International Journal of Thermophysics, Vol. 17, No. 4, 1996

Temperature Dependence of the Mixing Enthalpy and Excess Heat Capacity in the Liquid System Nickel–Zirconium

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Received October 2, 1995

The mixing enthalpy ΔH^{m} of the liquid system Ni–Zr was measured in the Ni-rich range at 1916 K up to $x_{Zr} = 0.34$ at % and for the first time in the Zr-rich range at 2270 K up to $x_{Ni} = 0.54$ at %. Using the thermodynamic-dapted power series, a composition- and temperature-dependent description of ΔH^{m} was given. Furthermore, the partial differentiation of $\Delta H^{m}(x, T)$ by T yielded the excess heat capacity $Cp^{xs}(x, T)$. The existence of chemical short-range order (associate) in the vicinity of Ni_7Zr_2 and NiZr was shown and was discussed with reference to $\Delta H^{m}(x, T)$ and $Cp^{xs}(x, T)$ (1748 to 2270 K). With decreasing temperature, the influence of chemical short-range order tended toward the composition NiZr.

KEY WORDS: binary alloys; emissivity; excess heat capacity; liquid metals; mixing enthalpy; Ni–Zr.

1. INTRODUCTION

The ability of an alloy system to transform to the amorphous state is facilitated by the presence of chemical short-range order (associate) in the melt [1]. Associate forming presupposes strong atomic interactions, which can be identified by the concentration- and temperature-dependent value of the mixing enthalpy $\Delta H^{m}(x, T)$. From this point of view, we are investigating the mixing enthalpy of the binary glass-forming systems Fe–Zr,

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0195-928X/96/0700-0959$09.50/0

Ni–Zr, and Co–Zr. For these systems, data were missing for the Zr-rich range and a temperature-dependent description of ΔH^{m} could not be given [2–7].

The first system investigated was Fe–Zr [8] and a description of $\Delta H^{\mathrm{m}}(x, T)$ was obtained by the regular associate model [9–11]. The composition of the intermetallic compound Fe_2Zr was identified as the predominant associate in the melt.

The experimentally observed composition range of amorphous phases in the Ni–Zr system [12] is 10–78 at % Zr [13]. Detailed information about the thermodynamic data and glass formation is given in the literature [6, 14]. Depending on the temperature and composition, it is to be expected that chemical short-range order for the melt can occur in the vicinity of the three intermetallic compounds Ni_7Zr_2 ($T_{\mathrm{m}} = 1713$ K), NiZr ($T_{\mathrm{m}} = 1533$ K), and $NiZr_2$ ($T_{\mathrm{m}} = 1393$ K).

2. EXPERIMENTS AND THEIR EVALUATION

The mixing experiments were carried out by levitating and melting a base sample A in the electromagnetic field of a levitation coil. With a circulating gas cooling system, the temperature of the sample was adjusted to the desired experiment temperature. Sixteen solid secondary samples B were in a revolving magazine which was mounted above the coil. These solid samples were gradually alloyed into the base sample by turning the magazine. The absolute temperature of the sample as well as the resulting temperature change of each mixing process was measured continuously with a quotient pyrometer, which operates simultaneously at 450 and 650 nm. The quotient pyrometer was calibrated by a partial-radiation

Table I. Temperature Dependence of the Normal Spectral Emissivity of Liquid Nickel and Zirconium

Metal	Temperature range (K)	Normal spectral emissivity	Ref.
Nickel	1789–2109	$\varepsilon_{488} = 0.2957 + 10.651 \times 10^{-5} T$	15
	1776–2063	$\varepsilon_{515} = 0.406 + 0.081 \times 10^{-5} T$	15
	1822–2143	$\varepsilon_{633} = 0.413 - 0.873 \times 10^{-5} T$	15
	1726	$\varepsilon_{650} = 0.395^{a}$	16
Zirconium	2175–2400	$\varepsilon_{633} = 0.41$	15
	2125, emissivities obtained in this work	$\varepsilon_{547} = 0.394^{a}$ $\varepsilon_{650} = 0.383^{a}$	Method given in Ref. 16

