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A CRITICAL THERMODYNAMIC EVALUATION OF THE SYSTEM MG-NI

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ABSTRACT Within the framework of COST Action 507 a critical thermodynamic analysis has been carried out of the system Mg-Ni. All thermodynamic data obtained in this action and existing data reported in the literature are described by the thermodynamic analysis. This thermodynamic evaluation is valid between 300 K and 1728 K (the melting temperature of Ni) and for the complete composition range. The purpose of the evaluation is to establish a firm basis for the thermodynamic description of the ternary system Cu-Mg-Ni.

1. Introduction

COST Action 507 was concerned with the measurement and evaluation of thermochemical and thermophysical properties to provide a database for the development of new light metal alloys. Amongst its achievements, this Action provided data of importance for the development of high-strength, hot-strength and wrought aluminium alloys. The thermodynamic evaluation of the ternary system Cu-Mg-Ni, and therefore the binary system Mg-Ni, represents a contribution to the development of this database.

Because the Laves phase MgNi_2 forms an extensive phase equilibrium field with liquid in the system Cu-Mg-Ni, a critical thermodynamic evaluation of the system Mg-Ni is indispensable to the elucidation of all phase equilibria in the ternary system.

A thermodynamic description of the system Mg-Ni has been presented by Nayeb-Hashemi and Clark[1] in 1985. This adequately describes the phase equilibria in the system and the then available thermodynamic data for the compound Mg_2Ni and the Laves phase MgNi_2 . A satisfactory thermodynamic description of the homogeneity range of the latter phase was not given however. Since 1991, accurate thermodynamic functions for many pure elements are available. These have been compiled by Dinsdale[2], and the Gibbs energy functions are incorporated in the present thermodynamic evaluation of the system. The ferromagnetic behaviour of Ni is also included in the thermodynamic description of the binary system.

Bagnoud and Feschotte[3] showed that the Laves phase MgNi_2 forms a single phase field with a homogeneity range of $0.662 \leq X_{\text{Ni}} \leq 0.673$. In the underlying work, a thermodynamic model is proposed which describes this homogeneity range. In order to achieve a more reliable description of the binary system

Mg-Ni, additional measurements were performed by several partners within COST Action 507. Using these measurements and existing information, a reliable thermodynamic description of the system is given. The results of a thermodynamic evaluation of the ternary system Cu-Mg-Ni will be presented in a separate paper.

2. Experimental data

2.1. Phase diagram data

The system Mg-Ni consists of the liquid, the stoichiometric compound Mg_2Ni , the Laves phase $MgNi_2$ with a narrow homogeneity range and the terminal solid solution phases Hcp_A3 and Fcc_A1. Haughton and Payne[4] showed that the solid solubility of Ni in Hcp_A3 is less than 0.04 mol% Ni at 773 K. Merica and Waltenberg[5] reported a solid solubility of Mg in Fcc_A1 of less than 0.2 mol% Mg at 1373 K. Because no exact values of the solid solubilities are given, we neglected the solid solubility of Mg in the Fcc_A1 phase and Ni in the Hcp_A3 phase.

The liquidus of the system has been investigated by Vos[6] using thermal analysis. Haughton and Payne[4] more accurately determined the liquidus in the composition range $0 \leq X_{Ni} \leq 0.34$ by means of cooling and heating curves. Within COST Action 507 the liquidus was measured by Micke and Ipser[7] in the composition range $0.30 \leq X_{Ni} \leq 0.34$ using an isopiëstic method. Their data are in good agreement with the liquidus data of Haughton and Payne[4].

As has been noted by Nayeb-Hashemi and Clark[1] there are reasons to believe that the liquidus data of Vos[6] are not reliable due to impurities of the used materials and a lack of homogeneity of the mixtures. Vos[6] is the only investigator who reported liquidus points in the composition range $0.33 \leq X_{Ni} \leq 1$. The number of liquidus points belonging to the liquid-Fcc_A1 and liquid- $MgNi_2$ equilibria do not allow an accurate estimation of the composition of the eutectic point however. The three phase equilibria have been investigated by Vos[6], Haughton and Payne[4], Bagnoud and Feschotte[3] and Merica and Waltenberg[5]. The melting temperature of $MgNi_2$ has been investigated by Vos[6], Bagnoud and Feschotte[3] and Lieser and Witte[8]. The range of homogeneity of $MgNi_2$ and the three phase equilibrium temperatures have been investigated by Bagnoud and Feschotte[3] by means of XRD, metallography, electron microprobe analysis and DTA. They claim that the homogeneity range extends from 66.2 mol% Ni at the peritectic three phase equilibrium of liquid, Mg_2Ni and $MgNi_2$ to 67.3 mol% Ni at the eutectic three phase equilibrium of $MgNi_2$, liquid and Fcc_A1.

