

**THERMODYNAMIC MODELING OF THE Mg-Cu-Ni TERNARY SYSTEM USING THE
MODIFIED QUASICHEMICAL MODEL**

*M. Mezbahul-Islam and M. Medraj

*Mechanical and Industrial Engineering Department
Concordia University
1455 de Maisonneuve Blvd West
Montreal, Canada H3G 1M8
(*Corresponding author: m_i@encs.concordia.ca)*

ABSTRACT

Thermodynamic modeling of the Mg-Cu-Ni system is carried out as a part of multi component thermodynamic database for Mg alloys. This system is being modeled for the first time using the modified quasicheical model, which considers the presence of short range ordering in the liquid. The thermodynamic descriptions of the binaries Mg-Cu, Cu-Ni and Mg-Ni have been extrapolated to the ternary Mg-Cu-Ni system using Toop geometric model. The constructed database has been used to calculate and predict thermodynamic properties, isothermal sections and liquidus projections of the Mg-Cu-Ni system, which showed very good consistency with the experimental data.



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INTRODUCTION

A complete thermodynamic assessment has been done on the Mg-Cu-Ni ternary system. Although this system has been modeled before by several investigators [1-3], none of them considered the presence of short range ordering in the liquid. Especially for the Mg-Cu and Mg-Ni binaries which show strong range ordering. Short range ordering is not considered for the binary systems may result in wrong extrapolation for the higher order systems. Therefore to provide a more scientific description of the Mg-Cu-Ni system, this work has been carried out.

In this work the Cu-Ni binary system has been modeled using the available literature data and the model parameters have been reported. The binary descriptions for the Mg-Cu [4] and Mg-Ni [5] systems have been taken from our earlier work. Extrapolation to the ternary Mg-Cu-Ni system has been done using the Toop [6] geometric model. Mg has been singled out as the asymmetric component since Cu-Ni system showed completely different thermodynamic characteristics than the Mg-Cu and Mg-Ni binary systems. The liquid phase has been modeled using the modified quasichemical model [7-9] which considers the presence of short range ordering. The sublattice model has been employed to describe the Mg_2Cu , $MgCu_2$, Mg_2Ni and $MgNi_2$ phases. The ternary solubility of these phases has been modeled considering the dependency of this solubility on temperature. The phase diagram and thermodynamic properties calculated using the current optimized parameters showed good agreement with the experimental data from the literature.

LITERATURE REVIEW

Cu-Ni Binary System

The equilibrium phases in the Cu-Ni system are the liquid phase and the fcc (Cu, Ni) phase. The liquid phase is miscible in all proportions. The solid Cu and Ni are also miscible until the critical (T_c) temperature below which this fcc phase changes from a paramagnetic to a ferromagnetic state. A complete assessment of this system was done by Hansen and Anderko [10] and later by Chakrabarti and Laughlin [11]. Recent studies on the phase equilibria of the Cu-Ni system was done by [12-14] by using XRD and microstructural analysis to establish the liquidus and solidus lines. All these results are in good agreement with each other and will be used during the present optimization.

The presence of the immiscibility in the fcc (Cu, Ni) phase is an important characteristic of this system. Several studies [15-18] on the electric, magnetic and structural properties of the alloys and their low temperature heat capacity confirmed the existence of this immiscibility. Mozer et al. [15] used neutron diffraction method and suggested that the critical miscibility gap is between 506 and 536 K. They [15] used a sample of 47.5 at.% Ni and examined it over a temperature range of 298 and 1298 K. While Ebel [16] employed X-ray analysis at 523 K and determined that the miscibility gap should exist between 10 to 90 at.% Ni at this temperature. Another neutron diffraction study by Vrijen and Radelaar [17] on compositions between 20 to 80 at.% Ni showed that the maximum of the miscibility gap should be located at 65 at.% Ni at a temperature between 613 and 623K. A summary of most of these analyses was done by Hansen and Anderko [10] who concluded that the critical immiscibility point lies below 627.5 K and may be shifted toward the Nickel rich region of the system. This conclusion along with other experimental data will be used as a guideline for the present optimization.