[a] Used for calibration of the quotient pyrometer.

pyrometer operating at 547 and 650 nm. The temperature dependence of the emissivity are low in the green spectrum range (515 and 547 nm) and the red range (633 and 650 nm) and the difference is small between the emissivity of liquid Ni and that of Zr (Table I). Therefore, the uncertainty in the absolute temperatures measured was estimated to be ±10 K. The magnitude of the temperature changes that occurred was in the range of 20–91 K.

The evaluation of the temperature–time curve led to a temperature difference ΔT_{L}, which is an important parameter of the energy balance for the mixing process [Eq. (1)]. A detailed description of the experimental method of levitation alloying calorimetry (LAC) and the problems involved is given in Ref. 17.

After j additions of secondary samples we obtain

$$\Delta h_j^{\mathrm{m}} = -\sum_{i=1}^{i=j} \left\{ n_{\mathrm{B}i}[H_{\mathrm{B}}(T_{\mathrm{g}}) - H_{\mathrm{B}}(T_{\mathrm{R}})] + \left(n_{\mathrm{A}} + \sum_{m=1}^{m=i} n_{\mathrm{B}_m} \right) Cp_i^{\mathrm{AB}}\, \Delta T_{\mathrm{L}i} \right\} \tag{1}$$

$$\Delta H_j^{\mathrm{m}} = \frac{\Delta h_j^{\mathrm{m}}}{n_{\mathrm{A}} + \sum_{i=1}^{i=j} n_{\mathrm{B}i}} \tag{2}$$

where n_{A} and n_{B} are the number of moles of the components, $H_{\mathrm{B}}(T_{\mathrm{g}})$ and $H_{\mathrm{B}}(T_{\mathrm{R}})$ are the enthalpies of the secondary sample at the experiments temperature and the room temperature, respectively, Cp^{AB} is the heat capacity of the alloy, and ΔH_j^{m} is the mixing enthalpy. With the exception of Cp_i^{AB}, all values in Eqs. (1) and (2) are known from the experiments and the literature. The heat capacity of an alloy is given as follows:

$$Cp^{\mathrm{AB}} = Cp^{\mathrm{AB}}(\mathrm{id}) + Cp^{\mathrm{AB}}(\mathrm{xs}) \tag{3}$$

with the Neumann–Kopp rule for the ideal heat capacity

$$Cp^{\mathrm{AB}}(\mathrm{id}) = x_{\mathrm{A}}\, Cp^{\mathrm{A}} + x_{\mathrm{B}}\, Cp^{\mathrm{B}} \tag{4}$$

where Cp^{A} and Cp^{B} are the heat capacities of the pure metals A and B. In the calculations, we used $Cp_{\mathrm{liq}}^{\mathrm{Ni}} = 43.095\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$ [18] and $Cp_{\mathrm{liq}}^{\mathrm{Zr}} = 40.7\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$ [19]. The highest experimental temperature that occurred was 2331 K. This value is 605 K above the melting point of Ni ($T_{\mathrm{m}} = 1726$ K) and is 206 K above the melting point of Zr ($T_{\mathrm{m}} = 2125$ K). Therefore, a temperature dependence of Cp, as reported by Margrave [20] for liquid metals, was not considered in the calculations. $Cp^{\mathrm{AB}}(\mathrm{xs})$ is the excess heat capacity of the alloy; its dependence on temperature and composition is generally unknown. The main problem is the consideration of $Cp^{\mathrm{AB}}(\mathrm{xs})$ for the evaluation of the experimental values of ΔH^{m}. This procedure is presented for the regular associate model in Ref. 17.

