Thermodynamic Evaluation of the Mg-Ni-Y Ternary System

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Abstract

Thermodynamic modeling of the Mg-Ni-Y system is carried out as a part of multicomponent thermodynamic database for Mg alloys. This system is being modeled for the first time using the modified quasichemical model which considers the presence of short range ordering in the liquid. A self-consistent thermodynamic database for this system is constructed by combining the thermodynamic descriptions of the constituent binaries. Mg-Ni and Ni-Y binary systems have been re-optimized based on the experimental phase equilibrium and thermodynamic data available in the literature. The optimized thermodynamic parameters for the Mg-Y system are taken from the previous thermodynamic assessment of the Mg-Cu-Y system by the same authors. The constructed database is used to calculate and predict thermodynamic properties, the binary phase diagrams and isothermal section of the ternary Mg-Ni-Y system. The calculated results are found to be in good agreement with the experimental data.

Introduction

Batteries can be a useful source of energy for spacecraft, military and defense, communication, power tools and consumer appliances because of their ability to store energy in a clean, convenient and efficient manner and hence there is a growing need for high-specific power, high-specific energy and low-cost batteries [1]. Currently nickel/cadmium rechargeable batteries are commonly used for these purposes. But due to the relatively low capacity and environmental concerns more efficient and safe substitutes for cadmium are urgently needed. The nickel-metal hydride battery (MH) with a hydrogen storage alloy as a negative electrode has shown a high potential in that aspect [1,2]. That is why, extensive attention has been paid to the utilization of magnesium-based alloys as hydrogen storage materials owing to their high storage capacity [3,4] and low specific weight. The Mg-Ni-Y system is considered one of the promising candidates [1]. Hence it is very important to know the phase diagram and the thermodynamic properties of this system which can be provided by a sound thermodynamic database. A thermodynamic database for the Mg–Ni-Y system has been constructed in this work. Two of the three constituent binaries, Mg–Ni and Ni-Y have been optimized using the modified quasichemical model [5-7] for the liquid phase. The Mg-Y system was optimized earlier [8] and has been used directly in this work. The toop [9] geometric model with Mg as the asymmetric component has been used for the extrapolation of the binaries to the ternary system. This database will provide valuable information about the entire ternary phase diagram and a better understanding of its alloys, which is necessary for their future technological application.

Literature Review

Ni-Y System

The phase diagram of the Ni-Y system was first investigated by Beaudry and Daane [10] and later by Domagala et al. [11]. Beaudry and Daane [10] used metallographic, thermal and X-ray diffraction (XRD) methods in their investigation and reported the existence of nine intermetallic compounds; Y_3Ni, Y_3Ni_2, YNi_2, YNi_3, Y_2Ni_7 YNi_4, Y_2Ni_{17}, YNi and YNi_5. Except the last two, all other compounds undergoe peritectic decomposition. Domagala et al. [11] reported eight compounds and missed the existence of Y_2Ni_7. But another investigation by Buschow [12] on several phases of the R-Ni (R = rare earth) shows that an R_2Ni_7 phase occurs in all the heavier R-Ni systems. So the existence of Y_2Ni_7 phase in the Ni-Y system is consistent with the general trend and been used in this work. They [11] also disagreed with [10] about the stoichiometry of the most Ni-rich intermediate phase reporting the composition to be YNi_9 not Y_2Ni_{17}. Studying the crystal structure data reported by Buschow [13] it is revealed that the stoichiometry should be Y_2Ni_{17}. This composition was also accepted by several other assessments [14-17] and hence it is used in the current analysis. The temperature and composition of the three eutectic reactions reported by [10] and [11] are close to each other and has been used in the current assessment with more weight for the data of [10] since the error associated with the data of [11] is higher.

Beaudry and Daane [10] reported the solubility of yttrium in nickel to be 0.1 at.% at 1250°C, while the solubility of nickel in yttrium to be 0.2 at.% at 900°C. Domagala et al. [11] reported it to be less than 1 wt.% in either terminal solutions.

The crystal structure and lattice parameters determined by different groups [10-13] were summarized by Nash [14] and are selected to be used in the present work.

The magnetic properties of the intermetallic compounds in the Ni-Y system were summarized by [12] and also by Gignoux et al. [18, 19]. None of the Ni-Y compounds has a magnetic ordering temperature above the room temperature. The highest value is found in Y_2Ni_{17} and is close to -113°C [20]. Also, Beaudry and Daane [10] did not find any of the intermetallic compounds to show magnetic behavior at room temperature. Hence magnetic contribution is not added in the optimization of this system.

