

Review Article

Essential Magnesium Alloys Binary Phase Diagrams and Their Thermochemical Data

Mohammad Mezbahul-Islam, Ahmad Omar Mostafa, and Mamoun Medraj

Department of Mechanical Engineering, Concordia University, 1455 de Maisonneuve Boulevard West, Montreal, QC, Canada H3G 1M8

Correspondence should be addressed to Mamoun Medraj; mmedraj@encs.concordia.ca

Received 30 November 2013; Revised 19 January 2014; Accepted 22 January 2014; Published 30 April 2014

Academic Editor: Alok Singh

Copyright © 2014 Mohammad Mezbahul-Islam et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Magnesium-based alloys are becoming a major industrial material for structural applications because of their potential weight saving characteristics. All the commercial Mg alloys like AZ, AM, AE, EZ, ZK, and so forth series are multicomponent and hence it is important to understand the phase relations of the alloying elements with Mg. In this work, eleven essential Mg-based binary systems including Mg-Al/Zn/Mn/Ca/Sr/Y/Ni/Ce/Nd/Cu/Sn have been reviewed. Each of these systems has been discussed critically on the aspects of phase diagram and thermodynamic properties. All the available experimental data has been summarized and critically assessed to provide detailed understanding of the systems. The phase diagrams are calculated based on the most up-to-date optimized parameters. The thermodynamic model parameters for all the systems except Mg-Nd have been summarized in tables. The crystallographic information of the intermetallic compounds of different binary systems is provided. Also, the heat of formation of the intermetallic compounds obtained from experimental, first principle calculations and CALPHAD optimizations are provided. In addition, reoptimization of the Mg-Y system has been done in this work since new experimental data showed wider solubility of the intermetallic compounds.

1. Introduction

Magnesium is the eighth most abundant metal in the earth outer surface at approximately 2.5% of its composition. It is an alkaline earth element (Group II) that crystallizes in a hexagonal structure (hcp-A3). Magnesium is the lightest metallic material used for structural applications with a density of 1.738 g/cm^3 in comparison with the densities of Al (2.70 g/cm^3) and Fe (7.86 g/cm^3). Magnesium alloys have an excellent combination of properties which includes excellent strength-to-weight ratio, good fatigue and impact strengths, and relatively large thermal and electrical conductivities [1–3] and excellent biocompatibility [4, 5]. This makes magnesium alloys one of the most promising light-weight materials for automotive [6], aerospace, consumer electronic (computer, camera, and cell phone), and biomedical applications due to its biodegradability. It is being used in the automotive industries in steering column parts, shift actuators, valve covers and housings, brackets, and intake manifold blades

[7]. In nonautomotive applications, small magnesium die cast components are appearing in small engines, electronic devices, power tools, and medical equipment, such as portable oxygen pumps [7]. Recently, Mg-rich Mg-Ca-Zn biocompatible metallic glass having small amounts of Ca (0–8 at.%) has been found to be suitable for the development of biodegradable implants [4, 5].

Some of the most common commercial Mg alloys are AZ series (Mg-Al-Zn), AM series (Mg-Al-Mn), AE series (Mg-Al-RE), EZ series (Mg-RE-Zn), ZK series (Mg-Zn-Zr), WE series (Mg-RE-Zr), AX or AXJ series (Mg-Al-Ca), and AJ series (Mg-Al-Sr) [8, 9]. For automotive applications, alloys of AM and AZ series are mainly used. AZ91D is the most widely used magnesium die-casting alloy. It has good combination of room-temperature strength and ductility, good salt-spray corrosion resistance, and excellent die-castability, compared to other Mg alloys.

It can be seen that most of the commercial alloys are multicomponent. The impact of each of the alloying element

TABLE 1: Effect of major alloying elements on Mg alloys [23].

Alloying element	Effects of Addition
Al	Increases hardness, strength, and castability while only increasing density minimally.
Ca	Improves thermal and mechanical properties as well as assists in grain refinement and creep resistance. Also, it reduces surface tension.
Ce	Improves corrosion resistance. Also, it increases plastic deformation capability, magnesium elongation, and work hardening rates. But it reduces yield strength.
Cu	Assists in increasing both room and high temperature strength.
Mn	Increases saltwater corrosion resistance within some aluminum containing alloys.
Ni	Increases both yield and ultimate strength at room temperature. Negatively impacts ductility and corrosion resistance.
Nd	Improves material strength.
Sr	Used in conjunction with other elements to enhance creep performance.
Sn	When used with aluminum it improves ductility and reduces tendency to crack during processing.
Y	Enhances high temperature strength and creep performance when combined with other rare earth metals.
Zn	Increases the alloys fluidity in casting. When added to magnesium alloys with nickel and iron impurities, it can improve corrosion resistance. Additions of 2 wt.% or greater tend to be prone to hot cracking.

is different and is needed to be understood. Table 1 provided by International Magnesium Association [23] shows a number of commonly used alloying elements alongside their effects upon the resulting alloy. Many alloying elements can be useful in a variety of different applications, whereas others are only ideal for very specific applications due to the change in properties.

In order to define the processing conditions for making various Mg-based alloys and subsequent treatments to obtain the optimum mechanical properties, knowledge of the phase diagram and thermodynamic properties of these alloys is essential. In addition, phase relations and phase stability under given conditions can be better understood through computational thermodynamic modeling. Precise description of the binary systems provides an opportunity to approach the phase equilibria aspects of alloy development and track of individual alloys during heat treatment or solidification by calculating the phase distributions and compositions.

Several researchers including the research group of the current authors [22, 32, 41–57] have been contributing to the development of thermodynamic multicomponent databases of Mg alloys. However, urgency was felt for an open access publication that contains the latest understandings of all the important Mg-based binary systems. This will provide the necessary information required for further assessment of these systems. Generally review papers on thermodynamic modeling do not contain some of the critical information like previous experimental data points and optimized model parameters. Sometimes it becomes very difficult to gather this information as some of the literature is very old and scattered in many different articles and not everyone has access to them. However these are crucial facts for the regeneration of phase diagram and other thermodynamic properties. Thus the main objective of this paper is to provide

all the necessary information of essential Mg binary systems in one place. In addition, brief but critical discussion of the previous experimental works on the phase diagrams as well as thermodynamic properties is provided to justify the latest understanding of this phase diagram.

This review paper focuses on some of the most important commercial Mg-based binary systems including Mg-Al/Zn/Mn/Ca/Sr/Y/Ni/Ce/Nd/Cu/Sn. Each of these systems has been discussed critically on the aspects of phase diagram and thermodynamic properties. The latest phase diagram information along with the optimized thermodynamic parameters is provided. Also, the crystallographic information of the intermetallic compounds in each system is summarized. All these binary systems have been optimized using most up-to-date experimental information. Each of the phases in any binary system has been assessed critically and based on the thermodynamic properties; proper thermodynamic model has been used. For example, the modified quasichemical model (MQM) [79] has been used to describe the liquid phase as this is the only scientific model that accounts for the presence of short range ordering, whereas sublattice modeling with in the compound energy formalism (CEF) [80] has been used to reproduce the homogeneity ranges of the intermetallic compounds.