The enthalpy of mixing of the liquid Cu-Ni had been done by several investigators [14, 19-23] using calorimetric methods. All these data except those of Predel [14] are closely associated and speak of their reliability and will be used in the present optimization. Activities of the components in the liquid state had been measured by [24-26] using different techniques. These data are also fairly reliable and will be used in this work. Experimental results for the enthalpy of mixing of the solid fcc (Cu-Ni) phase had been reported by [27-29]. The data of Leach and Bever [27] tend to be much higher than those of Oriani and Murphy [28] and Elford et al. [29]. For the present calculation the data of [28] and [29] will be used since these independent measurements are consistent with one another. Activity data for the solid Cu-Ni

alloys have been reported by several investigators [30-34]. All the data show large positive deviation from ideality and are in reasonable agreement within the limits of experimental uncertainty when compared at 1273 K. The present calculation will be compared with these data for justification.

The most recent work on this system was done by Turchanin et al. [35]. They modeled the system using Bragg-Williams model. However, all the other binaries in the Mg-Cu-Ni ternary system have been modeled using the modified quasicheical model in order to consider the short range ordering in the liquid and also, this model is more versatile and scientifically sound. Therefore, the Cu-Ni liquid phase is also described using this model.

Mg-Cu-Ni Ternary System

Mg-Cu-Ni system has been studied by several investigators and phase equilibria have been established through the determination of several isopleths, isothermal sections and liquidus projection. Experimental data on the thermodynamic properties of the liquid are also available. Comprehensive evaluation of these data was done by Gupta [36] and Lukas and Rokhlin [37].

Lieser and Witte [38] constructed a vertical section along 33.3 at.% Mg using thermal analysis, metallography and X-ray diffraction (XRD) methods. Mikheeva and Babayan [39] latter confirmed these liquidus temperatures within the experimental error. Karonik et al. [40] investigated the Mg-rich side of the Mg-Cu-Ni system using metallography and XRD methods and reported an isothermal section at 673 K. Their reported data will be used to determine the solubility of Cu in the Mg₂Ni compound in the present work. The compounds present in the Cu-Mg and Mg-Ni binary systems are extended to the ternary Mg-Cu-Ni system. Mikheeva and Babayan [39] suggested that complete solid solution exist in the MgCu₂-MgNi₂ quasibinary. But latter Lieser and Witte [38] by X-ray analysis showed that the crystal structures of MgCu₂ and MgNi₂ are not isotypic, making the formation of a complete solid solution impossible. MgCu₂ has fcc crystal structure of the type C16 while MgNi₂ is hcp with a C36 type crystal structure. Lieser and Witte [38] estimated that the solubility of Cu in the MgNi₂ phase is about 25 at.% in the temperature range 1193 K and 1423 K. Whereas Ipser et al. [41] and Fehrenbach et al. [42] confirmed that the solubility should be less than 5 at.% between 931 K and 1203 K. The solubility of Ni in MgCu₂ was estimated to be 26 at.% by Lieser and Witte [38] which is later supported by Fehrenbach et al. [42] who reported it to be 20 at.%. The results of Ipser et al. [41] also suggested that the solubility should be higher than 22 at.%. In the present work, the ternary solubilities for the MgNi₂ and MgCu₂ phases reported by Ipser et al. [41] and Fehrenbach et al. [42] were used during optimization. Fehrenbach et al. [42] according to their experimental data and also taking into account previous analysis of Lieser and Witte [38] proposed four isothermal sections at 1003, 1073, 1081 and 1123 K. Since the available information for the construction of the isothermal sections are limited at the time of their assessment, these phase relationships will be used for the current calculation unless they conflict with the other reliable experimental data from different resources. Ganasekaran and Ipser in a series of related works [43-45] constructed three vertical sections at content ratio, $x(\text{Cu})/x(\text{Ni}) = 2.0, 1.0$ and 0.5 and one vertical section at 71 at.% Mg using differential thermal analysis (DTA). They also identified two quasiperitectic and one ternary eutectic reactions. These data are reliable and will be used for the current thermodynamic optimization. Feufel and Sommer [46] measured the integral enthalpy of mixing of the ternary liquid for the Cu_xMg_{1-x}-Ni, Cu_xNi_{1-x}-Mg, Mg_xNi_{1-x}-Cu and Cu_xMg_{1-x}-Mg_{0.667}Ni_{0.333} compositions at 1008 K using calorimeter. Present calculation will be compared with these thermodynamic properties.

