite{19} 1784 K,\cite{22} 1838 K,\cite{22} 1916 K,\cite{23} 1963 K,\cite{24} and 2270 K.\cite{23} At low temperatures, the formation enthalpy of amorphous alloys was measured by Turchanin et al.,\cite{25} Spitz et al.,\cite{26} and Henaf et al.\cite{27} where there measurements are not in agreement. The formation enthalpy reported by Turchanin et al.\cite{25} is a more negative result and in this case the amorphous phase would be more stable than the intermetallic compounds.\cite{16} This originates from the large negative value measured at infinite dilution (Pure-Zr) of the thermal effect from experiments, $-235$ kJ/mol. Since Ansara et al.\cite{28} reported a less negative value, $-212.41$ kJ/mol, we recalculated the formation enthalpy in ref. 25 using the Ansara’s value.

Heat capacities of the liquid and amorphous phases have been measured by Witusiewicz and Sommer\cite{19} and by Ohsaka and Trinh.\cite{29} There are numerous measurements of both latent heats of crystallization from the undercooled liquid\cite{27,30-35} in the case of the Ni–Zr alloys, it is difficult to measure the glass transition temperature, which it was not detected on the DSC heating curve.\cite{29,36} Altounian et al.\cite{34} have pointed out that higher heating rates are required to observe the glass transition because the enthalpy change of the transition is much smaller than that of the crystallization. Although it is limited, there are some experimental data available in the literature\cite{33,37-39} which are used in the present assessment.

In the Ni–Zr system, the Gibbs free energies of the intermetallic compounds have been well established by Zaitsev et al.\cite{40} Thus, in the present study, the thermodynamic assessment of the liquid phase was carried out keeping these Gibbs free energies of the intermetallic phases fixed.

### 3. Results and Discussions

### 3.1 Results of the thermodynamic assessment

The optimized parameter set for the liquid phase is given in Table 1. The calculated phase diagram of the Ni–Zr system is shown in Fig. 1(a). Experimentally determined invariant reactions\cite{40} are reproduced well with the Gibbs free energy of the liquid phase assessed in the present work. The mixing enthalpy in the liquid has a strong temperature dependency and significantly decreases with decreasing temperature, due to the associate formation in the liquid, as shown in Fig. 1(b). Figure 1(c) shows the glass transition temperatures obtained in the present assessment and from experimental data, and clearly the glass transition temperatures are in good agreement with the experimental data. Furthermore, calculated mixing enthalpies in the liquid are in good agreement with the experimental data obtained over the temperature range from 2270 to 1565 K as shown in Fig. 2.

Calculated formation enthalpy of the amorphous phase from pure crystalline elements at 298 K and heat capacity reproduce experimental data very well as shown in Figs. 3(a) and (b). Calculated latent heats of crystallization from the undercooled liquid agree with experimental data although the experimental data are scattered as shown in Fig. 3(c). In Fig. 3(b), are evident in the heat capacity-temperature curve, the sharp peak at around 600 K is due to the glass transition given by eq. (3) and the broad peak at around 1300 K is explained by this increase in the amount of the associate. As shown in Fig. 3(d), the mole fraction of the associate starts to increase rapidly at around 1300 K with decreasing temperature.

### 3.2 The driving force of the crystallization

The phase having the largest driving force is expected to

| Table 1 Optimized thermodynamic parameters for the liquid in the Ni–Zr system (G and L in J/mol, and T and $\Omega$ in K). Parameters with an asterisk are taken from Shao\cite{20}. |
|---------------------|---------------------|---------------------|---------------------|---------------------|
| $G_{Ni,Zr}^{0}$ = $-72000 + 20 T$ |
| $L_{Ni,Zr}^{0}$ = $-170700 + 13.4 T$ |
| $L_{Ni,Zr}^{1}$ = $-90000 + 40 T$ |
| $G_{Ni,Ni,Zr}^{0}$ = $-295000 + 180 T$ |
| $L_{Ni,Ni,Zr,29}$ = $-278000 + 73 T$ |
| $T^{0}_{Ni}$ = 1035 |
| $T^{0}_{Zr}$ = 444 |
| $T^{0}_{Ni,Zr}$ = 855 |
| $\Omega_{Ni,Zr}^{0}$ = 32 |
| $\Omega_{Ni,Ni,Zr}^{0}$ = 15 |
| $\Omega_{Ni,Ni,Zr}^{0}$ = $-58$ |
| $\Omega_{Ni,Ni,Zr}^{0}$ = $-58$ |
form as the primary crystalline phase, at the crystallization temperature, $T_x$. Hence, the driving force is a candidate of an indicator to show the GFA. Figure 4(a) is the driving force of crystallization of intermetallic and solid solution phases at 800 K, as a function of the mole fraction of Zr. The local minima of the driving force at around 40 and 70 at%Zr suggests a higher GFA of alloys in this composition range.