2.2. Gibbs energy data

The Gibbs energy, enthalpy and entropy of formation of the Laves phase $MgNi_2$ can be derived from the data of Schmahl and Sieben[9] obtained by means of vapour pressure measurements using a transpiration method, Smith and Christian[10] by means of vapour pressure measurements using the Knudsen effusion method, King and Kleppa[11] by means of tin solution calorimetry and Lukashenko and Eremenko[12] by means of emf measurements. The heat capacity of $MgNi_2$ has been measured by Wollam and Wallace[13] in the range of 10.6-558 K. The enthalpy and heat capacity of $MgNi_2$ have been measured by Schubel[14]. According to Wollam and Wallace[13] and Buschow[15], the Laves phase $MgNi_2$ shows no ferromagnetic behaviour.

The enthalpy and entropy of formation of the compound Mg_2Ni were derived from the data of Schmahl and Sieben[9], Smith and Christian[10] and Lukashenko and Eremenko[12]. King and Kleppa[11] measured the heat of formation of this compound.

In order to establish a more reliable thermodynamic description within COST Action 507, Feufel[16] determined the heat capacities and enthalpies of formation of the two intermetallic phases. He also

determined the enthalpy of mixing and partial enthalpy of mixing of Ni in the liquid phase. The enthalpy of mixing was also measured by Sommer *et al.*[17]. Within COST Action 507, Mücke and Ipsier[7] determined the activity of Mg at several temperatures using an isopiestic method. They also determined the partial heat of mixing of Mg in the liquid. Partial enthalpies are also given by Tkhai and Serebryakov[18] and Hultgren[19]. Activities of the liquid were also established by Sieben and Schmahl[20] using vapour pressure measurements. The data of the latter authors are also reported by Hultgren[19].

3. Thermodynamic modelling

For the description of the thermodynamic functions of the pure elements in their stable and metastable states, we used the SGTE (Scientific Group Thermodata Europe) phase stability equations published by Dinsdale[2].

The Gibbs energy functions of the liquid, Fcc_A1 and Hcp_A3 phases are given as:

$$G^\varphi(T, x_i, x_j) = x_i \cdot \mu_i^{*\varphi} + x_j \cdot \mu_j^{*\varphi} + R \cdot T \cdot (x_i \cdot \ln(x_i) + x_j \cdot \ln(x_j)) + G^{E\varphi}(T, x_i, x_j) \quad (1)$$

where the thermodynamic potentials μ of substances i and j are only functions of temperature. The coefficients of the expressions used for μ_i and μ_j are listed in table 1. The symbol φ denotes a phase, R the gas constant, T thermodynamic temperature and x_j the mole fraction of substance j.

The excess Gibbs energy functions of these phases are described using a Redlich-Kister[21] expression:

$$G^{E\varphi}(T, x_i, x_j) = x_i \cdot x_j \cdot \sum_{v=0}^n (x_i - x_j)^v \cdot L_{ij}^{\varphi v}(T) \quad (2)$$

where:

$$L_{ij}^{\varphi v}(T) = A_{ij}^{\varphi v} + B_{ij}^{\varphi v} \cdot T \quad (3)$$

In the equations above, i = Mg, j = Ni and v and n are integers.

Schubert and Anderko[22,23] reported that the compound Mg_2Ni has a hexagonal, C16-type structure with 6 molecules per unit cell. No homogeneity range has been reported for this compound and it is modelled as a stoichiometric compound. The Gibbs energy expression which has been used in our analysis is given as:

$$G^\varphi(T) = G_1 + G_2 \cdot T + G_3 \cdot T \cdot \ln(T) + G_4 \cdot T^2 + G_5 \cdot T^{-1} \quad (4)$$

in which G_1 to G_5 are constants.