Thermodynamic assessment of this system was carried out by Gorsse and Shiflet [1]. But it cannot be reproduced due to undetectable type errors of some thermodynamic parameters. In 2008, two thermodynamic assessments of the Mg-Cu-Ni system were published by Miettinen [2] and Xiong [3]. Both of them are consistent with most of the experimental data. However due to the choice of a different thermodynamic model for the liquid phase and in order to reduce the number of ternary parameters, it is decided to re-optimize the system.

THERMODYNAMIC MODELS

The Gibbs energy function used for the pure elements i ($i = \text{Cu, Mg and Ni}$) are taken from the SGTE (Scientific Group Thermodata Europe) compilation of Dinsdale [47]. The Gibbs energy of a binary stoichiometric phase is given by:

$$G^\phi = x_i {}^0G_i^\phi + x_j {}^0G_j^\phi + \Delta G_f \quad (1)$$

where ϕ denotes the phase of interest, x_i and x_j are mole fractions of elements i and j which are given by the stoichiometry of the compound, ${}^0G_i^\phi$ and ${}^0G_j^\phi$ are the respective reference states of elements i and j in their standard state and $\Delta G_f = a + b.T$ represents the Gibbs energy of formation of the stoichiometric compound. The parameters a and b were obtained by optimization using experimental data.

The Gibbs energy for the terminal solid solution phases is described by the following equation:

$$G^\phi = x_i {}^0G_i^\phi + x_j {}^0G_j^\phi + RT[x_i \ln x_i + x_j \ln x_j] + {}^{ex}G^\phi + {}^{ex}G_{mag}^\phi \quad (2)$$

where ϕ denotes the phase of interest and x_i, x_j denote the mole fraction of components i and j , respectively. The first two terms on the right hand side of Eq. (2) represent the Gibbs energy of the mechanical mixture of the components, the third term is the ideal Gibbs energy of mixing, and the fourth term is the excess Gibbs energy, which is described by the Redlich-Kister polynomial model in this work and can be represented as:

$${}^{ex}G^\phi = x_i \cdot x_j \sum_{n=0}^{n=m} {}^nL_{i,j}^\phi (x_i - x_j)^n \quad (3)$$

$${}^nL_{i,j}^\phi = a_n + b_n \cdot T \quad (4)$$

Where a_n and b_n are the parameters of the model that need to be optimized considering the experimental phase diagram and thermodynamic data. The fifth term represents the magnetic contribution to the Gibbs energy of the \square phase and can be represented as:

$${}^{ex}G_{mag}^\phi = -RT(\ln \beta^\phi + 1)f(\tau) \quad (5)$$

Where $f(\tau) = T/T_c^\phi$, T_c^ϕ is the curie temperature of the alloy, β^ϕ is the mean magnetic moment of the alloy per atom. The function $f(\tau)$ is defined by:

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

$$f(\tau) = -\frac{1}{D} \left[\frac{\tau^{-5}}{10} + \frac{\tau^{-15}}{315} + \frac{\tau^{-25}}{1500} \right], \tau > 1 \quad (7)$$

Where $D = \frac{518}{1125} + \frac{11695}{15975} \left(\frac{1}{p} - 1 \right)$. The concentration dependence of the curie temperature T_c^ϕ and mean magnetic moment β^ϕ in the alloy can be described as follows:

$$T_c^\phi = x_i \text{}^o T_{c_i} + (1 - x_i) x_i \sum_{l=0}^n (1 - 2x_i)^l T_{c_i}^\phi \tag{8}$$

$$\beta^\phi = x_i \text{}^o \beta_i + (1 - x_i) x_i \sum_{l=0}^n (1 - 2x_i)^l \beta_i^\phi \tag{9}$$

Where $\text{}^o T_i$ is the curie temperature of i component and $\text{}^o \beta_i$ is the magnetic moment of that component ${}^1 T_{c_i}^\phi$ and ${}^1 \beta_i^\phi$ are the parameters to be determined.