2. Mg-Al (Magnesium-Aluminium)

This is the most important Mg binary phase diagram because Al is added to mg in most of the commercial types of Mg alloys. Several researchers [81–95] studied the liquidus, solidus, and solvus lines of the Mg-Al system. Murray [95] reviewed the Mg-Al system and his article provides a comprehensive discussion of the experimental results obtained by previous researchers. According to Murray [95] the assessed Mg-Al phase diagram consists of liquid, β -solid solution with

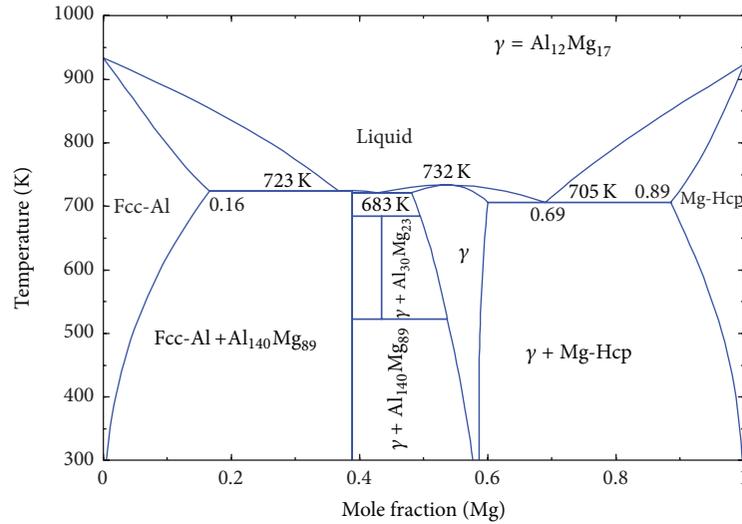


FIGURE 1: Mg-Al phase diagram.

hexagonal crystal structure, γ -solid solution with the αMn structure type, R phase with rhombohedral structure at 42 at.% Mg, Al solid solution with a maximum solubility of 18.9 at.% Mg at 723 K, and Mg solid solution with a maximum solubility of 11.8 at.% Al at 710 K. In view of the relative atomic radii of Al and Mg atoms, the ratio of the Al radius to that of Mg is 1.12 which suggests high mutual solid solubility. There is a good agreement between different authors regarding the solid solubility of Mg and Al, liquidus, solidus, and solvus lines.

Several efforts [96–100] have been made to calculate the Mg-Al phase diagram. In addition, Zhong et al. [101] reported a complete thermodynamic description of the Al-Mg binary system using a combined approach of CALPHAD and first-principles calculations. They also calculated the enthalpies of formation of $\text{Al}_{30}\text{Mg}_{23}$ (ϵ) and $\text{Al}_{12}\text{Mg}_{17}$ (γ) as well as the enthalpies of mixing of Al-fcc and Mg-hcp solution. But experimental measurement of the enthalpy of mixing of the Mg-Al liquid was carried out by [10, 12–14, 21, 102]. Belton and Rao [13] and Tiwari [21] obtained the enthalpy of mixing of Mg-Al liquid from emf measurements at 1073 K, while Bhatt and Garg [12] and Juneja et al. [14] derived the enthalpy of mixing from partial pressure measurements at 1073 K. Agarwal and Sommer [10] measured enthalpy of mixing of Mg-Al liquid using three different calorimetric methods at 943 K, 947 K, 948 K, and 973 K. In 1998, Moser et al. [11] measured the enthalpy of mixing at 1023 K using drop calorimetry. The thermodynamic activities of liquid alloys at 1073 K were determined by [12, 13, 18–21, 103] using emf measurements. The reported results are scattered but show small negative deviation from ideal solution.

Based on the available experimental data from the literature Aljarrah [104] made thermodynamic modeling of the Mg-Al system. Their reported parameters have been used to calculate the phase diagram and thermodynamic properties of the Mg-Al system as shown in Figures 1 and 2 as it provides the most accurate description of the system in

terms of phase diagram and thermodynamic properties. The crystallographic information of the intermetallic compounds and optimized parameters are listed in Tables 2 and 3. Also, the enthalpies and entropies of formation of the intermetallic compounds are listed in Table 4.

3. Mg-Zn (Magnesium-Zinc)

Zn is commonly alloyed with Mg in AZ, EZ, ZK and in smaller amounts in AM and AE series. The liquidus in the Mg-Zn phase diagram was determined by Boudouard [105] using thermal analysis. He [105] introduced a compound with Mg_4Zn formula. Grube [106] found that Boudouard's [105] measurements were in error due to contaminations and the Mg_4Zn compound did not exist. Moreover, he [106] found an intermetallic compound that corresponds to MgZn_2 and melts at 868 K. The compound forms a eutectic with pure Zn at 97 at.% Zn and 641 K. No solid solution areas were defined in the system [105, 106]. Chadwick [107] found a new solid solution β near the composition MgZn_5 and reported that MgZn_2 forms a wide range of solid solution. However, his [107] results showed higher content of zinc due to the presence of Si impurity. Chadwick [107] also measured the liquidus line in the Mg-Zn phase diagram using thermal analysis. The reported values agree reasonably with the liquidus suggested by Grube [106]. The compound MgZn_5 was first discovered by Chadwick [107] and later on replaced by $\text{Mg}_2\text{Zn}_{11}$ based on the more reliable X-ray analysis by Samson [108]. On the other hand, Park and Wyman [109] reported the maximum solubility of Zn in Mg as 2.5 at.% Zn at 340°C; also, they [109] measured the narrow homogeneity range of MgZn_2 as 1.1 at.% Zn (from 66 at.% Zn at 416°C to 67.1 at.% Zn at 654 K). Hume-Rothery [110] studied the system in the composition range of 30 to 100 at.% Zn using thermal analysis and microscopic inspection. Accordingly, the maximum limited solubility of Mg in Zn was determined as 0.3 at.% at 673 K. Laves [111] identified Mg_2Zn_3 phase

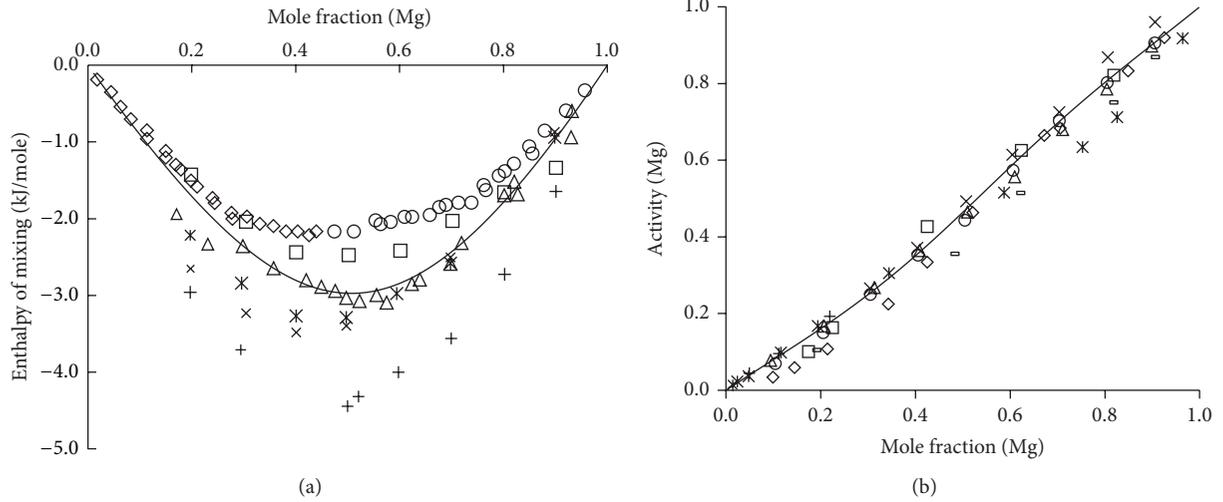


FIGURE 2: Calculated (a) enthalpy of mixing of liquid Mg-Al at 1073 K: \circ : [10] at 948 K, \diamond : [10] at 973 K, \triangle : [11] at 1073 K, \square : [12] at 1073 K, \times : [13] at 1073 K, $+$: [14] at 1073 K, $*$: [15] at 973 K, \square : [16] at 1002 K, \circ : [16] at 1008 K. (b) Activity of liquid Mg 1073 K: \circ : [14] at 1073 K, \triangle : [17] at 923 K, \times : [18] at 923 K, \square : [19] at 1073 K, \diamond : [13] at 1123 K, $*$: [20] at 1073 K, $+$: [12] at 1073 K, $*$: [21] at 1073 K.

TABLE 2: Crystal structure data for Mg-Al intermetallic compounds.

Phase	Prototype	Space group number	Space group	Lattice parameter (nm)			Reference
				a	b	c	
$\text{Al}_{30}\text{Mg}_{23}$ (ϵ)	$\text{Al}_{30}\text{Mg}_{23}$	148	$R\bar{3}h$	1.2825	1.2825	2.1748	[137]
$\text{Al}_{140}\text{Mg}_{89}$ (β)	$\text{Al}_{45}\text{Mg}_{28}$	227	$F\bar{D}\bar{3}m$	2.8300	2.8300	2.8300	[137]
$\text{Al}_{12}\text{Mg}_{17}$ (γ)	$\text{Al}_{12}\text{Mg}_{17}$	217	$I4\bar{3}m$	1.0544	1.0544	1.0544	[137]

TABLE 3: Optimized model parameters of the Mg-Al system [41].