Laves and Witte[24] reported that the Laves phase $MgNi_2$ has a hexagonal hP24-type (C36) crystal structure with 8 molecules per unit cell. This phase has been modelled using a two sublattice model written as $(Mg, Ni)_p : (Mg, Ni)_q$ as used in the ThermoCalc program[25]. The Gibbs energy of phase $\varphi = MgNi_2$ is written as:

$$G^\varphi = G_{id}^\varphi + G_f^\varphi + G^{E\varphi} \quad (5)$$

where:

$$G_{id}^\varphi = \frac{R \cdot T}{p + q} \cdot \left[p \cdot \left(y_{Mg}^1 \cdot \ln(y_{Mg}^1) + y_{Ni}^1 \cdot \ln(y_{Ni}^1) \right) + q \cdot \left(y_{Mg}^2 \cdot \ln(y_{Mg}^2) + y_{Ni}^2 \cdot \ln(y_{Ni}^2) \right) \right] \quad (6)$$

and

$$G_f^{\phi} = \left[y_{Mg}^1 \cdot y_{Mg}^2 \cdot G(Mg_p : Mg_q) + y_{Mg}^1 \cdot y_{Ni}^2 \cdot G(Mg_p : Ni_q) + y_{Ni}^1 \cdot y_{Mg}^2 \cdot G(Ni_p : Mg_q) + y_{Ni}^1 \cdot y_{Ni}^2 \cdot G(Ni_p : Ni_q) \right] \quad (7)$$

where the superscripts 1 and 2 denote sublattice 1 or 2. The functions $G(i_p:j_q)$ represent the Gibbs energies of formation of the ideal compound and of the fictitious compounds and are expressed as functions of temperature only. The variables y_j^1 and y_j^2 represent the site fractions of elements j on sublattice 1 or 2. The values of p and q are equal to 2/3 and 1/3 respectively. There are two possible ways in which the optimisation may proceed. In a first analysis, referred to as description 1, we assumed $G^{E\phi} = 0$, which means that the functions $G(i_p:j_q)$ had to be optimised. In order to establish a data set which is more applicable to modern databases we adopted the unaries description recommended by SGTE. In this second description, the functions $G(Mg_p:Mg_q)$ and $G(Ni_p:Ni_q)$ are fixed to certain expressions. In the latter case the function $G^{E\phi}$ had to be optimised. It is written as:

$$G^{E\phi} = y_{Mg}^1 \cdot y_{Ni}^1 \cdot (y_{Mg}^2 \cdot L_{Mg,Ni:Mg} + y_{Ni}^2 \cdot L_{Mg,Ni:Ni}) + y_{Mg}^2 \cdot y_{Ni}^2 \cdot (y_{Mg}^1 \cdot L_{Mg:Mg,Ni} + y_{Ni}^1 \cdot L_{Ni:Mg,Ni}) \quad (8)$$

TABLE 1.

Coefficients of the thermodynamic potentials of Mg and Ni in their stable and metastable phases taken from the work of Dinsdale[2]. The thermodynamic potentials are calculated using the expression: $\mu(T) = a + b \cdot T + c \cdot T \cdot \ln(T) + d \cdot T^2 + e \cdot T^3 + f/T + g \cdot T^7 + h \cdot T^9$. The coefficients are given in $J \cdot mol^{-1}$. T_{min} represents the minimum temperature from which the description starts.

Tmin/K	a	b	c	d·10 ⁴	e·10 ⁶	f	g·10 ²⁰	h·10 ⁻²⁸
Mg-Hcp_A3								
298.15	-8367.340	143.675547	-26.1849782	4.858	-1.393669	78950	0	0.000000
923.00	-14130.185	204.716215	-34.3088000	0.000	0.000000	0	0	1.038192
Mg-Liquid								
298.15	-165.097	134.838617	-26.1849782	4.858	-1.393669	78950	-8.0176	0.000000
923.00	-5439.869	195.324057	-34.3088000	0.000	0.000000	0	0	0.000000
Mg-Fcc_A1								
298.15	-5767.340	142.775547	-26.1849782	4.858	-1.393669	78950	0	0.000000
923.00	-11530.185	203.816215	-34.3088000	0.000	0.000000	0	0	1.038192
Ni-Fcc_A1								
298.15	-5179.159	117.854	-22.096	-48.407	0	0	0	0.00
1728.00	-27840.655	279.135	-43.100	0.000	0	0	0	1127.54
Ni-Liquid								
298.15	11235.527	108.457	-22.096	-48.407	0	0	0.382318	0
1728.00	-9549.775	268.598	-43.100	0.000	0	0	0	0
Ni-Hcp_A3								
298.15	-4133.159	119.109	-22.096	-48.407	0	0	0	0
1728.00	-26794.655	280.390	-43.100	0.000	0	0	0	1127.54

The functions denoted as "L" in equation (8) can be expressed in the same way as given by equation (3). Because Ni is a ferromagnetic element, a magnetic contribution to the Gibbs energies of Ni-Fcc_A1 and Ni-Hcp_A3 is required. This contribution has been defined by Hillert and Jarl[26] following the work of Inden[27,28] and is given by:

$$G_{mag} = R \cdot T \cdot \ln(B_0 + 1) \cdot g(\tau) \quad (9)$$

where $\tau = T/T_c$, T_c the curie temperature of Ni (633 K) and B_0 the average magnetic moment per Ni atom (0.52).