Not many experimental thermodynamic properties of the Ni-Y system could be found in the literature. Subramanian and Smith [15] determined the Gibbs energy of formation of the nine intermediate phases using the electromotive force (emf) measurements over the temperature range of 627 to 952°C. Estimations of the enthalpy of formation of various intermetallic compounds were done by [20-22] but these values are not consistent with the experimentally measured values by [15]. For the present work, only the values reported by [15] were used. Batalin et al. [23] measured the enthalpy of mixing of the liquid Ni-Y at 1700°C using differential thermal analysis (DTA).

Thermodynamic assessments were done on the Ni-Y system by Nash [14], Zhenmin and Weijing [16] and Mattern et al. [17]. However, none of the assessments considered the presence of short range ordering in the liquid. Hence it is decided to reoptimize this system.

Mg-Ni System

Voss [24] was the first researcher who investigated the Mg–Ni system by thermal analysis in the composition range $0.04 < X_{Ni} < 0.98$. But in his work, the purity of Mg was not specified and the purity of Ni was low (97.7 wt%). Later, Haughton and Payne [25] determined the liquidus temperature more accurately in the Mg-rich end ($0 \leq X_{Ni} \leq 0.34$) by thermal analysis with high purity of elements and homogeneity of mixtures. Bagnoud and Feschotte [26] investigated the system using XRD, metallography, electron microprobe analysis and DTA. Micke and Ipser [27] determined the magnesium vapor pressure over liquid Mg–Ni alloys in the composition range $X_{Mg} > 0.65$ by the isopiestic method and they obtained the liquidus curve between $0.30 < X_{Ni} < 0.40$. According to these investigations, there are two eutectic and one peritectic reactions in the Mg-Ni system. Two intermetallic compounds have been reported among them Mg_2Ni melts incongruently (760°C) and $MgNi_2$ melts congruently (1147±3°C). Bagnoud and Feschotte [26] investigated the homogeneity range of $MgNi_2$ and mentioned that the homogeneity range extends from 66.2 at.% Ni to 67.3 at.% Ni.

Different researchers reported different solid solubility between the two end members. Among them, Haughton and Payne [25] mentioned that the solid solubility of Ni in Mg is less than 0.04 at.% Ni at 500°C, whereas Merica and Waltenberg [28] reported that the solid solubility of Mg in Ni is less than 0.2 at.% Mg even at 1100°C. In the present work, the terminal solid solubility is considered negligible. Moreover, the ferromagnetic behavior of Ni is not included in the optimization as Wollam and Wallace [29] and Buschow [30] disputed the ferromagnetic behavior. They investigated the system by heat capacity and magnetic susceptibility measurements and did not find any anomaly in magnetic susceptibility of $MgNi_2$ or heat capacity at any temperature.

Laves and Witte [31] determined the crystal structure of the Laves phase $MgNi_2$ to be hexagonal *h*P24-type with 8 molecules per unit cell, and lattice parameters of a = 0.48147 and c = 1.58019 nm which are in good agreement with the reported values of Lieser and Witte [32], and Bagnoud and Feschotte [26]. The crystal structure of Mg_2Ni was determined by Schubert and Anderko [33] who reported a hexagonal, C16-type structure with 6 molecules per unit cell and lattice parameters of a = 0.514 and c = 1.322 nm which agree with the reported values by Buschow [30].

Feufel and Sommer [34] measured the integral enthalpy of mixing by calorimetric method at 729°C and 735°C. Micke and Ipser [27] determined the activity of Mg at several temperatures using the isopiestic method. Reasonable agreement was found between their [27] results and those of Sryvalin et al. [35] in the composition range $X_{Ni} \leq 0.30$. Sieben et al. [36] also measured the activity of Mg from Mg vapor pressure.

Enthalpy of formation for $MgNi_2$ and Mg_2Ni compounds were measured by Sieben et al. [36], Smith and Christian [37], King and Kleppa [38], and Lukashenko and Eremenko [39]. All these data are in reasonable agreement and will be compared with the current work.

Thermodynamic optimizations on this system were done by Nayeb-Hashemi and Clark [40], Jacobs and Spencer [41] and most recently by Islam and Medraj [42]. But since none of them accounted for the presence of short range ordering in the liquid, it is decided to re-optimize the system.

Mg-Ni-Y Ternary System

The isothermal section of the Mg-Ni-Y system (Ni ≥ 50%) was investigated by Yao et al. [43] who confirmed the existence of the two ternary compounds YMg_2Ni_9 and $YMgNi_4$ at 400°C. The compositions of these ternary compounds were reported earlier by Kadir et al. [44-46] and Aona et al. [47]. But the heat of formation or melting temperature of these ternary compounds have not been determined yet. No thermodynamic assessment on this system has yet been performed.

