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Zinc thermodynamic activities in Co–Ni–Zn β'_1 and β_1 phases

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Abstract

A dew point technique was used to determine the zinc activity in Co–Ni–Zn β'_1 and β_1 intermediate compounds in the range 873–1113 K. Active planning of the experiments was performed in order to obtain equations describing the compositional dependence of the zinc activity coefficients.

1. Introduction

A partial investigation of the Co–Ni–Zn phase diagram has been performed by Köster *et al.* [1] in the range 15–60 at.% Zn. Recently, an isothermal (1073 K) cross-section of this system has been constructed by Vassilev and Budurov [2]. The phase boundaries, at this temperature, between solid face-centred cubic (f.c.c.) solutions (α phase) and β'_1, β_1 and γ intermediate compounds have been drawn based on the respective binary structures [1–5]. In this study, we neglect the thermodynamic differences between the body-centred cubic (b.c.c.) β and face-centred tetragonal (f.c.t.) β_1 phases of the nickel-rich part of this equilibrium diagram, partly because the pertinent phase boundaries have not been drawn and partly because the zinc activities in both compounds may be very similar due to the anticipated narrow two-phase region [2, 3].

The thermochemical properties of the ternary Co–Ni–Zn f.c.c. solid solutions have been studied previously [6], applying active planning of the experiments, according to the method of Sheffe [7–9]. In order to study the thermodynamics of the β'_1 and β_1 intermediate phases, we use the same approach as described previously [6–9]. Thus only strictly necessary details about the planning procedure are given.

2. Experimental details

Tables 1 and 2 contain the simplex matrices for planning of the experiments for the β'_1 and β_1 phases respectively.

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TABLE 1

Simplex matrix for the planning and containment of the original components (β_1' phase): η_j points of the simplex lattice; Z_i, mole fractions of the pseudo components; X_i, mole fractions of the real components

η_j	Z_1	Z_2	Z_3	X_{Ni}	X_{Co}	X_{Zn}
η_1	1.0	0.0	0.0	0.1000	0.3900	0.5100
η_2	0.0	1.0	0.0	0.1800	0.3800	0.4400
η_3	0.0	0.0	1.0	0.0000	0.4900	0.5100
η_4	0.5	0.5	0.0	0.1400	0.3850	0.4750
η_5	0.5	0.0	0.5	0.0500	0.4400	0.5100
η_6	0.0	0.5	0.5	0.0900	0.4350	0.4750
η_7	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	0.0933	0.4200	0.4867
η_8	0.2	0.7	0.1	0.0460	0.4580	0.4960
η_8'	0.2	0.7	0.1	0.0460	0.4580	0.4960

TABLE 2

Simplex matrix for the planning and containment of the original components (β_1 phase): η_j points of the simplex lattice; Z_i, mole fractions of the pseudo components; X_i, mole fractions of the real components

η_j	Z_1	Z_2	Z_3	X_{Ni}	X_{Co}	X_{Zn}
η_1	1.0	0.0	0.0	0.5400	0.0000	0.4600
η_2	0.0	1.0	0.0	0.4600	0.0000	0.5400
η_3	0.0	0.0	1.0	0.4000	0.1000	0.5000
η_4	0.5	0.5	0.0	0.5000	0.0000	0.5000
η_5	0.5	0.0	0.5	0.4700	0.0500	0.4800
η_6	0.0	0.5	0.5	0.4300	0.0500	0.5200
η_7	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	0.4667	0.0333	0.5000
η_8	0.25	0.25	0.5	0.4500	0.0500	0.5000

The specimens (weighing $(10–15)\times10^{-3}$ kg) were prepared from powders of the pertinent metals (containing at least 99.9 wt.% Co, Ni or Zn, with particle diameters of less than 6.3×10^{-5} m). The required quantities (Tables 1 and 2) of the different components were weighed analytically, mixed, stirred and formed into bricks. They were then heated at 673 K for 2 h in a hydrogen atmosphere, and immediately sealed in quartz ampoules (length, 0.18 m) with a residual pressure of 1.3×10^{-4} N m^{-2}. The ampoules were placed in a cool furnace and the temperature was raised gradually for a week, up to 973 K, in such a way that no melting could occur. The specimens were kept at this temperature for a further week. It has been estimated that this period is sufficient for good homogenization, using the values of the diffusion and penetration coefficients in the relevant binary intermediate phases [10, 11]. The phase compositions of the specimens were checked by X-ray analysis after completion of all the experiments. Negligible weight losses were observed and therefore the chemical composition of the specimens can be considered to be unchanged.