The function $g(\tau)$ is defined as:

$$g(\tau) = 1 - \frac{1}{D} \cdot \left[\frac{79}{140 \cdot m \cdot \tau} + \frac{474 \cdot (1-m)}{497 \cdot m} \cdot \left(\frac{\tau^3}{6} + \frac{\tau^9}{135} + \frac{\tau^{15}}{600} \right) \right] \quad \tau \leq 1 \quad (10)$$

$$g(\tau) = -\frac{1}{D} \cdot \left[\frac{\tau^{-5}}{10} + \frac{\tau^{-15}}{315} + \frac{\tau^{-25}}{1500} \right] \quad \tau > 1 \quad (11)$$

where:

$$D = \frac{518}{1125} + \frac{11692 \cdot (1-m)}{15975 \cdot m}$$

The value of m depends on the structure and can be interpreted as the fraction of the magnetic enthalpy absorbed above the critical temperature. For Fcc_A1 and Hcp_A3 this value equals 0.28.

4. Results and discussion

The programs “BINGSS”[29] and “ThermoCalc”[25] have been used to evaluate the excess Gibbs energy of the liquid phase and the Gibbs energy functions of the intermetallic phases Mg_2Ni and $MgNi_2$. All data except the liquidus data of Vos[6] in the composition range $0 \leq X_{Ni} \leq 0.67$ have been used in the assessment of the system. The results of the two evaluations are given in table 2. Extra digits in the values are given to avoid stability problems when the results are used in higher order systems. Using these results the phase diagram has been calculated and plotted in figures 1 and 2 together with the experimental data of Vos[6], Haughton and Payne[4], Bagnoud and Feschotte[3] and Micke and Ipser[7]. The maximum deviation of the data of Haughton and Payne[4] is 15 K and the mean deviation is 4.7 K. The maximum deviation of the data of Micke and Ipser[7] is 10.2 K and the mean deviation is 3 K. The liquidus points of Vos[6] strongly deviate from the result of our calculation. Their liquidus points representing the equilibrium between liquid and Fcc_A1 are reproduced within 10 K. The experimental data of Bagnoud and Feschotte[3] are reproduced within their reported error in the compositions (± 0.3 at %) for both descriptions. From figure 2 it is seen that for description 2 the phase boundary separating the single phase field $MgNi_2$ from the two phase field Fcc_A1+ $MgNi_2$ is shifted to Mg rich compositions compared to that of description 1.

In table 3 a comparison is given of the calculated and experimental three phase equilibria present in the system. From this table it is clear that all data are reproduced excellently and that the difference between the two descriptions is small.

The calculated heats of formation of the two intermetallic phases are compared with the experimental data in table 4. From this table it is clear that the data of Feufel[16] are best reproduced. Directing the optimisation to lower values of the enthalpy of formation as indicated by other authors in table 4, leads to a poorer reproduction of the activity data of Micke and Ipser[7] and to poorer reproduction of the excess enthalpy data of Feufel[16] and Sommer *et al.*[17].

From table 4 it is clear that the calculated entropy of formation of $MgNi_2$ is close to the value given by Lukashenko and Eremenko[12] but more negative than the values of King and Kleppa[11] and Smith and Christian[10]. To obtain their result, the latter authors used the heat capacity of Ni at temperatures above the Curie temperature using the data of Kelley[30].

TABLE 2

Coefficients and functions describing the thermodynamic properties of the system Mg-Ni. All coefficients and functions are given in Joule per mole of atoms.