Thermodynamic Modeling

Unary phases

The Gibbs Energy function used for the pure elements i (i = Mg, Ni, and Y) in a phase ϕ is described by the following equation:

$$^{0}G_{i}^{\phi}(T) = a + bT + cT\ln T + dT^{2} + eT^{3} + fT^{-1} + gT^{7} + hT^{-9} \qquad (1)$$

Where, $G_i^{\phi}(T)$ is the Gibbs energy of the pure element at standard state, T is the absolute temperature. The values of the coefficients *a* to *h* are taken from Dinsdale [48].

Stoichiometric Phases

The Gibbs energy of a binary stoichiometric phase is given by equation 2.

$$G^{\phi} = x_i\,{}^0G_i^{\phi_1} + x_j\,{}^0G_j^{\phi_2} + \Delta G_f \tag{2}$$

$$\Delta G_f = a + b.T \tag{3}$$

Where, x_i and x_j are mole fractions of elements *i* and *j* which are given by the stoichiometry of the compound, ${}^0G_i^{\phi_1}$ and ${}^0G_j^{\phi_2}$ are the respective reference states of elements *i* and *j*, and ΔG_f is the Gibbs energy of formation per mole of atoms of the stoichiometric compound, which is expressed by equation 3. The parameters *a* and *b* are to be determined through optimization.

Liquid phases

Modified Quasichemical Model

The modified quasichemical model [5-7] has been chosen to describe the liquid phases of the constituent binaries. From the literature survey, it is found that all the three binary systems have very high negative enthalpy of mixing for the liquid which indicates the presence of short range ordering [5]. The energy of pair formation in the modified Quasichemical model can be expressed by using equation 4.

$$\Delta g_{AB} = \Delta g_{AB}^{o} + \sum_{i\geq 1} g_{AB}^{i0} X_{AA}^{i} + \sum_{j\geq 1} g_{AB}^{0j} X_{BB}^{j} \tag{4}$$

Where, Δg_{AB}^{o}, Δg_{AB}^{i0} and Δg_{AB}^{0j} are the parameters of the model and can be expressed as functions of temperature ($\Delta g_{AB}^{o} = a + bT$). Also, the atom to atom coordination number Z_A and Z_B, can be expressed as function of composition and can be presented by the following equations:

$$\frac{1}{Z_A} = \frac{1}{Z_{AA}^{A}}\left(\frac{2n_{AA}}{2n_{AA}+n_{AB}}\right) + \frac{1}{Z_{AB}^{A}}\left(\frac{n_{AB}}{2n_{AA}+n_{AB}}\right) \tag{5}$$

$$\frac{1}{Z_B} = \frac{1}{Z_{BB}^{B}}\left(\frac{2n_{BB}}{2n_{BB}+n_{AB}}\right) + \frac{1}{Z_{BA}^{B}}\left(\frac{n_{AB}}{2n_{BB}+n_{AB}}\right) \tag{6}$$

n_{ij} is the number of moles of (*i-j*) pairs, Z_{AA}^{A} and Z_{AB}^{A} are the coordination numbers when all nearest neighbors of an A atom are A or B atoms, respectively. Similarly, for Z_{BB}^{B} and Z_{BA}^{B}. The composition of maximum short range ordering is determined by the ratio $\frac{Z_{BA}^{B}}{Z_{AB}^{A}}$. Values of Z_{AB}^{A} and Z_{BA}^{B} are unique to the A-B binary system and should be carefully determined to fit the thermodynamic experimental data (enthalpy of mixing, activity etc.). The selected values for the present work are given in table 1. The value of Z_{AA}^{A} is common for all systems containing A as a component. The same is true for all components. In this work, the value of Z_{MgMg}^{Mg} , Z_{CuCu}^{Cu} and Z_{YY}^{Y} was chosen to be 6 because it gave the best possible fit for many binary systems and is recommended by Dr. Pelton's group [5-7].