Phase	Parameters
	Δg^0 and 0L in J/mole, ${}^0\Delta H$ in J/mole-atom and ${}^0\Delta S$ in J/mole-atom·K
Liquid	$Z_{\text{MgAl}}^{\text{Mg}} = 6, Z_{\text{AlMg}}^{\text{Al}} = 4$ $\Delta g_{\text{MgAl}}^0 = -4495.5 + 2.85T; \Delta g_{\text{MgAl}}^{10} = 436.8 + 0.42T;$ $\Delta g_{\text{MgAl}}^{01} = 732.5$
Mg-hcp	${}^0L^{\text{Mg-hcp}} = 1950.8 - 2.0T; {}^1L^{\text{Mg-hcp}} = 1480.6 - 2.1T;$ ${}^2L^{\text{Mg-hcp}} = 3501.5$
Al-fcc	${}^0L^{\text{Al-fcc}} = 4973.1 - 3.5T; {}^1L^{\text{Al-fcc}} = 900.4 + 0.42T;$ ${}^2L^{\text{Al-fcc}} = 950.4$
$\text{Al}_{30}\text{Mg}_{23}$ (ϵ)	${}^0\Delta H_{\text{AlMg}}^{\text{Al}_{30}\text{Mg}_{23}} = -991.8; {}^0\Delta S_{\text{AlMg}}^{\text{Al}_{30}\text{Mg}_{23}} = 3.27$
$\text{Al}_{140}\text{Mg}_{89}$ (β)	${}^0\Delta H_{\text{AlMg}}^{\text{Al}_{140}\text{Mg}_{89}} = -1075.0; {}^0\Delta S_{\text{AlMg}}^{\text{Al}_{140}\text{Mg}_{89}} = 2.95$
$\text{Al}_{12}\text{Mg}_{17}$ (γ) $(\text{Mg})_5(\text{Al}, \text{Mg})_{12}(\text{Al}, \text{Mg})_{12}$	${}^0L_{\text{Mg:Al;Al,Mg}}^{\gamma} = 3901.7 - 0.50T; {}^0L_{\text{Mg:Mg;Al,Mg}}^{\gamma} = 3901.7 - 0.50T$

by means of XRD and metallography inspection; he also proved that the phase is at equilibrium with Mg terminal solid solution at room temperature. The phase equilibria in the Mg-Zn system from 0 to 67.8 at.% Zn were determined by Clark and Rhins [112] using XRD and microscopic analysis. They confirmed the thermal stability range of MgZn from 366 to 608 K. In addition, they identified the temperature of the eutectoidal decomposition $\text{Mg}_7\text{Zn}_3 \rightleftharpoons \alpha\text{-Mg} + \text{MgZn}$ at near

598 K. After careful crystal structure study, Higashi et al. [113] replaced the compound Mg_7Zn_3 by $\text{Mg}_{51}\text{Zn}_{20}$ using XRD techniques. Afterwards, the Mg-Zn system was assessed by Clark et al. [114] based on the experimental work of [107, 109, 110]. Using computational thermodynamics, Agarwal et al. [26], Liang et al. [115], Wasiur-Rahman and Medraj [47], and Ghosh et al. [22] performed phase diagram calculations on the Mg-Zn system. Five intermetallic compounds $\text{Mg}_{51}\text{Zn}_{20}$,

TABLE 4: Enthalpy and entropy of formation of the Mg-Al intermetallic compounds.

Compound	Enthalpy of formation (kJ/mole-atom)	Entropy of formation (J/mole-atom-K)	Reference
Al ₃₀ Mg ₂₃ (ϵ)	-3.42		[101] Cal. (F.P.)
	-0.99	3.27	[104] Cal. (Calphad)
	-2.47		[138] Exp.
Al ₁₄₀ Mg ₈₉ (β)	-1.22		[139] Exp.
	-1.08	2.95	[104] Cal. (Calphad)
	-3.80		[138] Exp.
Al ₁₂ Mg ₁₇ (γ)	-1.01		[139] Exp.
	-3.60		[101] Cal. (F.P.)

Mg₁₂Zn₁₃, Mg₂Zn₃, MgZn₂, and Mg₂Zn₁₁ and two terminal solid solutions were reported in their models. Agarwal et al. [26] modeled the compounds as stoichiometric phases, whereas, Liang et al. [115], Wasiur-Rahman and Medraj [47] and Ghosh et al. [22] considered MgZn₂ as intermediate solid solution achieving consistency with the experimental results of [109, 114].

Based on the assessed thermodynamic parameters by Ghosh et al. [22], the phase diagram and thermodynamic properties of the Mg-Zn system are calculated as shown in Figures 3, 4, and 5. They [22] considered all the available experimental data including the recent measurements of enthalpy and entropy of formation and heat capacity (cp) of the intermediate compounds by Morishita et al. [129–132]. The crystallographic data of the intermetallic compounds as well as the thermodynamic parameters of the Mg-Zn system are listed in Tables 5 and 6, respectively. The enthalpies and entropies of formation of the intermetallic compounds are listed in Table 7.

4. Mg-Mn (Magnesium-Manganese)

Mg-Mn system is characterized by a wide miscibility gap in the liquid. Very limited experimental data are available on this system and the available data are inconsistent among one another. Most of the available data are on the Mg-rich side describing the limited solid solubility of Mn in Mg. According to Tiner [37], the maximum solid solubility of Mn in Mg is 2.0 at.% Mn at 924 K. But Petrov et al. [133] reported much lower solubility limit as 1.03 at.% Mn in Mg using X-ray analysis. Nayeb-Hashemi and Clark [134] critically assessed the partial equilibrium phase diagram of the Mg-Mn system from 0 at.% Mn to 3.0 at.%. Their evaluation was based on thermal analysis, microscopic observation, and hardness measurements of Petrov et al. [133]. They [134] reported the solubility limit of Mn in Mg as 0.996 at.% Mn. No intermediate compounds between Mg and Mn terminal sides were detected; this supports the presence of the large miscibility gap in the liquid phase, indicating that Mg and Mn atoms prefer to be separated in the liquid and solid phases. The complete Mg-Mn phase diagram was determined by Gröbner et al. [135] using differential thermal analysis (DTA) and thermodynamic modeling. Their estimated solubility limit of Mn in Mg was in good agreement with Nayeb-Hashemi

and Clark [134]. Two invariant reactions were observed: the peritectic reaction $L + (\alpha\text{-Mn}) \rightarrow \text{Mg}$ at 0.85 at.% Mn and just below 923 K and the monotectic reaction $L' \rightarrow L' + (\delta\text{-Mn})$ at 96 at.% Mn and 1471 K. The calculations of Gröbner et al. [135] are consistent with the measurements of Petrov et al. [133] for both the liquidus curve and the solubility limit of Mn in Mg. Later, Kang et al. [136] reoptimized the Mg-Mn phase diagram. Their optimized phase diagram agrees well with the DTA results of Gröbner et al. [135]. No experimental data on the consolute temperature of the liquid miscibility gap was found, and the available values are based only on the thermodynamic calculations. Kang et al. [136] calculated the temperature of the liquid miscibility gap as 2175 K, which is lower than that calculated by Gröbner et al. [135] as 3475 K and by Asgar-Khan and Medraj [32] as 3688 K. The liquid miscibility gap temperature was lowered in the work of Kang et al. [136] to enable good agreement with their work on the Mg-Mn-Y system without using any ternary adjustable parameter for the liquid phase. Recently, a self-consistent thermodynamic model of the Mg-Mn phase diagram was developed by Asgar-Khan and Medraj [32]. In most of the cases, they reported consistent calculations with the experimental observations [135].

The crystallographic data of this system and the optimized thermodynamic parameters reported by Asgar-Khan and Medraj [32] are listed in Tables 8 and 9. The calculated phase diagram is shown in Figures 6 and 7.

