Ni – Zn (Nickel – Zinc)

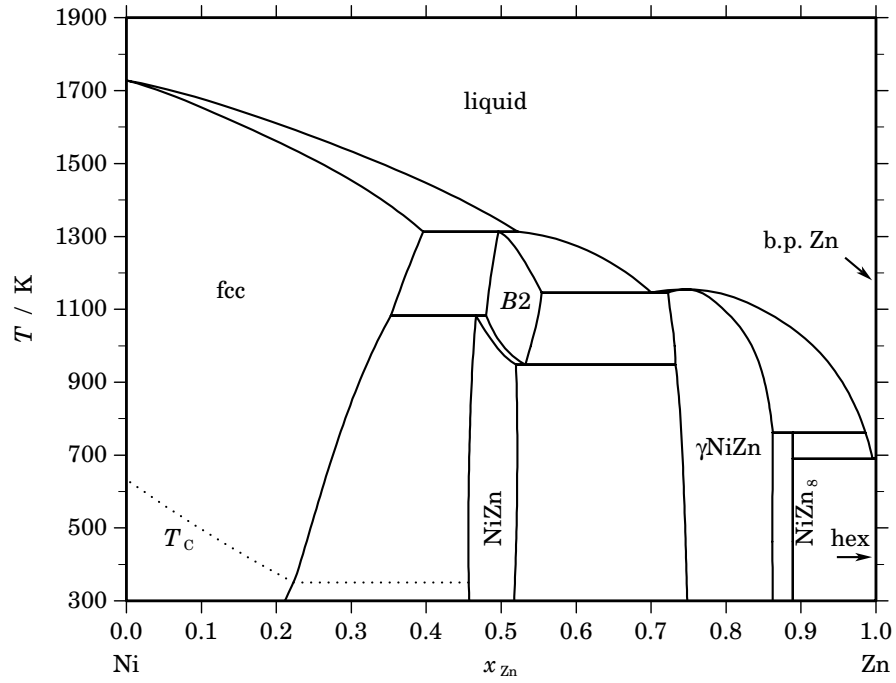

Fig. 1. Calculated phase diagram for the system Ni-Zn.

The Ni-Zn system is of interest for galvanising of high silicon steels where Ni is added to the bath in order to reduce coating thickness and to improve the coating adhesion and its appearance. The Ni-Zn system has been reviewed in [1991Nas] as well as by [2000Vas, 2002Su, 2003Mie] who also reported optimised thermodynamic datasets. Over the years, numerous studies of the Ni-Zn have been published and the optimisations [2000Vas, 2002Su, 2003Mie] are based essentially on the same experimental data but they differ in the thermodynamic modelling, especially the description of the non-stoichiometric intermetallic phases.

Data on the phase equilibria have been measured over the complete composition range and temperatures from the liquidus down into the subsolidus regions. Furthermore there are numerous studies of the zinc activity in the liquid as well as in the solid solution phases and enthalpies of formation have been determined at several temperatures.

In [2000Vas] the deviation from stoichiometry on the Zn-deficient side of the $B2$ and NiZn phases and on the Ni-poor side of γNiZn has been modelled by introducing vacancies into one of the sublattices. In [2002Su] it has been criticised that these phases contain unphysically high vacancy concentrations even at low temperatures and alternative modelling of these phases has been presented. However, the overall fit of the phase diagram and the thermodynamic data is still best in the assessment of [2000Vas] and therefore, this dataset is presented here.

Table I. Phases, structures and models.

Phase	Struktur-bericht	Prototype	Pearson symbol	Space group	SGTE name	Model
liquid					LIQUID	$(Ni,Zn)_1$
fcc	$A1$	Cu	$cF4$	$Fm\overline{3}m$	FCC_A1	$(Ni,Zn)_1$
$B2$	$B2$	CsCl	$cP2$	$Pm\overline{3}m$	NIZN_B2	$(Ni,Zn)_1(Zn,\Box)_1$
NiZn	$L1_0$	AuCu	$tP2$	$P4/mmm$	NIZN_L10	$(Ni,Zn)_1(Zn,\Box)_1$
γNiZn	$D8_2$	Cu_5Zn_8	$cI52$	$I4\overline{3}m$	NIZN_GAMMA	$(Ni,\Box)_2(Ni,Zn)_{11}Ni_2Zn_{11}$
$NiZn_8$	$\cdots$	$\cdots$	$mC28$	$C2/m$	NIZN8	Ni_1Zn_8
hex	$A3$	Mg	$hP2$	$P6_3/mmc$	HCP_ZN	Zn_1

Table II. Invariant reactions.