Table 1: Atom-Atom "coordination numbers" of the liquid

A	B	Z_{AB}^{A}	Z_{AB}^{B}
Mg	Mg	6	6
Y	Y	6	6
Ni	Ni	6	6
Mg	Ni	2	4
Y	Ni	6	5

Solid Solution Phases

The Gibbs energy of an ordered solution phase is described by the compound energy formalism as shown in equations [7-10].

$$G = G^{ref} + G^{ideal} + G^{excess} \quad (7)$$

$$G^{ref} = \sum y_i^l y_j^m ....y_k^q \, {}^0G_{(i:j:...:k)} \quad (8)$$

$$G^{ideal} = RT\sum_l f_l \sum_i y_i^l \ln y_i^l \quad (9)$$

$$G^{excess} = \sum y_i^l y_j^l y_k^m \sum_{\gamma=0} {}^{\gamma}L_{(i,j):k} \times (y_i^l - y_j^l)^{\gamma} \quad (10)$$

Where *i, j, ...k* represent components or vacancy, *l, m* and *q* represent sublattices, y_i^l is the site fraction of component *i* on sublattice *l*, f_l is the fraction of sublattice *l* relative to the total lattice sites, ${}^0G_{(i:j:..k)}$ represents a real or a hypothetical compound (end member) energy, and ${}^{\gamma}L_{(i,j)}$ represent the interaction parameters which describe the interaction within the sublattice.

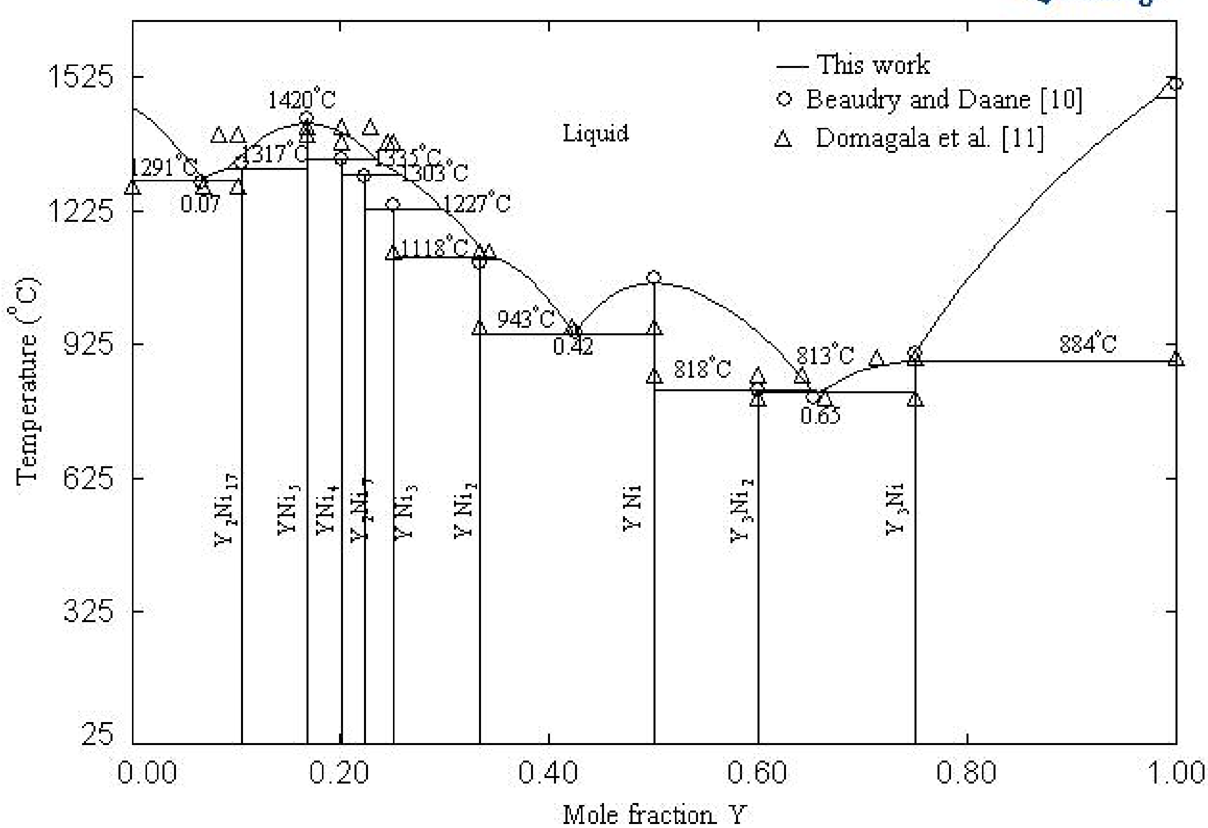

Figure 1 Ni-Y phase diagram

Results and Discussion

All the calculations in this work have been done using the FactSage Software [49]. The calculated Ni-Y phase diagram with the experimental data from [10,11] is shown in figure 1**.** The optimized parameters for the liquid and intermetallic compounds are given in table 2. The mutual solubility between Y and Ni is considered negligible.