5. Mg-Ca (Magnesium-Calcium)

The first work on phase diagram was reported by Baar [145] who determined the liquidus curves for the Mg-Ca system. But it was found later that the starting materials were of low purity. The melting point of the starting Ca he used was 1081 K and for Mg was 905.6 K, compared to 1115 and 923 K [146] for pure Ca and Mg, respectively. Further work on this system was carried out by Paris [147] while he was studying the Mg-Ca-Zn ternary system. Their [147] results differ slightly from those of Baar [145]. However, Paris [147] did not mention the purity of the starting materials. Haughton [148] determined the liquidus temperatures in the Mg-rich region in the composition range of 0 to 26 at.% Ca. They found that the liquidus temperatures in this composition range are in fair agreement with Vosskühler [149] and Klemm

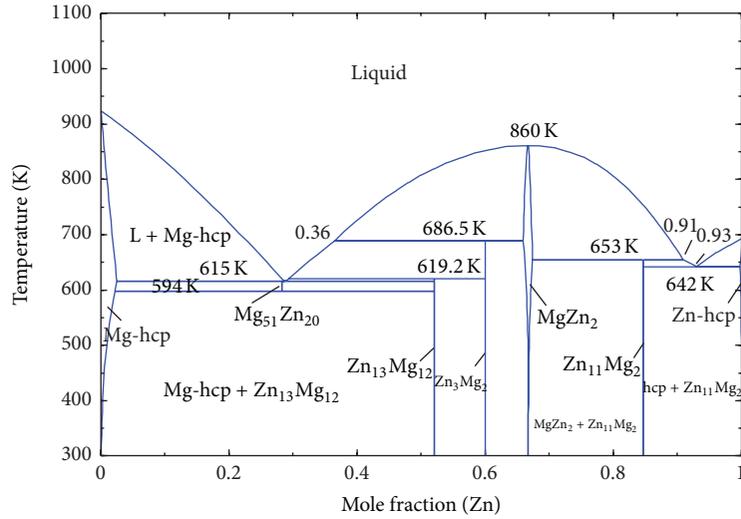


FIGURE 3: Mg-Zn phase diagram [22].

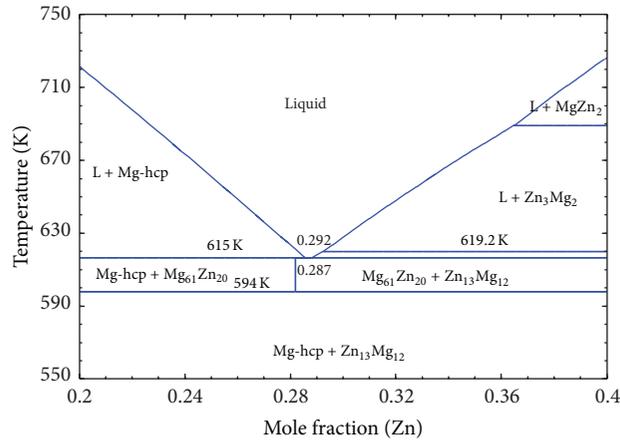


FIGURE 4: Magnified part of the Mg-Zn phase diagram [22].

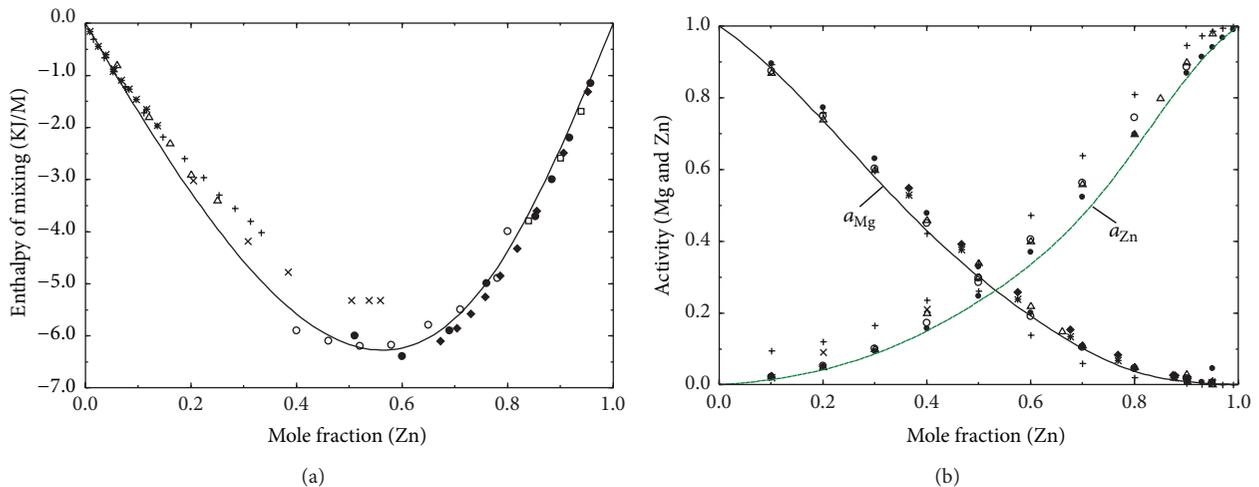


FIGURE 5: Calculated (a) enthalpy of mixing of liquid Mg-Zn at 923 K: ○: [24] at 893 K, □: [24] at 842 K, △: [24] at 931 K, ●: [25] at 1073 K, ◆: [26] at 873 K, ×: at 933 K, +: at 933 K, *: at 940 K; (b) Activity of liquid Mg and Zn 923 K: ○: [27] at 933 K, +: [28] at 680 K, ●: [28] at 880 K, *: [29] at 923 K, ◆: [29] at 1000 K, △: [30], ×: [31] at 943 K.

TABLE 5: Crystal structure data for Mg-Zn intermetallic compounds.

Phase	Prototype	Space group number	Space group	Lattice parameter (nm)			Reference
				<i>a</i>	<i>b</i>	<i>c</i>	
Mg ₅₁ Zn ₂₀		71	<i>Immm</i>	1.4025			[140, 141]
Mg ₂₁ Zn ₂₅		167	<i>R3̄ch</i>	2.5776		0.8762	[140, 141]
Mg ₄ Zn ₇		12	<i>C12/m1</i>	2.5960	0.5240	1.4280	[140, 141]
MgZn ₂	MgZn ₂	164	<i>P6₃/mmc</i>	0.5220		0.8566	[140, 141]
Mg ₂ Zn ₁₁	Mg ₂ Zn ₁₁	200	<i>Pm3̄</i>	0.8552			[140, 141]

TABLE 6: Optimized model parameters of the Mg-Zn system [22].

Phase	Parameters	
	Δg^0 and 0L in J/mole, ${}^0\Delta H$ in J/mole-atom and ${}^0\Delta S$ in J/mole-atom·K	
Liquid	$Z_{MgZn}^{Mg} = 6, Z_{ZnMg}^{Zn} = 4;$	
	$\Delta g_{MgZn}^0 = -8326.2 + 3.19T; \Delta g_{MgZn}^{10} = -4602.4 - 3.26T;$ $\Delta g_{MgZn}^{01} = -62.8 - 3.76T$ (J/mole)	
Mg-hcp (Mg in Zn-hcp, Zn in Mg-hcp)	${}^0L^{Mg-hcp} = -3502.5 + 5.64T;$ ${}^1L^{Mg-hcp} = -6129.9 + 5.66T;$	
Mg ₂ Zn ₁₁	${}^0\Delta H_{Mg,Zn}^{Mg_2Zn_{11}} = -6601.2; {}^0\Delta S_{Mg,Zn}^{Mg_2Zn_{11}} = -1.82$	
Mg ₂ Zn ₃	${}^0\Delta H_{Mg,Zn}^{Mg_2Zn_3} = -10989.9; {}^0\Delta S_{Mg,Zn}^{Mg_2Zn_3} = -1.3$	
Mg ₁₂ Zn ₁₃	${}^0\Delta H_{Mg,Zn}^{Mg_{12}Zn_{13}} = -10019.9; {}^0\Delta S_{Mg,Zn}^{Mg_{12}Zn_{13}} = -1.92$	
Mg ₅₁ Zn ₂₀	${}^0\Delta H_{Mg,Zn}^{Mg_{51}Zn_{20}} = -4718.3; {}^0\Delta S_{Mg,Zn}^{Mg_{51}Zn_{20}} = 0.16$	
MgZn ₂ (Mg%, Zn) (Mg, Zn%) ₂	${}^0G_{Mg:Mg}^{MgZn_2} = 43508.7; {}^0G_{Mg:Zn}^{MgZn_2} = -55979.2 + 380.9T - 74T \ln T + 0.00085T^2 - 3.333 \times 10^{-6} T^3;$	
	${}^0\Delta H^{MgZn_2} = -33815; {}^0S^{MgZn_2} = 115.005; c_p = 70 - 0.0017T + 2 \times 10^{-5} T^2$	
	${}^0G_{Zn:Mg}^{MgZn_2} = 30012.9; {}^0G_{Zn:Zn}^{MgZn_2} = 20008.6;$	
	${}^0L_{Mg,Zn:Mg}^{MgZn_2} = {}^0L_{Mg,Zn:Zn}^{MgZn_2} = {}^0L_{Mg:Mg,Zn}^{MgZn_2} = {}^0L_{Zn:Mg,Zn}^{MgZn_2} = 1.0$	