The liquid phase has been modeled using the modified quasi-chemical model. This model uses the energy for pair formation to express the excess Gibbs energy which can be expressed as:

$$\Delta G_{AB} = \Delta G_{AB}^\circ + \sum_{i>1} g_{AB}^{ij} X_{AA}^i + \sum_{j>1} g_{AB}^{ij} X_{BB}^j \tag{10}$$

Where, ΔG_{AB}° , Δg_{AB}^{ij} and Δg_{AB}^{ij} are the parameters of the model and can be stated as functions of temperature ($\Delta g_{AB}^\circ = a + bT$). The model also use the atom to atom coordination number 'Z' to express the short range ordering in the liquid and can be defined as:

$$\frac{1}{Z_A} = \frac{1}{Z_{AA}^A} \left(\frac{2n_{AA}}{2n_{AA} + n_{AB}} \right) + \frac{1}{Z_{AB}^A} \left(\frac{n_{AB}}{2n_{AA} + n_{AB}} \right) \tag{11}$$

$$\frac{1}{Z_B} = \frac{1}{Z_{BB}^B} \left(\frac{2n_{BB}}{2n_{BB} + n_{AB}} \right) + \frac{1}{Z_{BA}^B} \left(\frac{n_{AB}}{2n_{BB} + n_{AB}} \right) \tag{12}$$

Z_{AA}^A and Z_{AB}^A are the values of Z_A when all nearest neighbors of an A atom are A's, and when all nearest neighbors of A atom are B's, respectively. Similarly for Z_{BB}^B and Z_{BA}^B . The coordination numbers used for the different binary systems are given in table 1. The Gibbs energy of an ordered solution phase is described by the compound energy formalism which has been explained elaborately elsewhere [4,5].

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

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

RESULTS AND DISCUSSION

Cu-Ni System

The calculated Cu-Ni phase diagram is shown in figure 1 in comparison with the available experimental data from the literature. The liquid phase has been modeled using the modified quasi-chemical model while the fcc (Cu, Ni) phase has been modeled using the Bragg-Williams model presented in Redlich-Kister form. All the parameters have been included in table 2. The liquid phase shows very good agreement with all the available experimental data.

Table 2 - Optimized model parameters of the Cu-Ni system

Phase	Terms
Liquid	$\Delta G_{\text{CuNi}}^{\text{L}} = 5,797.33 - 0.21T$ (J/mole), $G_{\text{CuNi}}^{\text{Cu}} = -1,172.02$ (J/mole)
	${}^0L^{\text{fcc}} = 6790.48 + 4.64 T$ (J/mole), ${}^1L^{\text{fcc}} = 1655.13$ (J/mole)
Fcc (Cu, Ni)	${}^0T_{\text{c}}^{\text{fcc}} = -467.5$, ${}^1T_{\text{c}}^{\text{fcc}} = -297.5$
	${}^0\beta_{\text{Cu-Ni}}^{\text{fcc}} = -0.7316$, ${}^0\beta_{\text{Cu-Ni}}^{\text{fcc}} = -0.317$

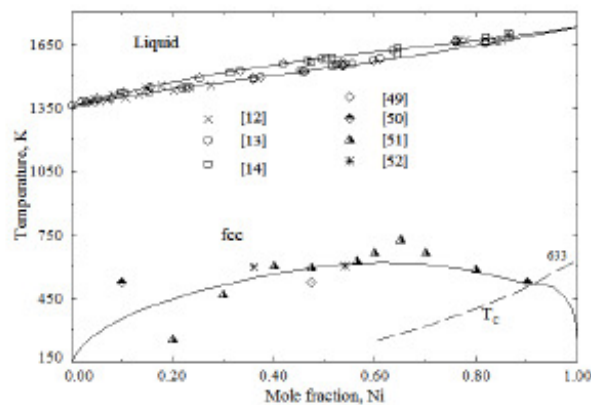


Figure 1 - Calculated Cu-Ni phase diagram

The miscibility gap in the fcc (Cu, Ni) phase has been determined using the available experimental data as a guideline. It is worth noting that it is very difficult to obtain very accurate experimental results at such low temperature due to the difficulty in obtaining equilibrium conditions. Hence lower weight is given to these data during optimization. The magnetic contribution to the Gibbs energy of the fcc phase especially at a lower temperature has a substantial influence on the shape of the miscibility gap. This has been taken into consideration during optimization. Due to the magnetic transition the miscibility gap showed a hump (Nishizawa horn) near the Ni rich corner on the T_c line. The critical temperature of the miscibility gap is determined to be 621 K near 60 at.% Ni which is consistent with the data of Vrijen and Radelaar [17].