A concentration- and temperature-dependent description of ΔH^{m} has been carried out with the thermodynamic-adapted power series by Tomiska et al. [21, 22]. The representation of ΔH^{m} is

$$\Delta H^{\mathrm{m}}(x, T) = (1 - x) \sum_{n=1}^{N} x^{n} \sum_{\varepsilon=1}^{E} C_{n, 1-\varepsilon} T^{1-\varepsilon} \tag{5}$$

and with

$$\frac{\partial \Delta H^{\mathrm{m}}(x, T)}{\partial T} = Cp^{\mathrm{xs}}(x, T) \tag{6}$$

one obtains

$$Cp^{\mathrm{xs}}(x, T) = (1 - x) \sum_{n=1}^{N} x^{n} \sum_{\varepsilon=1}^{E} (1 - \varepsilon) C_{n, 1-\varepsilon} T^{-\varepsilon} \tag{7}$$

where N is the degree of the series and E is the number of parameters to consider the temperature dependence. According to Eqs. (5) and (7), measurements at two temperatures ($E \geqslant 2$) are necessary.

3. RESULTS AND DISCUSSION

The measurements were carried out in the Ni-rich range at 1916 K up to $x_{\mathrm{Zr}} = 0.34$ at % Zr and in the Zr-rich range at 2270 K up to $x_{\mathrm{Ni}} = 0.54$ at % Ni. The major error ($\sim 10\%$) can be attributed to nickel evaporation during the experiments. According to Eq. (5), we obtain

$$\Delta H^{\mathrm{m}} = (1 - x_{\mathrm{Zr}}) \left[\left(-177.984 + \frac{1159.5}{T} \right) x_{\mathrm{Zr}} + \left(-61.488 - \frac{436{,}384}{T} \right) x_{\mathrm{Zr}}^{2} + \left(472.508 + \frac{825{,}888}{T} \right) x_{\mathrm{Zr}}^{3} + \left(-304.332 - \frac{428{,}248}{T} \right) x_{\mathrm{Zr}}^{4} \right] \tag{8}$$

where ΔH^{m} is in $\mathrm{kJ \cdot mol^{-1}}$ and T is in K. Figure 2 shows the available literature data for the Ni-rich range and our experimental results. The solid curves represent the calculated functions for 1916 and 2270 K according to Eq. (8), the dashed curves represent the polynomial representation according to the subregular approximation by Arpshofen et al. [6] [Eqs. (9) and (10)], and the dotted curve represents the five-term fit by Sidorov et al. [5] [Eq. (11)]. The dashed-dotted curve was calculated based on thermodynamic and phase equilibrium data of Charles et al. [23]. Their calculation is described by Eq. (12). All values are given in $\mathrm{kJ \cdot mol^{-1}}$.

$$\varDelta H^{\mathrm{m}}_{1740} = x_{\mathrm{Zr}} x_{\mathrm{Ni}} (-240.6972 + 4.241797 x_{\mathrm{Zr}}) \tag{9}$$

$$\varDelta H^{\mathrm{m}}_{1838} = x_{\mathrm{Zr}} x_{\mathrm{Ni}} (-285.4671 + 255.1141 x_{\mathrm{Zr}}) \tag{10}$$

$$\varDelta H^{\mathrm{m}}_{1963} = x_{\mathrm{Zr}} x_{\mathrm{Ni}} (-221.8 - 192.3 x_{\mathrm{Zr}} + 1014 x_{\mathrm{Zr}}^2 - 553 x_{\mathrm{Zr}}^3 - 508 x_{\mathrm{Zr}}^4) \tag{11}$$

$$\varDelta H^{\mathrm{m}} = x_{\mathrm{Zr}} x_{\mathrm{Ni}} [-243.75 + 47.950(2x_{\mathrm{Zr}} - 1) + 5.9(6x_{\mathrm{Zr}}^2 - 6x_{\mathrm{Zr}} + 10)] \tag{12}$$