TABLE 7: Enthalpy and entropy of formation of the Mg-Zn intermetallic compounds.

Compound	Enthalpy of formation (kJ/mole-atom)	Entropy of formation (J/mole-atom·K)	Reference
Mg ₅₁ Zn ₂₀	-4.72	0.16	[22] Cal. (Calphad)
	-10.5 ± 3.1		[142] Exp.
Mg ₁₂ Zn ₁₃	-8.9 ± 0.4		[77] Exp.
	-12.14 ± 3		[130] Exp.
	-10.02	-1.92	[22] Cal. (Calphad)
	-7.9 ± 3.1		[143] Exp.
Mg ₂ Zn ₃	-13.96 ± 3		[130] Exp.
	-10.99	-1.3	[22] Cal. (Calphad)
MgZn ₂	-17.6		[144] Exp.
	-15.05 ± 1.1		[142] Exp.
	-10.9 ± 0.4		[77] Exp.
	-13.8 ± 3		[130] Exp.
	-18.66		[22] Cal. (Calphad)
Mg ₂ Zn ₁₁	-10.4 ± 1.5		[143] Exp.
	-10.0 ± 2.5		[142] Exp.
	-8.96 ± 3		[130] Exp.
	-6.60	-1.82	[22] Cal. (Calphad)

TABLE 8: Crystal structure data for Mg-Mn system.

Phase	Prototype	Space group number	Space group	Lattice parameter (nm)			Reference
				<i>a</i>	<i>b</i>	<i>c</i>	
(Mg)	Mg	194	$P6_3/mmc$	0.31997		0.51969	[134]
(α Mn)	α Mn	217	$I\bar{4}3m$	0.89219			[134]
(β Mn)	β Mn	213	$P4_132$	0.63152			[134]
(γ Mn)	Cu	225	$Fm\bar{3}m$	0.38624			[134]
(δ Mn)	W	229	$Im\bar{3}m$	0.30806			[134]

TABLE 9: Optimized model parameters of the Mg-Mn system [32].

Phase	Parameters Δg^0 and 0L in J/mole
Liquid	$Z_{MgMn}^{Mg} = 4, Z_{MnMg}^{Mg} = 6;$ $\Delta g_{MgMn}^0 = -22\,973.4 + 0.81T; \Delta g_{MgMn}^{10} = -11\,995.2;$
Mg-hcp	${}^0L^{Mn-fcc} = 4\,785.2 - 8.83T; {}^1L^{Mg-hcp} = -3\,323.5$
Mn-fcc	${}^0L^{Mn-fcc} = 83\,716.0$
δ -fcc	${}^0L^{\delta-Mn} = 83\,716.0$

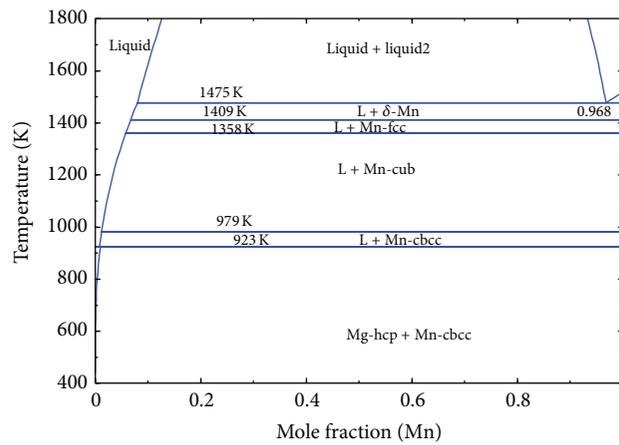


FIGURE 6: Mg-Mn phase diagram [32].

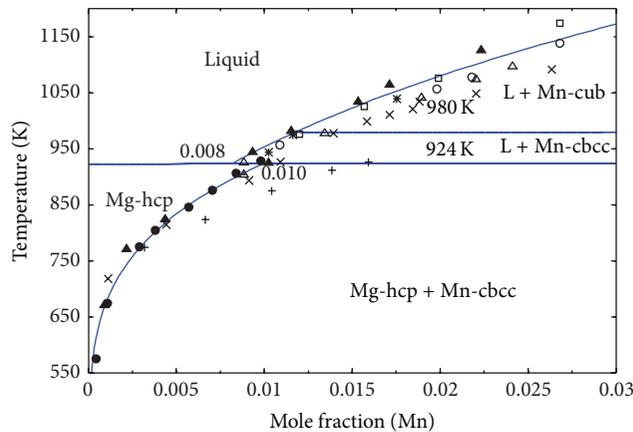
FIGURE 7: Mg-rich side of the Mg-Mn phase diagram [32]. \circ : [33], \blacktriangle : [34], \square : [35], \triangle : [36], $*$: [37], \times : [38], \bullet : [39], $+$: [40].

TABLE 10: Crystal structure data for Mg-Ca intermetallic compound.

Phase	Prototype	Space group number	Space group	Lattice parameter (nm)			Reference
				<i>a</i>	<i>b</i>	<i>c</i>	
Mg ₂ Ca	MgZn ₂	194	<i>P6₃/mmc</i>	0.6253	0.6253	1.0144	[137]

TABLE 11: Optimized model parameters of the Mg-Ca system [41].

Phase	Parameters	
	Δg^0 and 0L in J/mole, ${}^0\Delta H$ in J/mole-atom and ${}^0\Delta S$ in J/mole-atom·K	
Liquid	$Z_{\text{MgCa}}^{\text{Mg}} = 5, Z_{\text{CaMg}}^{\text{Ca}} = 4;$ $\Delta g_{\text{MgCa}}^0 = -13\,206.20 + 9.37T; \Delta g_{\text{MgCa}}^{10} = 6918.14 - 21.03T; \Delta g_{\text{MgCa}}^{01} = 8911.57 - 15.11$	
Mg-hcp	${}^0L_{\text{Mg-hcp}}^{\text{Mg}} = 7153.98 - 9.41T$	
Mg ₂ Ca	${}^0\Delta H_{\text{Mg,Ca}}^{\text{Mg}_2\text{Ca}} = -13\,468.63; {}^0\Delta S_{\text{Mg,Ca}}^{\text{Mg}_2\text{Ca}} = -1.93$	

and Dinkelacker [150] but differ slightly from those given by Baar [145]. Haughton [148] reported that the invariant reaction in the Mg-rich region occurs at 10.5 ± 0.5 at.% Ca and 790 K, compared to Baar's results as 12.46 at.% Ca and 787 K. Whereas, Klemm and Dinkelacker's [150] values are 10.5 at.% Ca and 789.5 K which are in good accord with Haughton [148].

Several researchers [148–150, 159–161] measured the solubility of Ca in Mg. Among them Burke [160] and Vosskühler [149] reported limited solubility and their results agree fairly well, whereas other researchers reported larger solubility.