Redlich-Kister model (equations (2,3))						
Phase	ν	A_{ij} in $\text{J}\cdot\text{mol}^{-1}$	B_{ij} in $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	Phase	ν	A_{ij} in $\text{J}\cdot\text{mol}^{-1}$ B_{ij} in $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
Liquid	0	-50910.00	25.79995	Fcc_A1	0	100000 0
	1	-14989.95	13.24788	Hcp_A3	0	100000 0
Phase: $1/3 \text{Mg}_2\text{Ni}$: Stoichiometric model: equation (4)						
	G_1	G_2	G_3	G_4	G_5	
	-20320.40	138.49311	-24.9354	$-1.5385\cdot 10^{-3}$	133805	
Phase: $1/3 \text{MgNi}_2$: Two sublattice model (<i>first description</i>): equations (5,6,7)						
$G(\text{Mg}_{1/3}:\text{Ni}_{2/3})$	G_1	G_2	G_3	G_4	G_5	(See equation (4))
	-24688.46	147.27013	-25.7998	$-2.46496\cdot 10^{-3}$	111575.5	
$G(\text{Mg}_{2/3}:\text{Mg}_{1/3}) = 764.7058861 + 20.5882353\cdot T + \mu(\text{Mg-Hcp_A3})$						
$G(\text{Mg}_{2/3}:\text{Ni}_{1/3}) = 1000 + 2/3\cdot\mu(\text{Mg-Hcp_A3}) + 1/3\cdot\mu(\text{Ni-Fcc_A1})$						
$G(\text{Ni}_{2/3}:\text{Ni}_{1/3}) = 5254.902 + 6.862745\cdot T + \mu(\text{Ni-Fcc_A1})$						
Phase: $1/3 \text{MgNi}_2$: Two sublattice model (<i>second description</i>): equations (5,6,7,8)						
$G(\text{Mg}_{1/3}:\text{Ni}_{2/3})$ and $G(\text{Mg}_{2/3}:\text{Ni}_{1/3})$: same as the first description						
$G(\text{Mg}_{2/3}:\text{Mg}_{1/3}) = 5000 + \mu(\text{Mg-Hcp_A3})$						
$G(\text{Ni}_{2/3}:\text{Ni}_{1/3}) = 5000 + \mu(\text{Ni-Fcc_A1})$						
$L_{\text{Mg,Ni:Mg}} = L_{\text{Mg,Ni:Ni}} = 10100$						
$L_{\text{Mg,Mg:Ni}} = L_{\text{Ni,Mg:Ni}} = -3346.79669 + 19.96183\cdot T$						

TABLE 3.

Comparison of calculated and experimental characteristics of the phase diagram Mg-Ni. Only the compositions of the liquid and the MgNi_2 phases are given because it is assumed that there is no mixing of Mg atoms in the Fcc_A1 phase and no mixing of Ni atoms in the Hcp_A3 phase. Differences between the two descriptions are indicated.

Phases	T/K	$X_{\text{Ni}}(\text{Liq})$	$X_{\text{Ni}}(\text{MgNi}_2)$	Reference
Hcp_A3+Liq+ Mg_2Ni	781.41	0.1106	--	This work
	785	0.176	--	Vos[6]
	781	0.113	--	Haughton and Payne[4]
	779	--	--	Bagnoud and Feschotte[3]
Liq+ Mg_2Ni + MgNi_2	1032.31	0.2964	0.6620	This work
	1041	0.260	--	Vos[6]
	1033	0.290	--	Haughton and Payne[4]
	1033	--	0.662	Bagnoud and Feschotte[3]
Liq+Fcc_A1+ MgNi_2	1368.28	0.7961	0.6734	This work 1st description
	1368.04	0.7960	0.6735	This work 2nd description
	1355	0.772	--	Vos[6]
	1368	--	--	Merica and Waltenberg[5]
	1370	--	0.673	Bagnoud and Feschotte[3]
Liq+ MgNi_2 (maximum)	1420.60	0.6665	0.6665	This work 1st description
	1420.58	0.6686	0.6686	This work 2nd description
	1368	--	--	Merica and Waltenberg[5]
	1416	--	--	Lieser and Witte[8]
	1420±3	--	--	Bagnoud and Feschotte[3]

Because the data of Smith and Christian[10] deviate from our results and because SGTE data, as compiled by Dinsdale[2], give a reliable heat capacity of Ni taking its ferromagnetic behaviour into account, we used the published vapour pressure measurements to recalculate the formation properties of MgNi_2 and Mg_2Ni . For Mg in the vapour state we used an ideal value of the heat capacity of $20.763 \pm 0.2 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, which describes its variation in the temperature range of 298 K to 3000 K. We used the same calculation procedure as given by Smith and Christian[10]. For MgNi_2 , the recalculated formation properties are in good agreement with our results from the thermodynamic analysis. For Mg_2Ni however, our calculated enthalpy of formation from the analysis is higher than the recalculated enthalpy of formation.

