Thermodynamics of the ternary Co–Ni–Zn f.c.c. solutions

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Abstract

A dew point technique has been used to determine the zinc activity in Co–Ni–Zn f.c.c. solutions in the range 1023–1173 K. Active planning of the experiments has been applied. Various thermodynamic quantities have been calculated with the aid of several models.

1. Introduction

We constructed experimentally an isothermal cross-section of the equilibrium Co–Ni–Zn phase diagram at 1073 K [1] finding a large region of f.c.c. (α) solutions. This evidence is consistent with our earlier investigations of the Ni–Zn [2] and Co–Zn [3] phase diagrams. The recent achievements in the description of the thermochemical properties of the relevant binary systems [4–6], in the lattice stabilities of the pure components [7–9], and in the planning of experiments [10–12] come together in such a way that an adequate thermodynamic description can be obtained from a small number of new experiments only.

2. Results and discussion

2.1. Planning of the experiments with ternary alloys

Active planning has been applied according to the method of Sheffe [10, 11]. The matrix simplex is shown in Table 1, and the relevant region of the ternary phase diagram is marked on Fig. 1. The summits Z_1, Z_2, Z_3 lie on the binary phase diagrams Ni–Zn (Z_1, Z_3) or Co–Zn (Z_2) and are considered to be independent components (pseudocomponents), *e.g.*

$$Z_1 + Z_2 + Z_3 = 1 \tag{1}$$

where $0 \leqslant Z_i \leqslant 1$.

The matrix (Table 1) has been composed by supposing that the dependence of the investigated thermodynamic properties on the composition is described by a polynomial of degree 2 or 2.5. The pertinent coefficients and the transformations to the real components concentrations can be determined with the aid of well-known expressions [10–12].

TABLE 1

Matrix simplex for the planning and the containment of the original components

	Z_1	Z_2	Z_3	X_{Ni}	X_{Co}	X_{Zn}
η_1	1.0	0.0	0.0	0.9500	0.0000	0.0500
η_2	0.0	1.0	0.0	0.0000	0.9500	0.0500
η_3	0.0	0.0	1.0	0.7000	0.0000	0.3000
η_4	0.5	0.5	0.0	0.4750	0.4750	0.0500
η_5	0.5	0.0	0.5	0.8250	0.0000	0.1750
η_6	0.0	0.5	0.5	0.3500	0.4750	0.1750
η_7	1/3	1/3	1/3	0.5500	0.3166	0.1334

η_j, points of the simplex lattice; Z_i, mole fractions of the pseudocomponents; X_i, mole fractions of the real components.
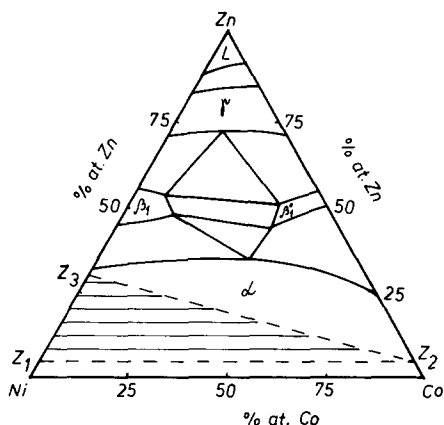

Fig. 1. The phase diagram Co–Ni–Zn at 1073 K. The shaded area represents the matrix triangle with the summits Z_1, Z_2 and Z_3.

2.2. Thermochemical properties of the Ni–Zn, Co–Zn, Co–Ni and Co–Ni–Zn f.c.c. solutions

The thermodynamic properties of the Ni–Zn and Co–Zn f.c.c. solutions have been optimized earlier [4, 5] by applying a polynomial description (Table 2).

For the temperature and compositional dependence of the excess integral molar Gibbs energy of the Co–Ni f.c.c. alloys the following expression proposed by Kaufman and Nesor [6] was used:

$$G_{CoNi}^{E,\,f.c.c.} = X_{Ni}X_{Co}(4602 - 5.3815 \times 10^{-3}T^2 + 2.8689 \times 10^{-6}T^3) \qquad (2)$$

The activity coefficients γ_{Zn} of zinc in the ternary Co–Ni–Zn alloys have been measured experimentally for the points η_4, η_6, and η_7 (see Table 1) using a dew point method described previously [3]. The values of γ_{Zn} are shown in Table 3. The slope of the linear regression of the zinc activities in the coordinates $\ln(a_{Zn})$–$(1/RT)$ gives the values of the partial molar enthalpies

TABLE 2

Excess Gibbs energy coefficients for the solid (α, f.c.c.) phases of the Ni–Zn and the Co–Zn systems