Agarwal et al. [166] measured the enthalpy of mixing of liquid Mg-Ca alloy calorimetrically at 1023 K and heat contents of Mg₂Ca between 750 and 1150 K. They used these values together with the experimental phase equilibria from [148–150] to calculate the phase diagram of the Mg-Ca system. The enthalpy of mixing measured by Sommer et al. [58] was not used since it contradicts with their measurement. Many efforts had been made to measure the heat of formation of the compound Mg₂Ca [77, 144, 151–155, 166, 167]. The crystallographic information of this compound is listed in Table 10. Mashovets and Puchkov [59] and Sommer [60] determined the activity of Mg and Ca in Mg-Ca liquid at 1080, 1200, and 1010 K using vapor pressure measurement.

Nayeb-Hashemi and Clark [177] critically assessed this system based on the liquidus temperatures and the eutectic reactions of Vosskühler [149] and Klemm and Dinkelacker [150]. However, they [177] placed the melting point of Mg₂Ca at 988 K which is the average temperature measured by Baar [145] and Vosskühler [149].

Zhong et al. [156] used first principle calculations based on the density functional theory to assess the Mg-Ca system. They determined the total energies of the pure elements of various stable phases at 0 K. They also calculated the enthalpies of formation of the four end-members of Mg₂Ca which were then used as input data in the optimization process. Their results are in good agreement with those from Zhang et al. [71] and Yang et al. [157] who also performed first principle calculations.

Later, Aljarrah and Medraj [41] optimized the Mg-Ca system using all the available experimental data. Their [41] assessed parameters are listed in Table II. The Mg-Ca phase

diagram and thermodynamic properties in Figures 8 and 9 are calculated based on their [41] reported parameters as they showed better agreement with the available experimental data. The enthalpy and entropy of formation of Mg₂Ca obtained from different sources are summarized in Table 12.

6. Mg-Sr (Magnesium-Strontium)

Nayeb-Hashemi and Clark [178] reviewed the Mg-Sr system and their article provides a comprehensive discussion of all the experimental results obtained by previous researchers [150, 178–181]. The liquidus surface of the Mg-Sr system was established based on the experimental work of [150, 180–182]. Zhong et al. [158] provided a fine assessment of the liquids experimental data and select them according to the accuracy of the experiments during their optimization. The solid solubility of Mg in Sr has been investigated by Brown [180] and Ray [181]. But according to Nayeb-Hashemi and Clark [178] despite the possibility of hydrogen contamination of Brown's [180] samples, the solidus temperatures he obtained were more realistic than those of Ray [181]. Thermal and metallographic analysis by Brown [180] indicated a very small solid solubility of Sr in Mg (< 0.5 at.% Sr). This was considered negligible in the optimization of the Mg-Sr phase diagram by Chartrand and Pelton [96].

King and Kleppa [77] used calorimetric method to measure the heat of formation of Mg₂Sr. Zhong et al. [158] predicted the heat of formation of all the intermetallic compounds in the Mg-Sr system using first-principles calculations. Sommer et al. [58] determined the enthalpy of mixing of the liquid alloys at 1080 K, using high temperature calorimetry. The thermodynamic activities of liquid alloys at 1054 K were determined by Sommer [61] using a modified Ruff boiling technique.

Zhong et al. [158] utilized the results of first principle calculations on the heat of formation along with other experimental data and provided a set of Gibbs energy parameters for the Mg-Sr system. The heat of formation reported by Zhong et al. [158] is in fair agreement with this of Yang et al. [157] who also employed first principles calculations to study the structural, heat of formation, elastic property, and density state of this compound.

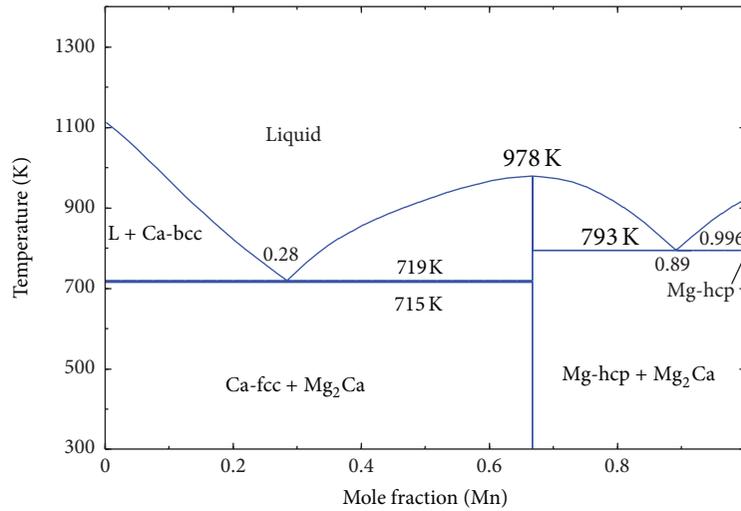
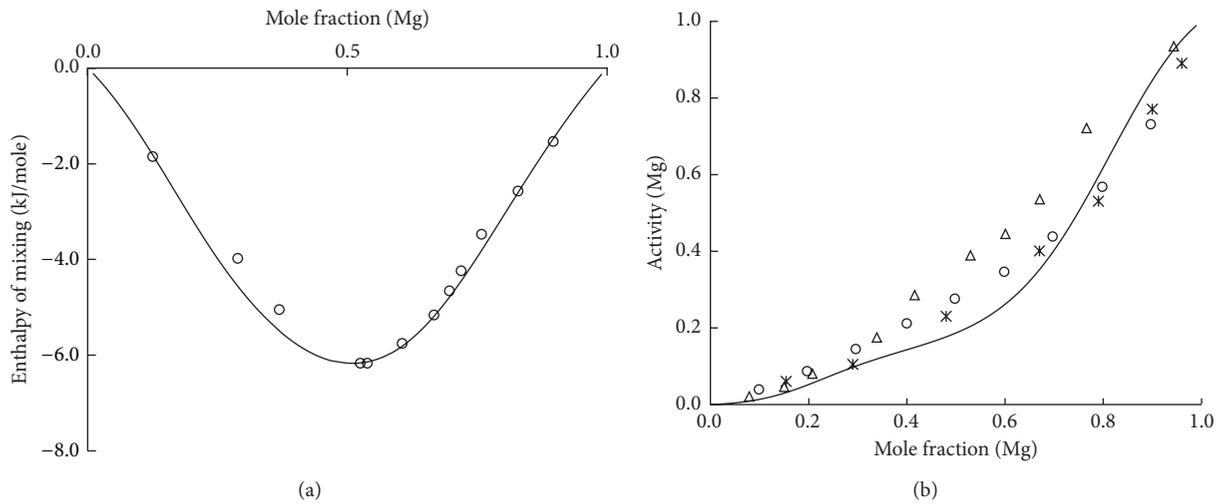


FIGURE 8: Mg-Ca phase diagram [41].

FIGURE 9: Calculated (a) enthalpy of mixing of liquid Mg-Ca at 1150 K: \circ : [58]. (b) Activity of liquid Mg at 1100 K: \triangle : [59] at 1200 K, $*$: [59] at 1080 K, \circ : [60] at 1010 K.TABLE 12: Enthalpy and entropy of formation of Mg_2Ca .

Enthalpy of formation (kJ/mole-atom)	Entropy of formation (J/mole-atom·K)	Reference
-13.47	-1.93	[41] Cal. (<i>Calphad</i>)
-11.72 \pm 3.77		[151] Exp.
-14.59		[152] Exp.
-19.56		[153] Exp.
-19.56		[154] Exp.
-13.39		[77] Exp.
-20.97		[155] Exp.
-11.72		[156] Cal. (<i>F.P.</i>)
-12.14		[71] Cal. (<i>F.P.</i>)
-12.85		[157] Cal. (<i>F.P.</i>)

TABLE 13: Crystal structure data for Mg-Sr system.

Phase	Prototype	Space group number	Space group	Lattice parameter (nm)			Reference
				<i>a</i>	<i>b</i>	<i>c</i>	
Mg ₂ Sr	MgZn ₂	194	<i>P6₃/mmc</i>	0.6475	0.6475	1.0433	[137]
Mg ₃₈ Sr ₉	Mg ₃₈ Sr ₉	194	<i>P6₃/mmc</i>	1.0500	1.0500	2.8251	[137]
Mg ₂₃ Sr ₆	Th ₆ Mn ₂₃	225	<i>Fm$\bar{3}$m</i>	1.5000	1.5000	1.5000	[137]
Mg ₁₇ Sr ₂	Th ₂ Ni ₁₇	194	<i>P6₃/mmc</i>	1.0530	1.0530	1.0408	[137]

TABLE 14: Optimized model parameters of the Mg-Sr system [41].