The experimental values and the corresponding polynomial representations yield a qualitatively correct description of $\varDelta H^{\mathrm{m}}$. The value of $\varDelta H^{\mathrm{m}}$ increases with decreasing temperature and the maximum tends to the composition NiZr. Moreover, the high value of $\varDelta H^{\mathrm{m}}$ in connection with its concentration and temperature dependence indicates strong interactions between Ni and Zr. These facts verify the statement of Arpshofen et al. [6] that the liquid system has a distinct tendency toward chemical short-range order. But this tendency toward the composition NiZr cannot be as strong as represented by $\varDelta H^{\mathrm{m}}$. This is pointed out by interpreting the excess heat capacity of the system. According to Eq. (7), we obtain

$$Cp(\mathrm{xs}) = (1 - x_{\mathrm{Zr}}) \left[-\frac{1159.5}{T^2} x_{\mathrm{Zr}} + \frac{436{,}384}{T^2} - \frac{825{,}888}{T^2} x_{\mathrm{Zr}}^3 + \frac{428{,}248}{T^2} x_{\mathrm{Zr}}^4 \right] \tag{13}$$

where $Cp(\mathrm{xs})$ is in kJ · mol^{-1} and T is in K. The curves in Fig. 3 represent the results of calculations corresponding to our experimental temperatures

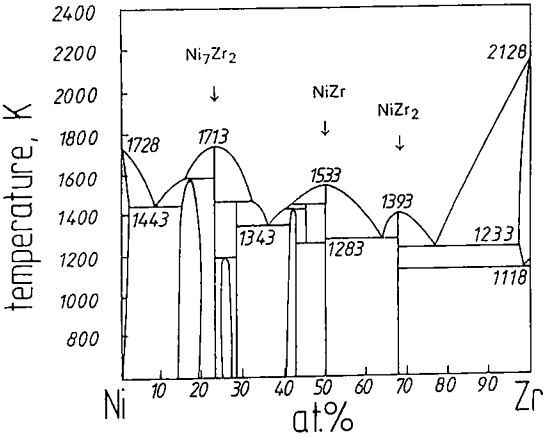

Fig. 1. Ni–Zr phase diagram; redrawn from Ref. 12.