The calculated enthalpy of mixing of the liquid phase at 1750 K in figure 2(a) shows reasonable agreement with the available experimental data. The data of Predel and Mohs [14] shows less endothermic values than other experimental data. Hence, it is decided not to consider their data. The data of Iguchi et al. [20] shows an asymmetric enthalpy of mixing curve with the maximum values towards the Cu-rich corner. This is an indication of the presence of short range ordering in the solution. But this system is expected to have symmetric enthalpy curve due to the absence of any compound. Hence it is decided to be consistent with the data of Turchanin et al. [23] which is symmetric in nature and is also the most recent reported experimental data.

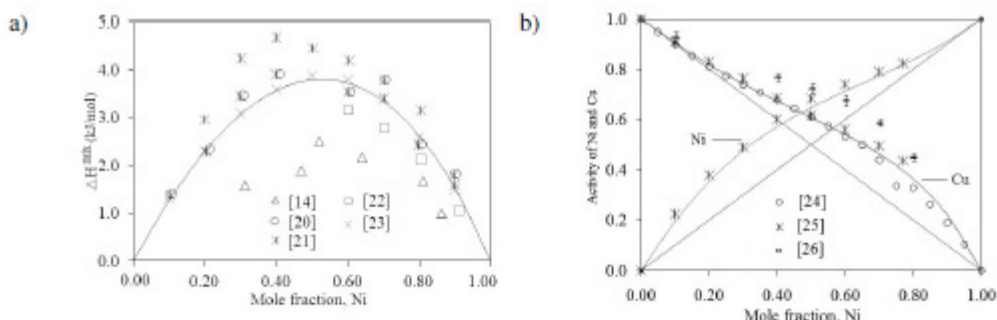


Figure 2 - Calculated (a) enthalpy of mixing at 1750 K and (b) activities of the liquid Cu and Ni in the Cu-Ni system at 1750 K

The activities of Cu and Ni in the liquid are presented in figure 2(b) and show good agreement with the experimental data. The activity of Cu shows deviation from the experimental data of [26] but since the two other data sets of [24] and [25] are consistent with each other, it is decided to follow the latter two. The calculated enthalpy of mixing of the fcc phase at 800 K is shown in figure 3(a) and compared with the experimental data of [28] at 973 K and [29] at 773 K. Both sets of data show an unusual break in the curve near 65 at.% Ni. According to [29] this is due to a non-equilibrium effect. Accepting this argument, it can be said that the present optimized parameters can reproduce the experimental results satisfactorily.

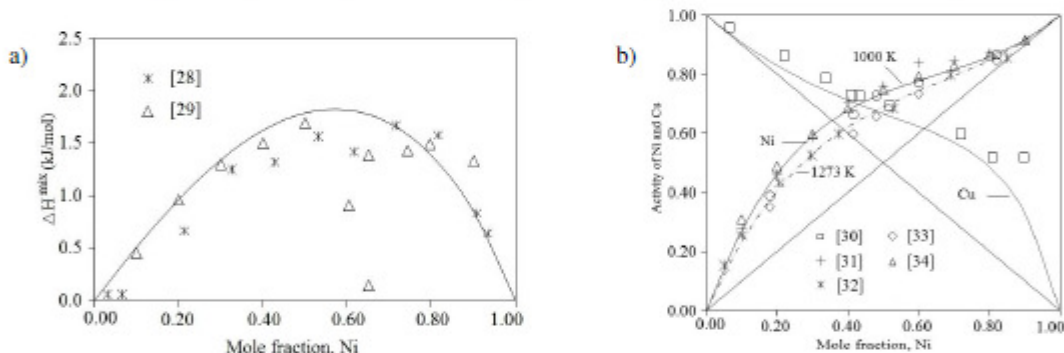


Figure 3 - Calculated (a) enthalpy of mixing of the solid phase at 800 K and (b) activities of the fcc phase components at 1000 K

Activities for the solid Cu and Ni have been calculated using the present optimized parameters as shown in figure 3(b). The dotted line in this figure shows the activity of Ni at 1273 K which is compared with the data of [32] and [33]. The activity of Ni at 1000 K as represented by the solid line is also in good agreement with the data of [31] at 973 K, [33] at 1073 K and [34] at 1000 K. The calculated activity of Cu at 1000 K shows good consistency with the data of [30] except for one point at 90 at.% Ni. This kind of flat activity can be expected in the solution due to the presence of immiscibility. But no other experimental evidence could be found in the literature which suggests that the miscibility gap exists at such a high temperature. Hence it is decided not to consider this point for the present calculation.