Phase	Parameters	
	Δg^0 in J/mole, ${}^\circ\Delta H$ in J/mole-atom and ${}^\circ\Delta S$ in J/mole-atom·K	
Liquid	$Z_{MgSr}^{Mg} = 4, Z_{SrMg}^{Sr} = 6;$ $\Delta g_{MgSr}^0 = -7\,425.6 + 2.59T;$ $\Delta g_{MgSr}^{10} = -1\,417.3 + 0.54T;$ $\Delta g_{MgSr}^{01} = 1\,938.0$	
Mg ₂ Sr	${}^\circ\Delta H_{Mg,Sr}^{Mg_2Sr} = -10\,300.0;$	${}^\circ\Delta S_{Mg,Sr}^{Mg_2Sr} = -1.88$
Mg ₃₈ Sr ₉	${}^\circ\Delta H_{Mg,Sr}^{Mg_{38}Sr_9} = -6\,038.3;$	${}^\circ\Delta S_{Mg,Sr}^{Mg_{38}Sr_9} = -0.25$
Mg ₂₃ Sr ₆	${}^\circ\Delta H_{Mg,Sr}^{Mg_{23}Sr_6} = -6\,496.5;$	${}^\circ\Delta S_{Mg,Sr}^{Mg_{23}Sr_6} = -0.39$
Mg ₁₇ Sr ₂	${}^\circ\Delta H_{Mg,Sr}^{Mg_{17}Sr_2} = -3\,631.6;$	${}^\circ\Delta S_{Mg,Sr}^{Mg_{17}Sr_2} = 0.01$

Aljarrah and Medraj [41] reoptimized the Mg-Sr system in the CALPHAD approach considering all the available experimental data on the phase diagram, enthalpy of mixing, and the activities of Mg and Sr in the liquid. They [41] used modified quasichemical model to describe the liquid phase. The intermetallic compounds were considered as stoichiometric. The heat of formation of the intermetallic compounds calculated by Aljarrah and Medraj [41] deviated from those of Zhong et al. [158] due to the use of different entropy values as can be seen in Table 15. The crystallographic data of the intermetallic compounds as well as the optimized model parameters by [41] are listed in Tables 13 and 14. The phase diagram in Figures 10 and 11 and thermodynamic properties in Figure 12 are calculated using these parameters as it provides the most accurate description of the Mg-Sr system. The enthalpies and entropies of formation of the intermetallic compounds are listed in Table 15.

7. Mg-Y (Magnesium-Yttrium)

Gibson and Carlson [183] were the first to report the Mg-Y phase diagram. They determined the maximum primary solid solubility of Y in Mg as 2.63 at.% Y at the eutectic temperature (840 K). This agrees well with the results of Sviderskaya and Padezhnova [64] who used thermal analysis to study the Mg-rich region of the Mg-Y system. Another investigation by Mizer and Clark [184] on this system using thermal analysis and metallography showed that the maximum solubility of Y in solid Mg was approximately 3.79 at.% Y at 838.5 K. This is, also, in good accord with the results of [64, 183].

Smith et al. [65] investigated the crystallography of MgY(γ), Mg₂Y(δ), and Mg₂₄Y₅(ϵ) intermediate phases.

The crystallographic data of the compounds are listed in Table 17. Smith et al. [65] also reported the homogeneity ranges of Mg₂₄Y₅(ϵ) and MgY(γ). The Mg₂Y(δ) compound was predicted as stoichiometric by [65, 183]. But their results do not agree with Flandorfer et al. [63], who employed XRD, optical microscopy, and microprobe analyses to study the Ce-Mg-Y isothermal section at 773 K. Recently, in 2011, Zhao et al. [62] published new information on this system based on diffusion couple and key sample analysis in the temperature range 573–773 K. The homogeneity ranges of Mg₂₄Y₅(ϵ) and Mg₂Y(δ) are listed in Table 16. These measurements by [62] showed significantly different solubility ranges especially for Mg₂Y(δ) than those from the previous publications [63, 65]. Also, the solubility of Y in the Mg-hcp has been adjusted by Zhao et al. [62].

Agarwal et al. [67] measured calorimetrically the enthalpy of mixing of the Mg-Y liquid near the Mg-rich region (up to 21.8 at.% Y) at different temperatures. Activity of Mg was measured by Gansen et al. [68] using the vapour pressure technique. Their results are in agreement with those of Gansen and Isper [69] who used the same method for the measurement. The enthalpy of formation of the three compounds was determined calorimetrically by Pyagai et al. [70]. Their results are in reasonable agreement with the calorimetric data of Smith et al. [65] except MgY(γ), for which the value of Pyagai et al. [70] is twice more negative than that obtained by Smith et al. [65]. This is due to the difficulties in measuring the enthalpy of formation when yttrium content increases resulting in more exothermic reactions. Also, Y has a high melting point compared to Mg and this leads to the sublimation of Mg during fusion of the metals [67]. The first principle calculation by Zhang et al. [71] and Tao et al. [162] for all the intermetallic compounds in the Mg-Y system showed similar enthalpy of formation values as those of Smith et al. [65].

Thermodynamic modeling of the Mg-Y system has been carried out by Ran et al. [185], Fabrichnaya et al. [186], Al Shakhshir and Medraj [52], Meng et al. [187], Guo et al. [188], Kang et al. [189], and Mezbahul-Islam et al. [66]. Also, Okamoto [190] published the Mg-Y phase diagram based on the assessment of Meng et al. [187]. But, only Kang et al. [189] and Mezbahul-Islam et al. [66] used modified quasi chemical model (MQM) to describe the liquid. Since Mg-Y system showed strong short range ordering in the liquid it is more reliable to use MQM in the optimization as it generally provides better predictions in the ternary and higher-order systems [189]. However, the new experimental results on the Mg-Y phase diagram reported by Zhao et al. [62] were not included in any of the previous assessments.

TABLE 15: Enthalpy and entropy of formation of the Mg-Sr intermetallic compounds.

Compound	Enthalpy of formation (kJ/mole-atom)	Entropy of formation (J/mole-atom·K)	Reference
Mg_2Sr	-7.12		[77] Exp.
	-10.62		[158] Cal. (FP)
	-10.3	-1.88	[41] Cal. (Calphad)
	-11.34		[157] Cal. (FP)
$\text{Mg}_{38}\text{Sr}_9$	-6.27		[158] Cal. (FP)
	-6.74		[157] Cal. (FP)
	-6.04	-0.25	[41] Cal. (Calphad)
$\text{Mg}_{23}\text{Sr}_6$	-7.74		[158] Cal. (FP)
	-8.52		[157] Cal. (FP)
	-6.50	-0.39	[41] Cal. (Calphad)
$\text{Mg}_{17}\text{Sr}_2$	-4.80		[158] Cal. (FP)
	-5.60		[157] Cal. (FP)
	-3.63	0.01	[41] Cal. (Calphad)

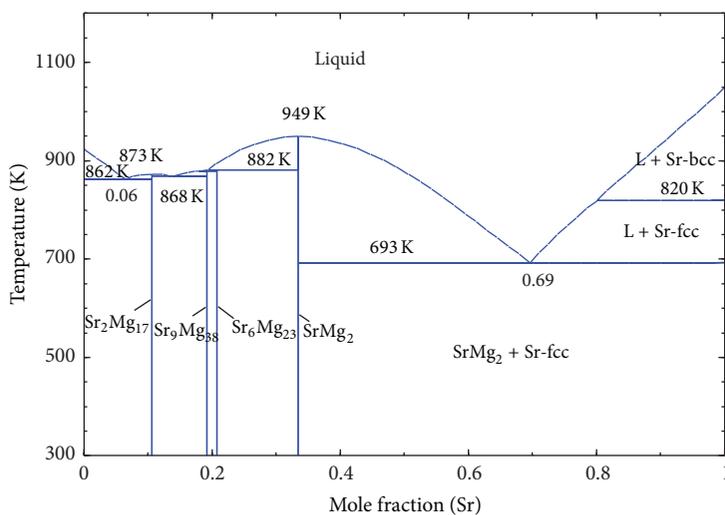


FIGURE 10: Mg-Sr phase diagram.