Table 2: Optimized model parameters for the Ni-Y system

Phase	Terms	a (J/mol)	b (J/mol. K)
Liquid	Δg^{0}_{AB}	-33,653.83	1.61
	g^{i0}_{AB}	-1,339.46	1.26
	g^{0j}_{AB}	-17,538.50	0.00
Phase	Terms	a (J/mol atom)	b (J/mol.K)
$Ni_{17}Y_2$	ΔG_f	-15,884.11	-2.41
Ni_5Y	ΔG_f	-25,450.90	-1.96
Ni_4Y	ΔG_f	-31,015.9	-0.12
Ni_7Y_2	ΔG_f	-32,229.91	-0.30
Ni_3Y	ΔG_f	-32,934.90	-0.74
Ni_2Y	ΔG_f	-33,899.93	-1.84
NiY	ΔG_f	-33,779.95	-1.25
Ni_2Y_3	ΔG_f	-28,159.96	-0.57
NiY_3	ΔG_f	-17,509.98	-1.45

The calculated enthalpy of mixing curve at 1700°C with the experimental data of [23] is shown in figure 2. Large deviation between the calculated and experimental results can be seen. However it was impossible to maintain the consistency between these results and to reproduce the experimental phase diagram in the same time. Therefore it is decided to be consistent with the phase diagram which is more preciously determined. The calculated Gibbs energy of formation of the intermetallic compounds at 700°C with the experimental data of [15] is shown in figure 3.