Using the Gibbs energies of the compound Mg_2Ni and the Laves phase MgNi_2 given in table 2, heat capacity curves were calculated. The result of the calculation for the compound Mg_2Ni is compared with the experimental data of Feufel[16] in figure 3. Their data are reproduced within $0.086 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ which is within their experimental error limits. The result of the calculation for MgNi_2 is compared with the experimental data of Wollam and Wallace[13] (maximum deviation 0.85, mean deviation $0.47 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$), Schubel[14] (maximum deviation 0.25, mean deviation $0.20 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) and Feufel[16] (maximum deviation 0.43, mean deviation $0.06 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) in figure 4. Directing the optimisation towards the data of Wollam and Wallace[13] results in a poorer description of the excess enthalpy data of Feufel[16] and Sommer *et al.*[17] and the activity data of Micke and Ipser[7].

TABLE 4
Comparison of calculated and experimental formation properties of the two intermetallic phases.

$\Delta_f H(\text{Mg}_2\text{Ni})$ $\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_f S(\text{Mg}_2\text{Ni})$ $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\Delta_f H(\text{MgNi}_2)$ $\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_f S(\text{MgNi}_2)$ $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	Reference
-35.555	-2.323	-48.086	-7.504	<i>This work</i>
-60.29	-27.63	-77.87	-32.66	Schmahl and Sieben[9]
-66.99 ± 9.20	-25.12 ± 12.14	-55.68 ± 6.28	-2.51 ± 5.86	Smith and Christian[10]
-56.29 ± 5.23	-8.97 ± 5.77	-55.65 ± 4.61	-5.63 ± 4.80	recalculated from [10] (see text)
-39.57 ± 1.26		-55.27 ± 2.1	-2.5	King and Kleppa[11]
-48.46	-14.89	-59.91	-11.68	Lukashenko and Eremenko[12]
-36.36 ± 6.24		-53.22 ± 10		Feufel[16]

In figure 5, we compare the calculated heat of mixing with the data of Feufel[16] (maximum deviation 0.13, mean deviation $0.05 \text{ kJ}\cdot\text{mol}^{-1}$) and Sommer *et al.*[17] (maximum deviation 1.79, mean deviation $0.65 \text{ kJ}\cdot\text{mol}^{-1}$).

In figure 6 the calculated partial heat of mixing is compared with the data of Feufel[16] (maximum deviation 3.3, mean deviation $1.5 \text{ kJ}\cdot\text{mol}^{-1}$) and Micke and Ipser[7] (maximum deviation 2.6, mean deviation $1.1 \text{ kJ}\cdot\text{mol}^{-1}$). The data of Hultgren[19] are reproduced within $0.8 \text{ kJ}\cdot\text{mol}^{-1}$ and the data of Tkhai and Serebryakov[18] within $0.8 \text{ kJ}\cdot\text{mol}^{-1}$.

In figure 7 the calculated activity of Mg in the liquid is compared with the data of Micke and Ipser[7] (maximum deviation 0.05, mean deviation 0.02). After their isopiestic measurements, they obtained their activity data for different sample temperatures and compositions and converted these to a common temperature of 1073 K. Each experimental run represents a different reservoir temperature (which is not equal to the sample temperature). The data of Sieben and Schmahl[20] as compiled by Hultgren[19] are reproduced within 0.05.

5. Conclusions

A thermodynamic evaluation of the system Mg-Ni has been presented. New thermodynamic data and phase diagram data obtained in COST Action 507 as well as existing data were used in the assessment of the system. The assessment of the system results in two possible descriptions of the Laves phase MgNi_2 . In the first description we have assumed that $G^E = 0$ which is to our idea the most straightforward description. In

the second description we have adopted the unaries description recommended by SGTE which results in a data set which is more applicable to modern databases. The two descriptions lead to almost identical results. Our results are in excellent agreement with the experimental data with the exception of the formation properties of Mg_2Ni . For this compound, our calculations reproduce the published calorimetric measurements well, whereas the reproduction of vapour pressure measurements is relatively poor. In the assessment of the system, an excellent description of the homogeneity range of the Laves phase MgNi_2 has been obtained.

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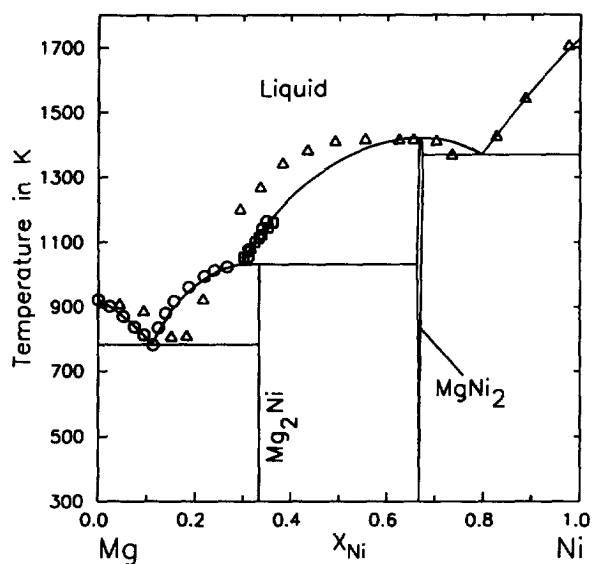


FIG. 1

Calculated phase diagram of the system Mg-Ni together with the liquidus data of: Δ Vos[6], \circ Haughton and Payne[4] and \square Micke and Ipser[7].