Mg-Cu-Ni System

The thermodynamic descriptions of the binaries Mg-Cu, Cu-Ni and Mg-Ni are extrapolated to the ternary Mg-Cu-Ni system using Toop [6] geometric model. As described earlier, Mg has been singled out as the asymmetric component since Cu-Ni system shows completely different thermodynamic

characteristics than Mg-Cu and Mg-Ni binary systems. A self-consistent set of parameters has been determined for the Mg-Cu-Ni system and is shown in table 3.

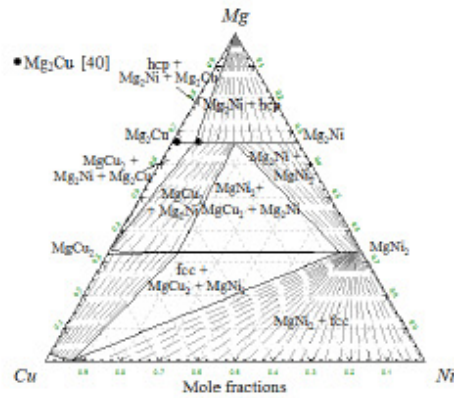


Figure 4 - Calculated isothermal section of the Mg-Cu-Ni system at 673 K

Good consistency between the present calculation and the experimental work of Karonik et al. [40] can be seen in the isothermal section at 673 K shown in figure 4. Also, it has been visually compared with the proposed isothermal section by Fehrenbach et al. [42] and the phase relationships are found to be exactly the same. However the phase boundaries are more or less different from those of [42]. But since there is no experimental evidence for the accurate positions of the proposed phase boundaries by Fehrenbach et al. [42] this small deviation is acceptable.

Table 3 - Parameters for the Mg-Cu-Ni ternary system

Phase	Terms (J/mole)
Liquid	$\Delta_G^{001}{}_{CuMg(Ni)} = -9236.80$, $\Delta_G^{011}{}_{CuMg(Ni)} = 7842.10$, $\Delta_G^{111}{}_{CuMg(Ni)} = 2023.71$
Mg ₂ Cu (Mg) ₂ (Ni, Cu%)	${}^0G_{MgCu}^{CuMg_2} = -28512.25$, ${}^0G_{MgNi}^{CuMg_2} = -29012.49 + 12.14 T$ ${}^0L_{Mg:Ni,Cu}^{Cu,Mg_2} = 6266.69$
Mg ₂ Ni (Mg) ₂ (Ni%, Cu)	${}^0G_{MgNi}^{Mg_2Ni} = -48227.11 + 13.98 T$, ${}^0G_{MgCu}^{Mg_2Ni} = -26011.19 + 1.0 T$ ${}^0L_{Mg:Ni,Cu}^{Mg_2,Ni} = 70274.18 + 55.96 T$, ${}^1L_{Mg:Ni,Cu}^{Mg_2,Ni} = -14256.08$
MgCu ₂ (Cu%, Mg, Ni) ₂ (Cu, Mg%, Ni)	${}^0G_{CuCu}^{Cu_2Mg} = 16743.0$, ${}^0G_{CuMg}^{Cu_2Mg} = -36160.93$, ${}^0G_{CuNi}^{Cu_2Mg} = 15000.0$ ${}^0G_{MgCu}^{Cu_2Mg} = 10000.00$, ${}^0G_{MgMg}^{Cu_2Mg} = 15000.0$, ${}^0G_{MgNi}^{Cu_2Mg} = 14865 - 13.86 T$, ${}^0G_{NiCu}^{Cu_2Mg} = 15000.0$, ${}^0G_{NiMg}^{Cu_2Mg} = 15000.0$ ${}^0G_{NiMg}^{Cu_2Mg} = -43000 + 71.39 T + 66.49 * 10^{-4} T^2 + 20 * 10^4 T^{-1} - 9.39 T \ln T$ ${}^0L_{Cu,Mg:Cu}^{Cu_2Mg} = {}^0L_{Cu,Mg:Mg}^{Cu_2Mg} = {}^0L_{Cu,Mg:Ni}^{Cu_2Mg} = 13005.75$ ${}^0L_{Cu:Cu,Mg}^{Cu_2Mg} = {}^0L_{Mg:Cu,Mg}^{Cu_2Mg} = {}^0L_{Ni:Cu,Mg}^{Cu_2Mg} = 6596.61$ ${}^0L_{Mg:Ni,Cu}^{Cu_2Mg} = {}^0L_{Mg:Ni:Mg}^{Cu_2Mg} = {}^0L_{Mg:Ni:Ni}^{Cu_2Mg} = 10000 + 90 T$ ${}^0L_{Cu:Mg,Ni}^{Cu_2Mg} = {}^0L_{Cu:Mg:Ni}^{Cu_2Mg} = {}^0L_{Ni:Mg,Ni}^{Cu_2Mg} = 30000$ ${}^0L_{Cu:Ni:Mg}^{Cu_2Mg} = -23750 + 21 T$ ${}^1L_{Cu:Ni:Mg}^{Cu_2Mg} = -51000$ ${}^0L_{Cu:Ni,Cu}^{Cu_2Mg} = {}^0L_{Cu:Ni:Ni}^{Cu_2Mg} = 10000 + 21 T$