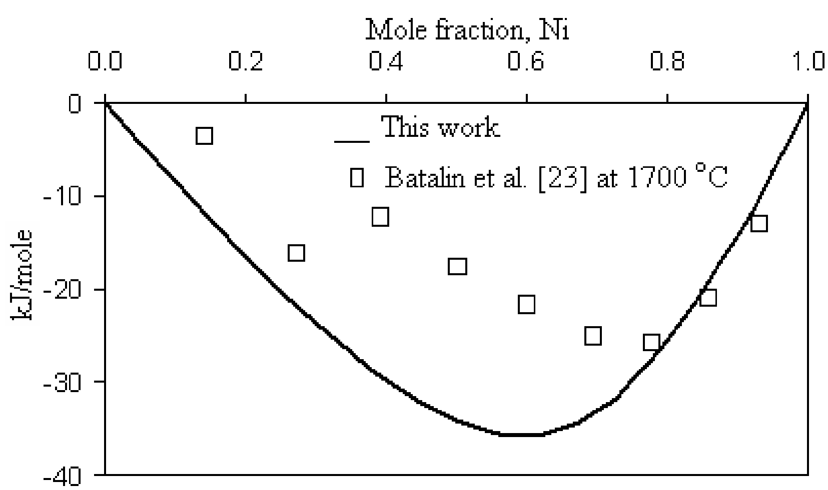

Figure 2: Calculated Enthalpy of Mixing of Liquid Ni-Y at 1700°C

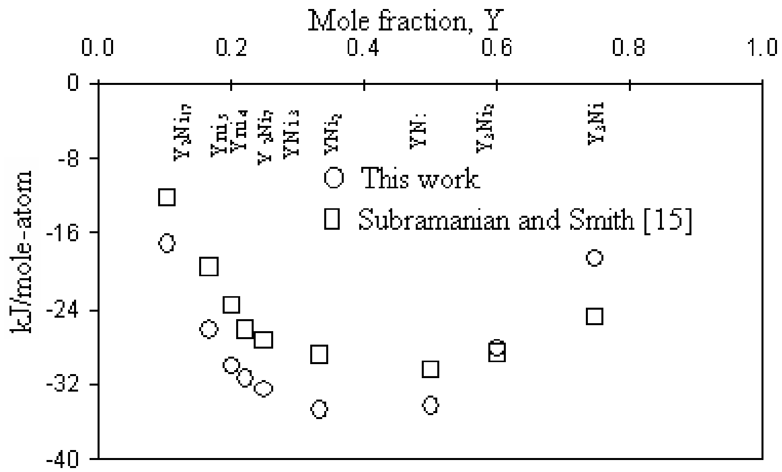

Figure 3: Gibbs Energy of Formation of the Intermetallic Compounds at 700°C

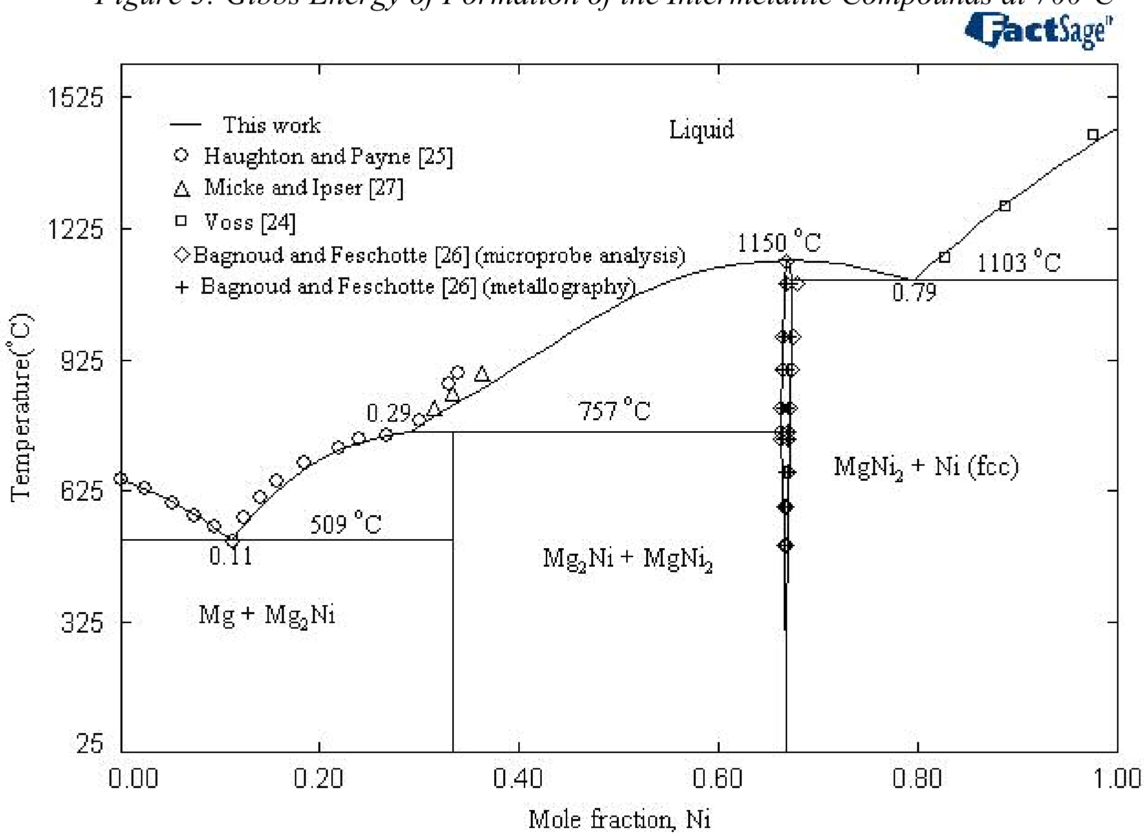

Figure 4: Mg-Ni Phase Diagram

The calculated Mg-Ni phase diagram with the available experimental data from literature is shown in figure 4. There is a lack of experimental data for the liquidus curve in the region between Mg_2Ni and $MgNi_2$. Experiments in this region are necessary for a better optimization of this system. Nevertheless the rest of the phase diagram shows very good agreement with the experimental data. The optimized parameters for the liquid, and the intermetallic compounds are given in table 3. A two sublattice model for the $MgNi_2$ as reported by Islam and Medraj [42] has been used to reproduce the homogeneity range of this phase.

Table 3: Optimized model parameters for the Mg-Ni system

Phase	Terms	a (J/mole)	b (J/mole K)
Liquid	Δg^{0}_{MgNi}	-16,829.43	5.02
	g^{Mg0}_{MgNi}	-15,864.18	10.49
	g^{0Ni}_{NiMg}	-16,345.55	0.00
Phase	**Terms**	**a (J/mole. atom)**	**b (J/mole K)**
Mg_2Ni	ΔG_f	-16,568.80	4.46
$MgNi_2$	${}^{0}G^{MgNi_2}_{Mg:Mg}$	8,333.33	12.66
(Mg%, Ni)$_1$ (Mg, Ni%)$_2$	${}^{0}G^{MgNi_2}_{Mg:Ni}$	-21,944.04	5.76
	${}^{0}G^{MgNi_2}_{Ni:Mg}$	0.00	0.00
	${}^{0}G^{MgNi_2}_{Ni:Ni}$	5,466.66	6.73