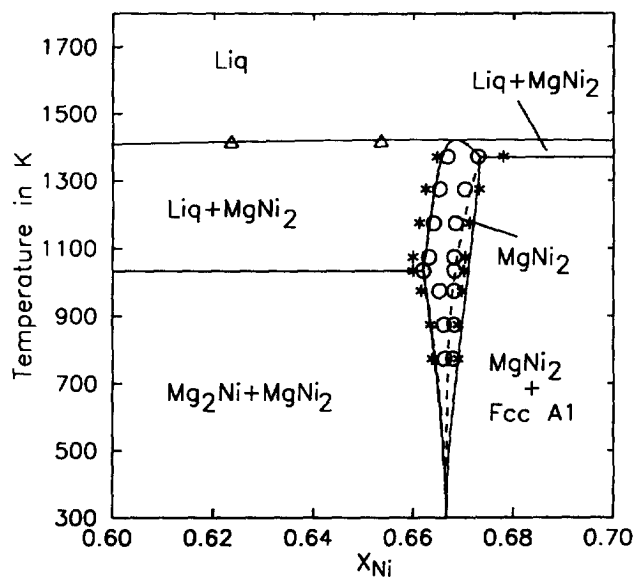


FIG. 2

Calculated phase diagram of the system Mg-Ni in the vicinity of the Laves phase MgNi₂ together with experimental data: Δ liquidus points of Vos[6], O, * Bagnoud and Feschotte[3] (O metallography and * microprobe analysis, the diameter of the symbols indicates the mean experimental error in the composition). Solid curves: description 1 and dashed curves: description 2

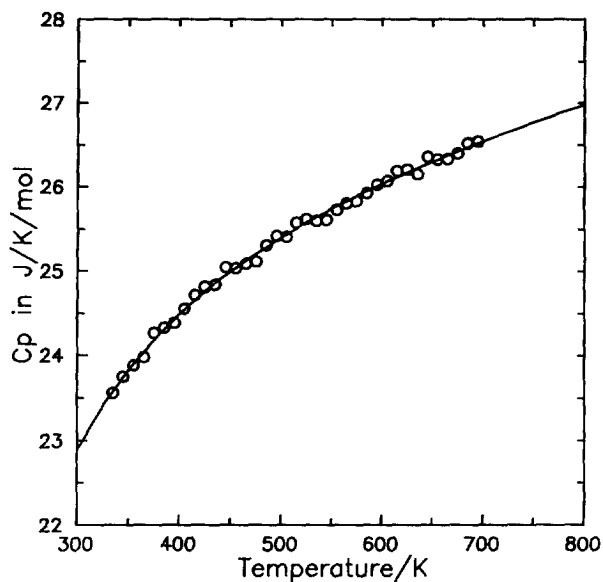


FIG. 3

Calculated heat capacity curve of the compound Mg_{2/3}Ni_{1/3} together with the data of: O Feufel[16].

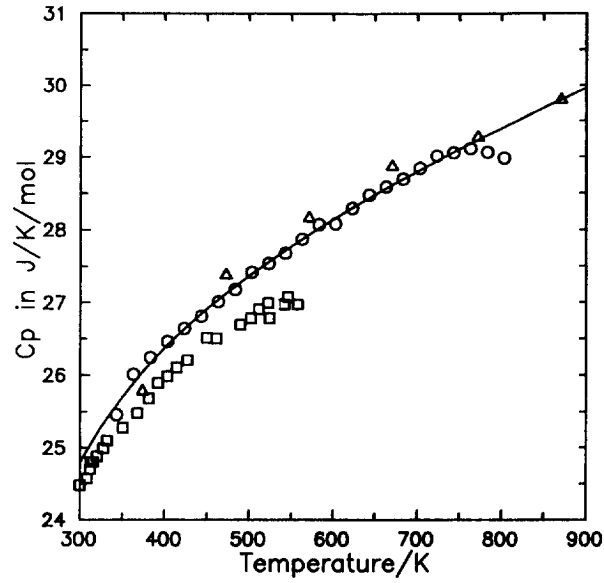


FIG. 4

Calculated heat capacity curve of the Laves phase $Mg_{1/3}Ni_{2/3}$ together with the data of: \square Wollam and Wallace[13], Δ Schubel[14] and \circ Feufel[16].