$$\begin{aligned}
 & {}^0G_{Cu:Cu}^{Ni_2Mg} = 15000.00, \quad {}^0G_{Cu:Mg}^{Ni_2Mg} = -4000+49.4T, \quad {}^0G_{Cu:Ni}^{Ni_2Mg} = 15000.00 \\
 & {}^0G_{Mg:Cu}^{Ni_2Mg} = 90970.00-16.46 T, \quad {}^0G_{Mg:Mg}^{Ni_2Mg} = 140000.00, \quad {}^0G_{Mg:Ni}^{Ni_2Mg} = 70000.00-7.0 T \\
 & {}^0G_{Ni:Cu}^{Ni_2Mg} = 15000.00, \quad {}^0G_{Ni:Mg}^{Ni_2Mg} = 13000.00 \\
 & {}^0G_{Ni:Mg}^{Ni_2Mg} = -64265.37+75.70 T+66.49*10^{-4} T^2+20*10^{-4} T^{-1}-9.39 T \ln T \\
 & \text{MgNi}_2 \\
 & (\text{Cu,Mg,Ni}\%)_2 \\
 & (\text{Cu,Mg}\%,\text{Ni}) \\
 & {}^0L_{Cu,Mg:Cu}^{Ni_2Mg} = {}^0L_{Cu,Mg:Mg}^{Ni_2Mg} = 20000.00, \quad {}^0L_{Cu,Mg:Ni}^{Ni_2Mg} = 5000.00 \\
 & {}^0L_{Cu:Cu,Mg}^{Ni_2Mg} = -24050.00, \quad {}^0L_{Mg:Cu,Mg}^{Ni_2Mg} = 6596.61 \quad {}^0L_{Ni:Cu,Mg}^{Ni_2Mg} = 14000.00 \\
 & {}^0L_{Mg,Ni:Cu}^{Ni_2Mg} = {}^0L_{Mg,Ni:Mg}^{Ni_2Mg} = {}^0L_{Mg,Ni:Ni}^{Ni_2Mg} = 10000.00+60 T \\
 & {}^0L_{Cu:Mg,Ni}^{Ni_2Mg} = {}^0L_{Mg:Mg,Ni}^{Ni_2Mg} = 20000.00, \quad {}^0L_{Ni:Mg,Ni}^{Ni_2Mg} = 30000.00 \\
 & {}^0L_{Cu,Ni:Cu}^{Ni_2Mg} = {}^0L_{Cu,Ni:Ni}^{Ni_2Mg} = 35000.00+30 T, \quad {}^0L_{Cu,Ni:Mg}^{Ni_2Mg} = -50000.00
 \end{aligned}$$

Figure 5(a), shows the calculated isopleth for X(Cu)/ X(Ni) = 2.0. Good agreement can be seen between the calculated liquidus temperatures and experimental data of Ipser et al. [41]. Besides most of the experimental points, such as phase field limits and invariant reactions are reasonably reproduced. Also, the calculated vertical section at 71 at.% Mg in figure 5(b) shows good agreement with the experimental data of Ipser et al. [41].