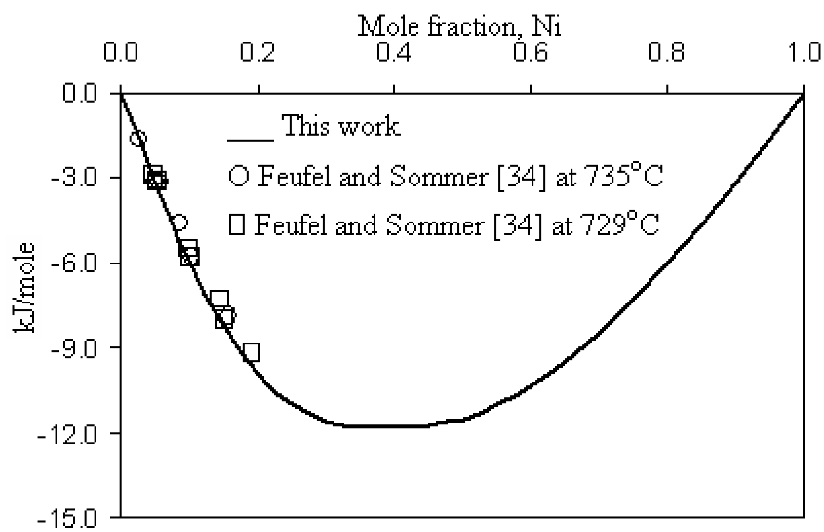

Figure 5: Calculated Enthalpy of Mixing of Liquid Mg-Ni at 735°C

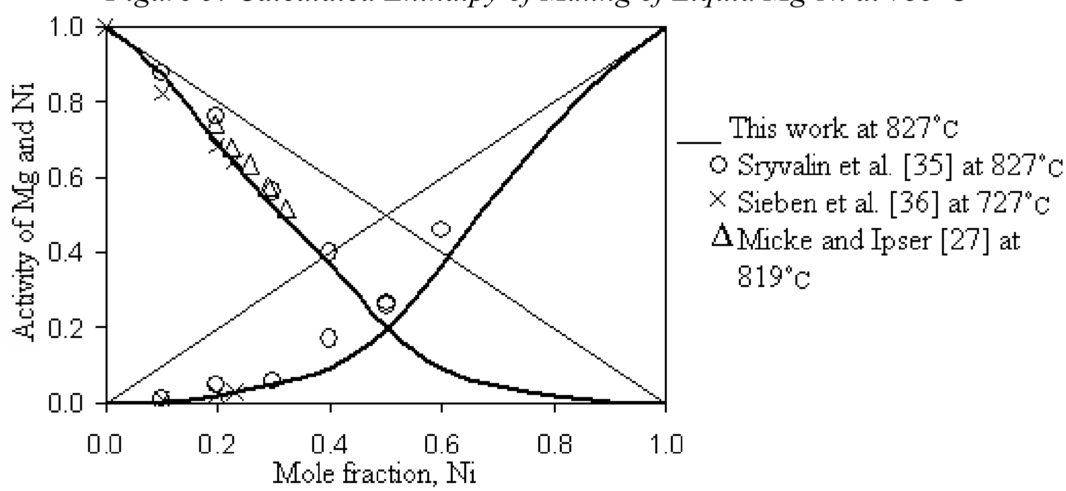

Figure 6: Calculated Activity of Liquid Mg and Ni at 827 °C

The calculated integral enthalpy of mixing of the liquid at 735^oC is given in figure 5 which shows very good agreement with the experimental data of [34]. The activity of liquid Mg and Ni calculated at 827^oC is shown in figure 6. Both the activity curves show reasonable agreement with the experimental data. The calculated enthalpy of formation at room for Mg_2Ni and $MgNi_2$ compared with the available experimental data is shown in figure 7.