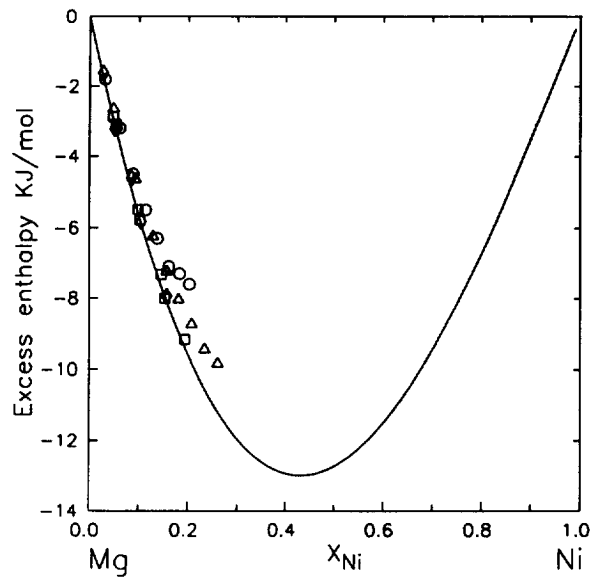


FIG. 5

Calculated excess enthalpy of the liquid phase together with the data of: \square Feufel[16] (1002 and 1008 K), Sommer *et al.*[17] (\circ at 1120 K, Δ at 980 K).

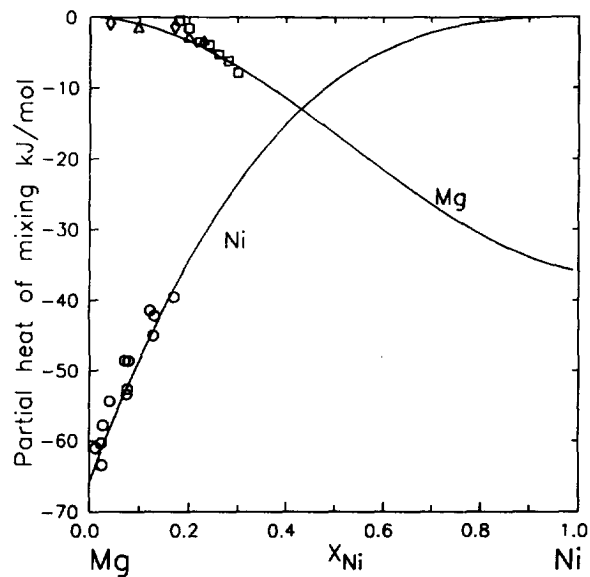


FIG. 6

Calculated partial heat of mixing of Mg and Ni together with the data of: \circ Feufel[16], \square Micke and Ipser[7], \diamond Tkhai and Serebryakov[18] and Δ Hultgren[19].

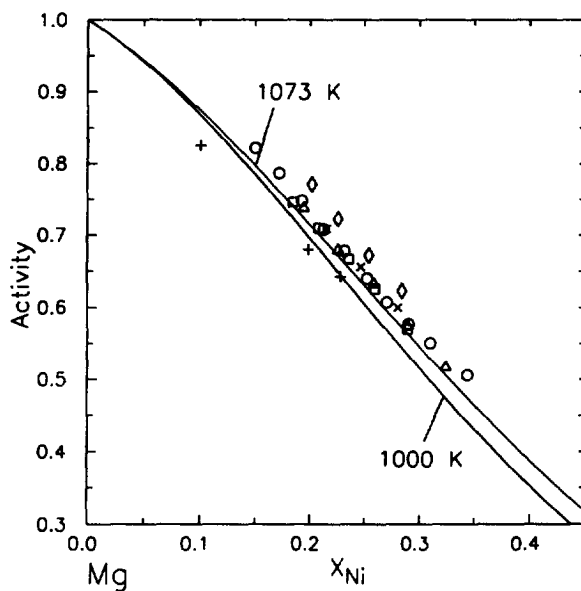


FIG. 7

Calculated activity curves of Mg in the liquid phase together with experimental data of: Micke and Ipser[7] at 1073 K (\diamond run 1, \square run 2, \times run 3, Δ run 4, \circ run 5), + Hultgren[19] at 1000 K.

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