By proceeding in this manner we were able to retain the porosity of the alloys in order to facilitate the establishment of a thermodynamic equilibrium between the liquid and solid phases during the dew point determination. The latter procedure is described in detail elsewhere [12–14]. Our experiments lasted about 8 h each, and during this period three to five dew point determinations were performed at a fixed temperature of the alloy. In general, the results were scattered (±3 K) and therefore a mean arithmetic value was taken; the specimen temperature was maintained constant (±1 K). Four temperatures were chosen: 873, 973, 1013 and 1113 K. Finally, the thermodynamic activity coefficients of zinc γ_{Zn} were calculated for every temperature and composition

$$\gamma_{Zn}(T_s) = P^0(T_{dp})/(\{P^0(T_s) \times X_{Zn}\} \qquad (1)$$

where T_s is the specimen temperature, T_{dp} is the relevant mean dew point temperature, P^0 is the vapour pressure of pure liquid zinc, calculated according to Barrow *et al.* [15] and X_{Zn} is the mole fraction of zinc in the alloy.

TABLE 3

Some thermodynamic properties of zinc in the Co–Ni–Zn β_1' phase at 1073 K. Reference state Zn(liq)

η_j point	A (slope)	B (intercept)	$\Delta\bar{H}_{Zn}$ (J mol^{-1})	γ_{Zn}
η_1	−1651±20.5	0.827±0.021	−13730±860	0.962±0.088
η_2	−502±26.5	−0.527±0.027	−4170±430	0.840±0.086
η_4	−247±40.9	−0.708±0.041	−2050±410	0.824±0.103
η_5	−572±20.2	−1.135±0.020	4760±270	1.074±0.094
η_6	−1691±21.6	0.865±0.022	−14060±880	1.034±0.096
η_7	−1536±25.3	0.789±0.025	−12770±850	1.081±0.107
η_8	667±64.7	−1.238±0.065	5550±820	1.088±0.191
η_8'	668±28.1	−1.227±0.028	5550±510	1.101±0.115

TABLE 4

Some thermodynamic properties of zinc in the Co–Ni–Zn β_1 phase at 1073 K. Reference state Zn(liq)

η_j point	A (slope)	B (intercept)	$\Delta\bar{H}_{Zn}$ (J mol^{-1})	γ_{Zn}
η_3	−2493±130	0.865±0.131	−20730±2120	0.465±0.143
η_5	−2738±70.0	1.012±0.070	−22760±1720	0.447±0.080
η_6	−2293±118	0.753±0.119	−19060±1930	0.522±0.138
η_7	−3015±126	1.341±0.126	−25070±2300	0.460±0.136
η_8	−2633±143	0.990±0.144	−21890±2280	0.463±0.153

The relative errors of the γ_{Zn} values, obtained using eqn. (2) derived from eqn. (1), were assessed to be about ±5%.

$$\Delta\gamma/\gamma = \Delta P^0_{Zn}(T_s)/P^0_{Zn}(T_s) + \Delta P^0_{Zn}(T_{dp})/P^0_{Zn}(T_{dp}) \tag{2}$$

Supplementary experiments performed with an ampoule containing pure zinc only have confirmed these estimations, which have been taken into account (Tables 3 and 4, see Section 3) together with the errors obtained by the regression analyses.

3. Results and discussion

The thermodynamic activities of zinc ($a_{Zn} = \gamma_{Zn} X_{Zn}$) were submitted to linear regression analyses (eqn. (3)) neglecting the temperature dependence of the zinc partial molar enthalpy $\Delta\bar{H}_{Zn}$:

$$\ln(a_{Zn}) = \Delta\bar{H}_{Zn}/RT + \text{constant} = A/T + B \tag{3}$$

where R is the universal gas constant and T is the absolute temperature.

The values of the variables A and B, calculated by the least-squares method, for a 0.95 confidence interval, are shown in Tables 3 and 4 for the ternary β'_1 and β_1 phase regions respectively. These tables also contain the smoothed values of the zinc activity coefficients at 1073 K (from which the excess chemical potential of zinc can be calculated, $\mu^E_{Zn} = RT\ \ln(\gamma_{Zn})$) and the corresponding partial molar enthalpies $\Delta\bar{H}_{Zn}$.

The analysis of the experimental results shows that the nickel-rich β_1 phase exhibits more negative deviations from ideality (*e.g.* Raoult's law) than the cobalt-rich β'_1 intermediate compound. It is probable that the nickel augments its thermodynamic stability and thus the latter can contain up to 20 at.% Ni, whereas the β_1 phase can contain no more than about 10 at.% Co at 1073 K [2].

Optimization of the literature data [14, 16, 17] on the binary Co–Zn β_1 phase was performed in order to obtain an expression (eqn. (4)) which could be used for the calculation of the zinc (or cobalt, see ref. 6) activity coefficients in the binary Co–Zn β_1 intermediate phase

$$\mu^{E,\ \beta_1}_{Zn} = (1 - X_{Zn})^2(U_0 + 2X_{Zn}U_1 + 3X_{Zn}{}^2U_2) \tag{4}$$

where $U_0 = -154\,600 + 200T$, $U_1 = 617\,940 - 780T$ and $U_2 = -883\,460 + 1020T$.