The experimental glass forming ranges (GFR)\(^{41,42}\) are also plotted in the figure. The experimental GFR data agree well with the composition range of the smaller driving forces of crystallization as presented in Fig. 4(a). Dong \textit{et al.}\(^{42}\) reported that the amorphous phase does not form at around the 50 at%Zr, where a relatively low GFA is expected from the high driving force of the formation of the NiZr compound.

In Fig. 4(b), a temperature dependency is observed in the driving force with the crystallization of NiZr from an Ni–50 at%Zr liquid. The linear temperature dependency is obtained in both the present and the previous assessments,\(^{16}\) where the degree of undercooling is small. As the temperature is decreased, however, around $T_g$ where short range ordering dominates, the linear relationship obviously gives an overestimation. In the present assessment, the driving force starts to deviate from the linear relationship at around 1300 K and gradually decreases, due to the formation of the associate as the temperature decreases.

### 3.3 Estimation of the critical cooling rate for the glass formation

Several attempts have been made to estimate the TTT curve of the crystallization.\(^{5,43-45}\) According to Saunders and Miodownik,\(^{5}\) the time, $t$, necessary to form the volume fraction of $X$ is given by the Johnson–Mehl–Avrami equation,

$$t = \frac{44.3\eta}{kT} \left\{ \frac{g^0Xe^{(G*/kT)}}{f^3N_e [1 - e^{(-G_m/RT)}]^3} \right\}^{1/4}, \quad (5)$$
where \( r_0, f, N_v, \eta, G^*, \) and \( G_m \) are the atomic radius, a structural constant, the number of atoms per unit volume, the viscosity, the free energy barrier for the nucleation and the driving force of crystallization from the liquid, respectively. The constants in the equation were taken as \( r_0 = 0.14 \text{ nm}, X = 10^{-6}, f = 0.1, \) and \( N_v = 5 \times 10^{28} \text{ atoms/m}^3.5\)

The thermodynamic factors, \( G^* \) and \( G_m \), were estimated from the optimized parameter set employing the same procedure as in ref. 5. For the viscosity of the undercooled liquid the Vogel–Fulcher equation was applied and the coefficients in the equation were fitted to reproduce experimental data,\(^{46}\) assuming that the viscosity at \( T_g \) is equal to \( 10^{11} \text{ Pa s} \) at \( T_g. \)\(^{47}\) The equation obtained is given in Fig. 5, with the experimental data.

In Fig. 6, TTT curves of the crystallization of NiZr from the undercooled liquid, calculated using the Gibbs free energies assessed in the present study and in the previous works. In the present assessment, the calculated driving force was found to be lower, compared to the previous works, because the low temperature data were included. Consequently, the nose of the TTT curve is shifted significantly to the longer time. The present results suggest strongly that the
thermodynamic data of the liquid, such as the latent heat of crystallization, the heat capacity of the undercooled liquid and the enthalpy of amorphous phase formation, are required for more precise thermodynamic assessments of the liquid phase in compound-forming systems and for the estimation of the TTT curves.

The critical cooling rate $R_c$, one of indicators of GFA, can be approximately estimated from the equation,

$$R_c = \frac{T_m - T_{nose}}{t_{nose}},$$

where $T_{nose}$ and $t_{nose}$ are the temperature and the time at the nose of the TTT curve, respectively. The critical cooling rate, $10^6$ K/s, was estimated for the Ni–Zr alloys.\(^{48}\) Cooling curves corresponding to the cooling rate is plotted in Fig. 6 as a dashed line. In the present case, although the experimental data obtained over a wide range of temperatures were taken into account, the critical cooling rate estimated in the present assessment, $5 \times 10^3$ K/s, is much slower than the experimental result, $10^6$ K/s. This suggests that the crystallization occurs much faster than predicted from the homogeneous nucleation theory. One possible explanation for this large discrepancy is that the heterogeneous nucleation from the undercooled liquid dominates where defects, inclusions, and short range ordered structures, such as an icosahedral cluster, are potential sites for heterogeneous nucleation. Thus, for more quantitative discussions, the investigations on atomic configurations in the undercooled liquids including the short range ordering and their relationship to the nucleation processes are required.

4. Conclusions

The thermodynamic assessment of the liquid phase in the Ni–Zr system was carried out using the thermodynamic quantities, such as the heat capacity, latent heats of crystallization from the undercooled liquid and the formation enthalpy of amorphous phase, obtained over a wide range of temperatures. The following results were obtained;

(1) The consistent set of parameters for the liquid phase in the Ni–Zr system was obtained. The calculated thermodynamic properties are in good agreement with the experimental data.

(2) When the degree of undercooling is small, a linear temperature dependency in the driving force is observed. At low temperatures, the linear relationship results in an overestimation, due to the formation of the short range ordering in the liquid. In the present assessment, the calculated driving force was found to be lower than the previous results because the low temperature data were taken into account. Consequently, the nose of the TTT curve is shifted significantly to the longer time.

(3) The critical cooling rate, $5 \times 10^3$ K/s, obtained in the present study for the crystallization of a Ni–50 at% Zr liquid is much slower than the experimental data, suggesting that the crystallization occurs much faster than that predicted from the homogeneous nucleation theory.

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