Reaction	Type	T / K	Compositions / x_{Zn}			$\Delta_{\mathrm{r}}H$ / (J/mol)
fcc + liquid $\rightleftharpoons$ $B2$	peritectic	1313.2	0.396	0.522	0.496	−14481
liquid $\rightleftharpoons$ γNiZn	congruent	1154.6	0.747	0.747		−11420
liquid $\rightleftharpoons$ $B2$ + γNiZn	eutectic	1146.2	0.700	0.554	0.723	−11825
fcc + $B2$ $\rightleftharpoons$ NiZn	peritectoid	1082.5	0.353	0.480	0.466	−2068
$B2$ $\rightleftharpoons$ NiZn + γNiZn	eutectoid	947.9	0.532	0.520	0.733	−2896
γNiZn + liquid $\rightleftharpoons$ $NiZn_8$	peritectic	762.0	0.862	0.986	0.889	−1686
liquid $\rightleftharpoons$ $NiZn_8$ + hex	eutectic	689.7	0.995	0.889	1.000	−7411

Table IIIa. Integral quantities for the liquid phase at 1800 K.

x_{Zn}	ΔG_{m} [J/mol]	ΔH_{m} [J/mol]	ΔS_{m} [J/(mol·K)]	$G_{\mathrm{m}}^{\mathrm{E}}$ [J/mol]	$S_{\mathrm{m}}^{\mathrm{E}}$ [J/(mol·K)]	ΔC_P [J/(mol·K)]
0.000	0	0	0.000	0	0.000	0.000
0.100	−7603	−5405	1.221	−2738	−1.482	0.000
0.200	−12565	−8753	2.117	−5076	−2.043	0.000
0.300	−16143	−10788	2.975	−7001	−2.104	0.000
0.400	−18536	−12010	3.626	−8464	−1.970	0.000
0.500	−19750	−12680	3.928	−9377	−1.835	0.000
0.600	−19687	−12819	3.815	−9614	−1.781	0.000
0.700	−18157	−12205	3.307	−9015	−1.772	0.000
0.800	−14866	−10373	2.496	−7377	−1.665	0.000
0.900	−9329	−6620	1.505	−4464	−1.198	0.000
1.000	0	0	0.000	0	0.000	0.000

Reference states: Ni(liquid), Zn(liquid)

Table IIIb. Partial quantities for Ni in the liquid phase at 1800 K.

x_{Ni}	ΔG_{Ni} [J/mol]	ΔH_{Ni} [J/mol]	ΔS_{Ni} [J/(mol·K)]	G^E_{Ni} [J/mol]	S^E_{Ni} [J/(mol·K)]	a_{Ni}	γ_{Ni}
1.000	0	0	0.000	0	0.000	1.000	1.000
0.900	−1778	−1173	0.336	−201	−0.540	0.888	0.987
0.800	−4142	−3579	0.313	−802	−1.543	0.758	0.948
0.700	−7223	−6094	0.627	−1885	−2.339	0.617	0.882
0.600	−11287	−8317	1.650	−3642	−2.597	0.470	0.784
0.500	−16754	−10571	3.435	−6380	−2.328	0.326	0.653
0.400	−24232	−13904	5.738	−10519	−1.881	0.198	0.495
0.300	−34609	−20086	8.068	−16590	−1.942	0.099	0.330
0.200	−49325	−31611	9.841	−25238	−3.541	0.037	0.185
0.100	−71680	−51700	11.100	−37220	−8.045	0.008	0.083
0.000	−∞	−84294	∞	−53405	−17.160	0.000	0.028

Reference state: Ni(liquid)