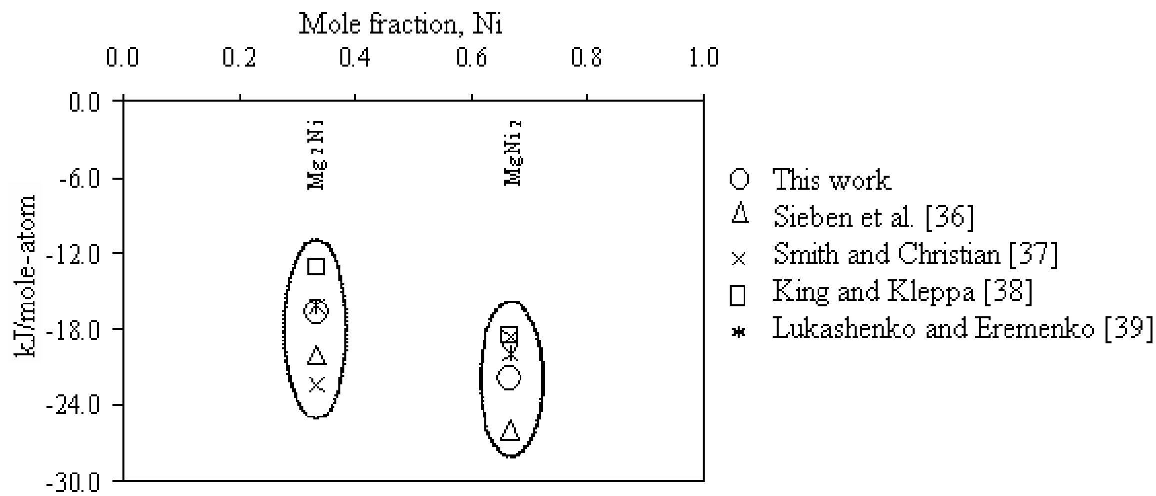

Figure 7: Enthalpy of Formation of the Intermetallic Compounds in the Mg-Ni System

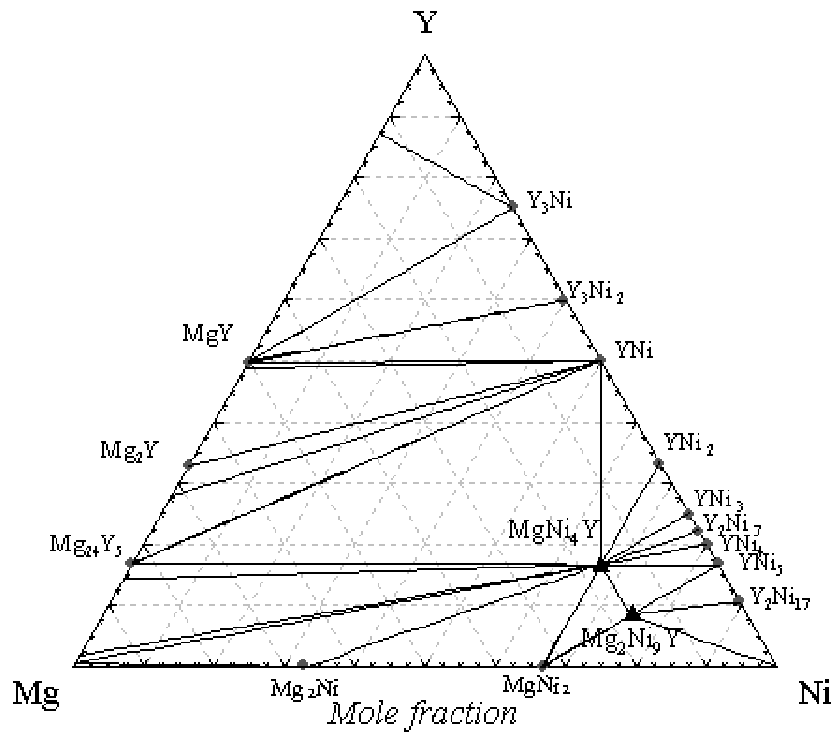

Figure 8: Isothermal Section of Mg-Ni-Y system at 400 ^oC

Mg-Ni-Y system

A self-consistent thermodynamic database for the Mg–Ni–Y system has been constructed by combining the thermodynamic descriptions of the three constituent binaries Mg–Ni, Ni–Y, and Mg–Y. According to Qiao et al. [50] if the excess thermodynamic properties in two of the three binary systems show similarity and significantly differ from the third one then the ternary system should be considered as asymmetric system and the common component in the two similar binary systems should be chosen as the asymmetric component. The enthalpy of mixing curves of liquid Mg-Ni and Mg-Y showed similar maximum negative value (-10 and -8 kJ/mole, respectively) while they differed from Ni-Y (-35 kJ). Therefore for the extrapolation to the ternary system, the toop geometric model [9] with Mg as the asymmetric component has been used.

No ternary interaction parameter is added since sufficient experimental data is not available. An isothermal section at 400 ^{o}C of the Mg-Ni-Y system is shown in figure 8. The two ternary compounds are included in the system by approximating the enthalpy of formation since no experimental data is available. The present calculated phase diagram agrees well with the reported experimental phase diagram of Yao et al. [43].

Conclusion

A self-consistent thermodynamic database for the Mg-Ni-Y system has been constructed by combining the thermodynamic descriptions of the binaries Mg-Ni, Ni-Y and Mg-Y using toop geometric model. No ternary interaction parameter has been used for the extrapolation. Among the three binaries, Mg-Ni and Ni-Y system have been optimized using the modified quasichemical model for the liquid phase in order to consider the presence of the short range ordering. The optimized parameters for the Mg-Y system using the same model have been taken from the previous work by the same authors.

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