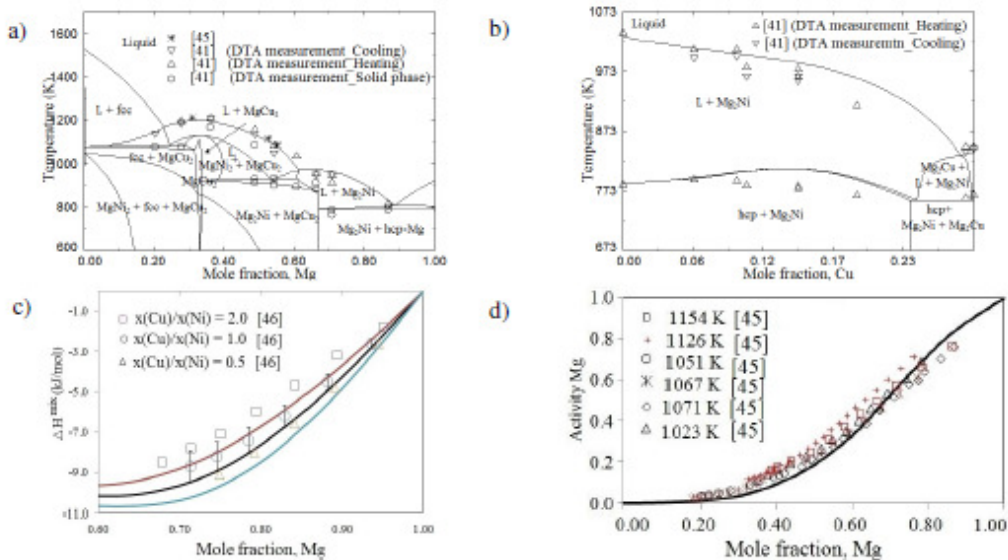


Figure 5 - Calculated vertical section for (a) x(Cu)/x(Ni)= 2.0 and (b) 71 at.% Mg, (c) Calculated enthalpy of mixing of the liquid at 1008 K and (d) Mg activity at 1100 K of the liquid for the component ratio of x (Cu)/ x(Ni)= 2.0

In figures 5(c) and (d), the thermodynamic properties, such as enthalpy of mixing of the liquid and Mg activity, are calculated using parameter set from the current work. It can be seen that the present calculation can represent all the thermodynamic properties within the claimed uncertainty limits of ± 0.3-0.8 kJ/mol with higher error for the higher concentrations.

A liquidus projection of the Mg-Cu-Ni system is shown in figure 6 with the experimental data of Fehrenbach et al. [42]. The system has three quasiperitectic and one ternary eutectic point.

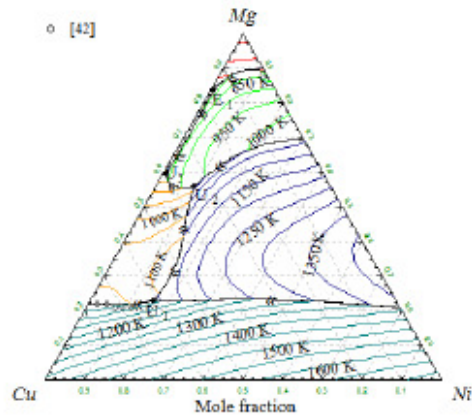


Figure 6 - Calculated projection of the Mg-Cu-Ni system (experimental data from [42])

CONCLUSIONS

A comprehensive thermodynamic assessment of the Mg-Cu-Ni system has been done using all the available information from the literature. Among the three binaries only Cu-Ni system has been modeled here. The optimized parameters for the other two binaries have been taken from our previous thermodynamic assessments of the Mg-Cu-Y and Mg-Ni-Y systems. The modified quasicheical model has been used for the first time to describe the liquid phase in the Mg-Cu-Ni system in order to consider the presence of short range ordering in the liquid. The ternary solubility of the binary compounds Mg_2Ni , $MgNi_2$, Mg_2Cu and $MgCu_2$ have been reproduced. All the optimized parameters have been reported. In order to be consistent with the experimental data from the literature three ternary parameters for the liquid phase have been used. The present optimized parameters could generate all the phase diagrams and thermodynamic properties within the experimental error.

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