System	ν	$\lambda^{(\nu)}$	$\psi^{(\nu)}$
Ni–Zn (α)	0	-45561	7.6957
	1	-75832	41.4700
	2	43457	23.6890
Co–Zn (α)	0	-18668	7.5132
	1	112335	-58.9783
	2	-100676	63.2216

Standard states Ni(f.c.c.), Zn(h.c.p.), Co(h.c.p.); $T = 273.15$ K, $P = 101.325$ kPa. X, mole fractions of zinc.

$$G^{E} = X(1 - X)\sum_{\nu=0}^{n} X^{\nu}U^{(\nu)}(T)$$

$$\bar{G}^{E,\text{f.c.c.}}_{\text{Co}} = X^{2}\{U_0 + (2X - 1)U_1 + (3X^2 - 2X)U_2\}$$

$$\bar{G}^{E,\text{f.c.c.}}_{\text{Zn}} = (1 - X)^2(U_0 + 2XU_1 + 3X^2U_2)$$

$$U^{(\nu)}(T) = \lambda^{(\nu)} + \psi^{(\nu)}T \qquad (\nu = 0, 1, 2)$$

TABLE 3

Experimental information on some partial thermochemical properties of zinc in the α-Co–Ni–Zn alloys

η_j	T (K)	γ_{Zn}	$\bar{G}^{E,\text{f.c.c.}}_{\text{Zn}}$ (J mol^{-1})	$\bar{H}^{\text{f.c.c.}}_{\text{Zn}}$ (J mol^{-1})
η_4, $X_{\text{Zn}} = 0.0495$	1023	0.331	-9400	
	1073	0.426	-7620	
	1103	0.477	-6790	$-44200 \quad \pm 800$
	1133	0.555	-5540	
	1173	0.643	-4310	
η_6, $X_{\text{Zn}} = 0.1750$	1023	0.465	-6510	
	1073	0.592	-4680	
	1100	0.684	-3450	-51000 ± 2000
	1133	0.828	-1780	
	1173	0.989	-110	
η_7, $X_{\text{Zn}} = 0.1335$	1023	0.100	-19600	
	1073	0.138	-17650	
	1103	0.162	-16670	-55600 ± 1300
	1133	0.186	-15860	
	1173	0.233	-14190	

Standard state Zn(h.c.p.).

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TABLE 4

The excess partial molar Gibbs free energy $\bar{G}_{Zn}^{E,\,f.c.c.}$ (J mol^{-1}) and the activity coefficients of zinc in the simplex lattice points at 1073 K referred to the standard state of Zn(h.c.p.)

	η_1	η_2	η_3	η_4	η_5	η_6	η_7
$\bar{G}_{Zn}^{E,\,f.c.c.}$	−36030	−5370	−18380	−7570	−28550	−4360	−17570
γ_{Zn}	0.018	0.548	0.127	0.428	0.041	0.613	0.140
Source	[4]	[5]	[4]	Eqn. (3a)	[4]	Eqn. (3b)	Eqn. (3c)

of zinc (Table 3). The temperature dependence of γ_{Zn} in the interval 1023–1173 K is represented by the equations

$$\gamma_{Zn}(\eta_4) = -1.8087 \mp 0.0949 + (2.0845 \times 10^{-3} \mp 8.61 \times 10^{-5})T \qquad (3a)$$

$$\gamma_{Zn}(\eta_6) = -3.1775 \mp 0.2971 + (3.5327 \times 10^{-3} \mp 2.69 \times 10^{-4})T \qquad (3b)$$

$$\gamma_{Zn}(\eta_7) = -0.7969 \mp 0.0582 + (8.7272 \times 10^{-4} \mp 5.28 \times 10^{-5})T \qquad (3c)$$

The zinc activity coefficients and its partial excess molar Gibbs energy at the points of the matrix simplex are represented in Table 4. The following equation based on these data describes γ_{Zn} as a function of the pseudo-components Z_j:

$$\gamma_{Zn}(Z_1,Z_2,Z_3) = 0.018Z_1 + 0.548Z_2 + 0.127Z_3 + 0.581Z_1 Z_2$$
$$- 0.127Z_1 Z_3 + 1.102Z_2 Z_3 - 7.125Z_1 Z_2 Z_3 \qquad (4)$$

The above coefficients are calculated as recommended in the specialized literature [10–12]. The transformation to the real molar concentrations of zinc for an alloy could be carried out [12] using the matrix expression

$$\begin{bmatrix} X_{Zn} \\ X_{Co} \\ X_{Ni} \end{bmatrix} = \begin{bmatrix} 0.05 & 0.05 & 0.30 \\ 0.00 & 0.95 & 0.00 \\ 0.95 & 0.00 & 0.70 \end{bmatrix} \begin{bmatrix} Z_1 \\ Z_2 \\ Z_3 \end{bmatrix} \qquad (5)$$