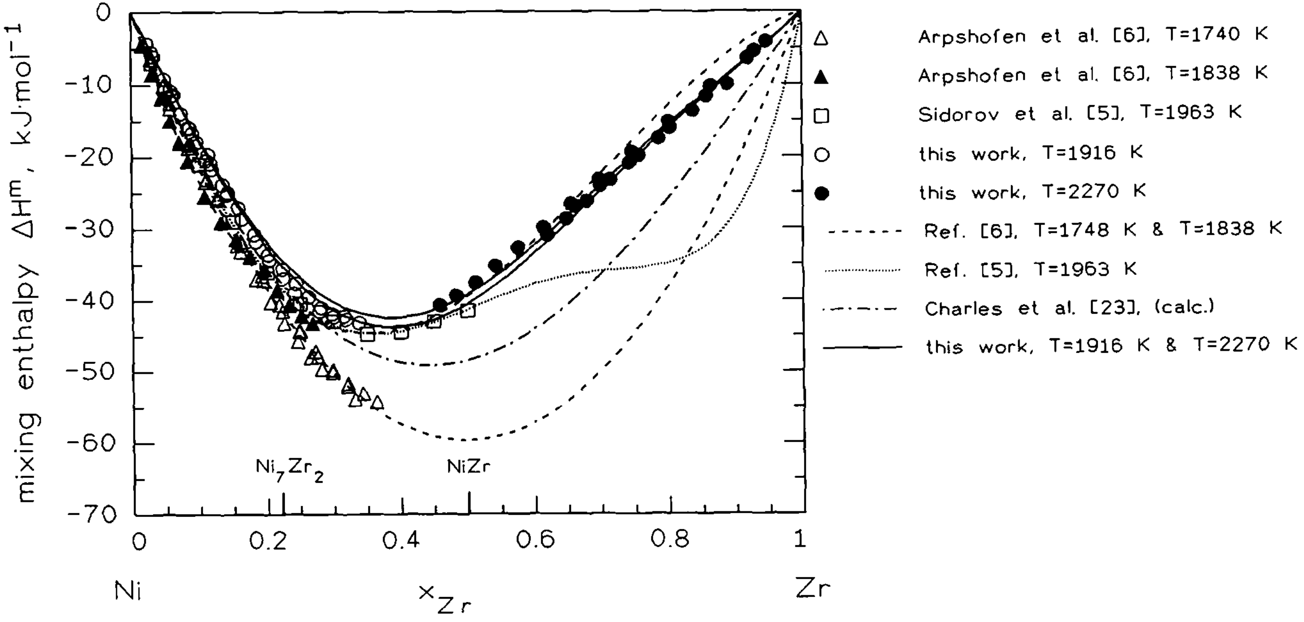

Fig. 2. Mixing enthalpy of liquid Ni–Zr alloys.

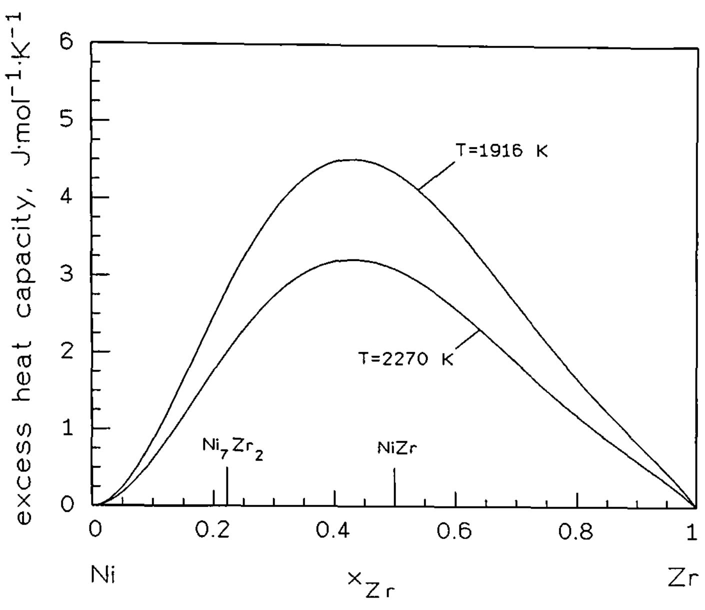

Fig. 3. Excess heat capacity of liquid Ni-Zr alloys.

1916 and 2270 K. The Maxima of the curves show no tendency toward any particular composition, i.e., in this temperature range no predominant influence of chemical short-range order can be seen. Moreover, the comparison of ΔH^{m} between the values at 1963 K [5] and those at 1740 K [6] in the vicinity of $x_{Zr} = 0.35$ at % Zr yields a difference of ~ 10 kJ · mol^{-1} for ΔH^{m}, which would mean a resulting Cp(xs) of ~ 50 kJ · mol^{-1}. The value obtained is unrealistic and suggests a smaller temperature dependence of ΔH^{m} as represented by the measurements at 1748 K. This may be due to Zr side reactions with the crucible material Al_2O_3 [6]. Under the assumption of lower values at this temperature, the tendency of the maximum value of ΔH^{m} toward NiZr would be smaller.

4. CONCLUSIONS

The temperature dependence of the mixing enthalpy and the excess heat capacity in the glass-forming system Ni-Zr were obtained and the influence of chemical short-range order on the mixing enthalpy was shown. With decreasing temperature, this influence tends toward the composition NiZr. The thermodynamic-adapted power series enables a temperature- and concentration-dependent description of the mixing enthalpy and the excess heat capacity.

ACKNOWLEDGMENT

We wish to thank the Deutsche Forschungsgemeinschaft (DFG) for their financial support.

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