Then, the coefficients of eqn. (5a), describing γ_{Zn} in the investigated area of the β'_1 phase as a function of the pseudo components Z_1, Z_2 and Z_3 for $T = 1073$ K, were derived as described elsewhere [7–9], using eqn. (4) (for the coefficient at the point η_3) and our experimental results at the points η_1, η_2, η_4, η_5 and η_6 (Table 3) for the other five coefficients

$$\begin{aligned}\gamma^{\beta'_1}_{Zn}(Z_1, Z_2, Z_3) = {} & (0.962 \pm 0.088)Z_1 + (0.840 \pm 0.086)Z_2 \\ & + (1.051 \pm 0.347)Z_3 + (-0.308 \pm 0.064)Z_1Z_2 \\ & + (0.270 \pm 0.494)Z_1Z_3 + (0.354 \pm 0.481)Z_2Z_3 \end{aligned} \tag{5a}$$

By disposing with the experimental results about another simplex lattice point, we can raise the degree of the polynomial from 2 to 2.5

$$\begin{aligned}\gamma_{\mathrm{Zn}}^{\beta_1'}(Z_1, Z_2, Z_3) = {} & (0.962 \pm 0.088)Z_1 + (0.840 \pm 0.086)Z_2 \\ & + (1.051 \pm 0.347)Z_3 \\ & + (-0.308 \pm 0.064)Z_1 Z_2 + (0.270 \pm 0.494)Z_1 Z_3 \\ & + (0.354 \pm 0.481)Z_2 Z_3 + (2.562 \pm 0.936)Z_1 Z_2 Z_3 \qquad (5b)\end{aligned}$$

The corresponding equations for the β_1 phase region are

$$\begin{aligned}\gamma_{\mathrm{Zn}}^{\beta_1}(Z_1, Z_2, Z_3) = {} & (0.316 \pm 0.104)Z_1 + (0.363 \pm 0.112)Z_2 \\ & + (0.465 \pm 0.143)Z_3 \\ & + (0.226 \pm 0.174)Z_1 Z_3 + (0.432 \pm 0.047)Z_2 Z_3 \qquad (6a)\end{aligned}$$

$$\begin{aligned}\gamma_{\mathrm{Zn}}^{\beta_1}(Z_1, Z_2, Z_3) = {} & (0.316 \pm 0.104)Z_1 + (0.363 \pm 0.112)Z_2 \\ & + (0.465 \pm 0.143)Z_3 + (0.226 \pm 0.174)Z_1 Z_3 \\ & + (0.432 \pm 0.047)Z_2 Z_3 + (0.156 \pm 0.834)Z_1 Z_2 Z_3 \qquad (6b)\end{aligned}$$

The polynomial coefficients before Z_1, Z_2 and Z_3 (belonging to the binary Ni–Zn β_1 phase) were assessed using previous experimental data [14]. The other coefficients were calculated with the data shown in Table 4.

The transformation from the mole fractions of the pseudo components (Z_i) to the mole fractions of the real components (X_i) can be performed [9] using the matrix equations (eqns. (7a) and (7b)) for the β_1' and β_1 phases respectively

$$\left|\begin{matrix} X_{\mathrm{Zn}} \\ X_{\mathrm{Co}} \\ X_{\mathrm{Ni}} \end{matrix}\right| = \left|\begin{matrix} 0.51 & 0.44 & 0.51 \\ 0.39 & 0.38 & 0.49 \\ 0.10 & 0.18 & 0.00 \end{matrix}\right| \times \left|\begin{matrix} Z_1 \\ Z_2 \\ Z_3 \end{matrix}\right| \qquad (7a)$$

$$\left|\begin{matrix} X_{\mathrm{Zn}} \\ X_{\mathrm{Co}} \\ X_{\mathrm{Ni}} \end{matrix}\right| = \left|\begin{matrix} 0.46 & 0.54 & 0.50 \\ 0.00 & 0.00 & 0.10 \\ 0.54 & 0.46 & 0.40 \end{matrix}\right| \times \left|\begin{matrix} Z_1 \\ Z_2 \\ Z_3 \end{matrix}\right| \qquad (7b)$$

TABLE 5

Comparison between experimental and calculated zinc activity coefficients in Co–Ni–Zn β_1' and β_1 phases at 1073 K. Reference state Zn(liq)

Phase	Simplex point	$\gamma_{\mathrm{Zn}}^{\mathrm{exp}}$	γ_{Zn} (eqn. (5a) or (6a))	γ_{Zn} (eqn. (5b) or (6b))
β_1'	η_7	1.081 ± 0.107	0.986 ± 0.289	1.081 ± 0.324
	η_8	1.088 ± 0.191	0.873 ± 0.165	0.908 ± 0.178
	η_8'	1.101 ± 0.115	0.873 ± 0.165	0.908 ± 0.178
β_1	η_7	0.460 ± 0.136	0.454 ± 0.145	0.460 ± 0.176
	η_8	0.463 ± 0.153	0.484 ± 0.153	0.489 ± 0.179

The model was checked for each phase region using the control points η_7 and η_8 (Table 5).

4. Conclusions

Equations (5a), (5b) and (6a), (6b) can be used for the description of the thermodynamic properties of zinc in the pertinent phases at 1073 K. Similar expressions, for other temperatures, can easily be obtained from the data given in Tables 3 and 4 and relevant data on the binary systems.

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