Table IIIc. Partial quantities for Zn in the liquid phase at 1800 K.

x_{Zn}	ΔG_{Zn} [J/mol]	ΔH_{Zn} [J/mol]	ΔS_{Zn} [J/(mol·K)]	G^E_{Zn} [J/mol]	S^E_{Zn} [J/(mol·K)]	a_{Zn}	γ_{Zn}
0.000	−∞	−67421	∞	−29433	−21.105	0.000	0.140
0.100	−60030	−43500	9.183	−25569	−9.961	0.018	0.181
0.200	−46256	−29452	9.336	−22169	−4.046	0.045	0.227
0.300	−36958	−21739	8.455	−18939	−1.555	0.085	0.282
0.400	−29410	−17548	6.590	−15697	−1.029	0.140	0.350
0.500	−22747	−14790	4.421	−12373	−1.342	0.219	0.437
0.600	−16657	−12097	2.533	−9011	−1.714	0.329	0.548
0.700	−11106	−8827	1.266	−5768	−1.700	0.476	0.680
0.800	−6251	−5064	0.660	−2912	−1.195	0.659	0.823
0.900	−2401	−1611	0.439	−824	−0.437	0.852	0.946
1.000	0	0	0.000	0	0.000	1.000	1.000

Reference state: Zn(liquid)

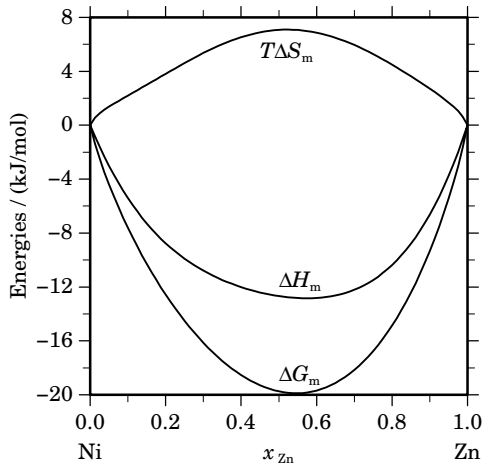

Fig. 2. Integral quantities of the liquid phase at T=1800 K.

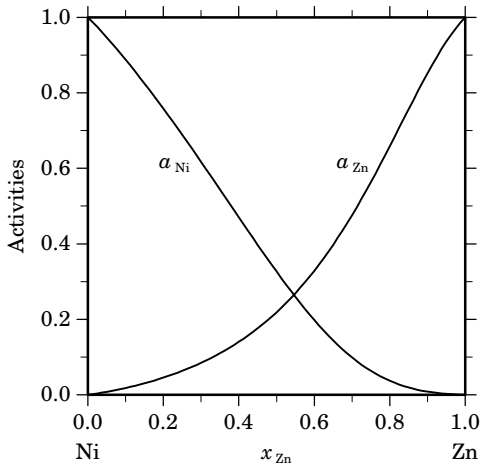

Fig. 3. Activities in the liquid phase at T=1800 K.

Table IV. Standard reaction quantities at 298.15 K for the compounds per mole of atoms.

Compound	x_{Zn}	$\Delta_{\mathrm{f}}G^{\circ}$ / (J/mol)	$\Delta_{\mathrm{f}}H^{\circ}$ / (J/mol)	$\Delta_{\mathrm{f}}S^{\circ}$ / (J/(mol·K))	$\Delta_{\mathrm{f}}C_P^{\circ}$ / (J/(mol·K))
$NiZn_8$	0.889	−10220	−10215	0.015	−0.085

References

[1991Nas] P. Nash, Y.Y. Pan in: "Phase Diagrams of Binary Nickel Alloys", P. Nash (ed.), ASM Intl., Materials Park, OH, 1991, pp. 382–390.
[2000Vas] G.P. Vassiliev, T. Gomez-Acebo, J.-C. Tedenac: J. Phase Equilibria **21** (2000) 287–301.
[2002Su] X. Su, N.-Y. Tang, J.M. Toguri: J. Phase Equilibria **23** (2002) 140–148.
[2003Mie] J. Miettinen: Calphad **27** (2003) 263–274.