Several geometrical models predicting the ternary thermodynamic properties in terms of the three corresponding binary solutions are known [13]. We have applied here the model of Toop [14] in order to calculate the molar excess integral Gibbs free energy $G_{CoNiZn}^{E,\,f.c.c.}$ using the two sets of coefficients from Table 2 and Toop's equation

$$G_{CoNiZn}^{E,\,f.c.c.} = [\{X_{Ni}/(1-X_{Zn})\}G_{NiZn}^{E,\,f.c.c.} + \{X_{Co}/(1-X_{Zn})\}G_{CoZn}^{E,\,f.c.c.}]_{X_{Zn}}$$
$$+ (1-X_{Zn})^2 (G_{CoNi}^{E,\,f.c.c.})_{X_{Co}/X_{Ni}} \qquad (6)$$

The results at 773 and 1073 K are shown in Table 5. Using these data we have derived the following equation predicting the temperature and compositional dependence of $G_{CoNiZn}^{E,\,f.c.c.}$:

$$G_{CoNiZn}^{E,\,f.c.c.} = (-2341 + 0.4667T)Z_1 + (-640 + 0.2333T)Z_2$$
$$+ (-13517 + 4.6667T)Z_3 + (-640 + 0.2T)Z_1 Z_2$$
$$+ (-1492 - 1.2T)Z_1 Z_3 + (16\,005 - 8.4667T)Z_2 Z_3 \qquad (7)$$

TABLE 5

The excess integral molar Gibbs free energy $G_{\mathrm{CoNiZn}}^{\mathrm{E,\ f.c.c.}}$ (J mol^{-1}) in the simplex lattice points at 773 and 1073 K referred to the standard states of Zn(h.c.p.), Co(h.c.p.) and Ni(f.c.c.)

T (K)	η_1	η_2	η_3	η_4	η_5	η_6	η_7
773	−1960	−460	−9910	−1380	−6550	−2820	−3360
1073	−1840	−390	−8510	−1260	−5870	−2720	−3110

The check performed with the aid of the above expression gives for the point η_7 $G_{\mathrm{CoNiZn}}^{\mathrm{E,\ f.c.c.}}$(1/3, 1/3, 1/3) = −3180 J mol^{-1}, while the value calculated from eqn. (6) is −3110 J mol^{-1} (Table 5). This is a satisfactory agreement and thus we have not increased the degree of eqn. (7).

3. Conclusion

An experimental and theoretical investigation of some thermochemical properties of the Co–Ni–Zn system has been performed applying active planning of the experiments and literature data about the pertinent binary systems. Two equations have been derived to calculate some partial and integral excess thermodynamic properties. Those results combined with the literature data about the lattice stabilities of the pure cobalt, nickel and zinc could be used for the calculation of phase equilibria in this or in other multicomponent systems.

References

1 G. Vassilev and S. Budurov, *Izv. Akad. Nauk. S.S.S.R.*, *Met.*, *2* (1980) 229 (in Russian).
2 S. Budurov, G. Vassilev and N. Nentchev, *Z. Metallkd.*, *65* (1974) 681.
3 S. Budurov and G. Vassilev, *Z. Metallkd.*, *67* (1976) 170.
4 G. Vassilev, Estimation of the thermodynamic equilibrium between solid and liquid Ni–Zn solutions, submitted to *Rev. Metall.*,
5 G. Vassilev, Assessment of the equilibrium between solid and liquid Co–Zn solutions, in preparation.
6 L. Kaufman and H. Nesor, *Calphad*, *2* (1978) 81.
7 S. An Mey, *Z. Metallkd.*, *78* (1987) 502.
8 A. F. Guillermet, *Int. J. Thermophys.*, *8* (1987) 481.
9 P. J. Spencer, *Calphad*, *10* (1986) 175.
10 H. Sheffe, *J. R. Statist. Soc. B*, *20* (1958) 344.
11 J. Gorman and J. Hinman, *Thermometrics*, *4* (1963) 463.
12 I. Vouchkov and H. Jonchev, *Planning and Analyses of Experiments*, Technika, Sofia, 1979, p. 353 (in Bulgarian).
13 K. Chou and Y. Chang, *Ber. Bunsenges. Phys. Chem.*, *93* (1989) 735.
14 G. Toop, *Trans. Metall. Soc. AIME*, *233* (1965) 850.