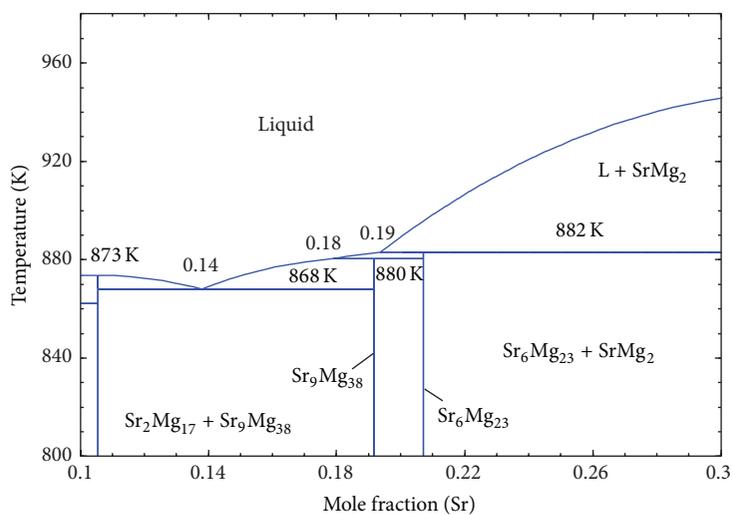


FIGURE 11: Magnified portion of the Mg-Sr phase diagram.

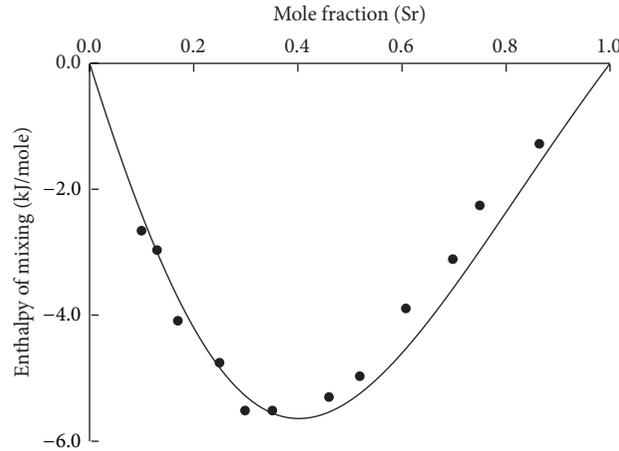


FIGURE 12: Calculated enthalpy of mixing of liquid Mg-Sr at 1080 K: ●: [61].

TABLE 16: Experimental data on the homogeneity ranges of Mg_{24}Y_5 (ϵ) and Mg_2Y (δ).

Temperature, K	Mg_{24}Y_5 (ϵ) at.% Y	Mg_2Y (δ) at.% Y	Reference
573	12.0–16.1	24.0–30.1	[62]
623	11.9–15.8	24.2–29.5	[62]
723	11.9–15.6	24.5–31.0	[62]
773	11.8–15.1	23.6–30.1	[62]
>800	12.0–16.0	33.4–34.5	[65]
773	12.1–16.1	25.0–34.5	[63]

The homogeneity ranges of the intermetallic compounds of this system considered in all the earlier assessments are based on very limited experimental data. Also, those data could have been associated with higher experimental error as they have been measured more than 40 years ago. Zhao et al. [62] used solid-solid diffusion couple technique to determine the solubility of the compounds which usually provides more accurate measurements. Therefore it is decided to consider the recent results of the solubilities of Mg_{24}Y_5 (ϵ) and Mg_2Y (δ) and reoptimize the Mg-Y system in this paper.

The optimized parameters for the Mg-Y system are listed in Table 18. During the optimization, the parameters reported by Mezbahul-Islam et al. [66] are used as the starting value as they provided good consistency with the experimental data of the phase diagram and the thermodynamic properties [63–65, 67–70, 183, 184]. These parameters are then reassessed in light of the recent experimental results of Zhao et al. [62]. Small modifications of the parameters for the liquid, Mg_{24}Y_5 (ϵ), and Mg_2Y (δ) were necessary to comply with the larger homogeneity range of the intermetallic compounds. The calculated Mg-Y phase diagram based on the recent assessment is shown in Figure 13 with the recently available experimental solubility data of Zhao et al. [62] as well those from Smith et al. [65] and Flandorfer et al. [63]. The phase diagram calculated from the previous optimization from the same authors [66] is shown using dotted line. The difference

between these two assessments is mainly along the solubility of the compounds. It can be seen that the present calculation can reproduce the experimental solubility range of Mg_{24}Y_5 (ϵ) and Mg_2Y (δ) as reported by Zhao et al. [62]. The solubility of Y in Mg-hcp obtained in this work is about 2.8 at.% at 773 K which was reported 4.0 at.% by Zhao et al. [62]. Attempt to obtain higher Y solubility in Mg-hcp resulted in poor agreement with the eutectic composition ($\text{L} \leftrightarrow \text{Mg-hcp} + \text{Mg}_{24}\text{Y}_5$ (ϵ)) and temperature data from several other experimental measurements [64, 183, 184]. Also, the authors [62] did not mention the error of measurement of the EPMA which is usually associated with an error of at least ± 1 at.%. Hence it is decided to accept the present assessment with lower Y solubility in Mg-hcp. The enthalpy of mixing of the liquid, activity of the liquid Mg, and enthalpy of formation of the intermetallic compounds are calculated as shown in Figures 14(a), 14(b), and 14(c). All the calculations show very good agreement with the available experimental data. The enthalpies and entropies of formation of the intermetallic compounds are listed in Table 19.

8. Mg-Ni (Magnesium-Nickel)

Voss [191] was the first researcher who investigated the Mg-Ni system by thermal analysis in the composition range $0.04 < X_{\text{Ni}} < 0.98$. 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 [192] determined the liquidus temperature more accurately in the Mg-rich side ($0 \leq X_{\text{Ni}} \leq 0.34$) by thermal analysis using high purity elements. Bagnoud and Feschotte [193] investigated the system using XRD, metallography, EPMA and DTA. Micke and Ipsier [73] determined the activity of magnesium over the Mg-Ni liquid in the $X_{\text{Mg}} > 0.65$ composition range by the isopiestic method. They also obtained the liquidus between $0.30 < X_{\text{Ni}} < 0.40$. According to these investigations, there are two eutectic and one peritectic reactions in the Mg-Ni system. Bagnoud and Feschotte [193] investigated the homogeneity range of MgNi_2 and mentioned that it extends from 66.2 at.% Ni at the peritectic three-phase equilibrium of liquid,

TABLE 17: Crystal structure data for Mg-Y intermetallic compounds.

Phase	Prototype	Space group number	Space group	Lattice parameter (nm)			Reference
				<i>a</i>	<i>b</i>	<i>c</i>	
Mg ₂₄ Y ₅ (ϵ)	Ti ₅ Re ₂₄	217	$\bar{I}43m$	1.1278	1.1278	1.1278	[137]
Mg ₂ Y (δ)	MgZn ₂	194	$P6_3/mmc$	0.6018	0.6018	0.9734	[137]
MgY (γ)	CsCl	221	$Pm\bar{3}m$	0.3797	0.3797	0.3797	[137]

TABLE 18: Optimized model parameters of the Mg-Y system (this work).

Phase	Parameters	
	Δg^0 and 0L in J/mole,	${}^0\Delta H$ in J/mole-atom and ${}^0\Delta S$ in J/mole-atom-K
Liquid	$Z_{MgY}^{Mg} = 2, Z_{YMg}^Y = 4;$	
	$\Delta g_{MgY}^0 = -13\,980.6 + 6.45T; \Delta g_{MgY}^{10} = -15\,445.6 + 8.87T;$ $\Delta g_{MgY}^{01} = 5\,274.1 + 2.09T;$	
Mg-hcp	${}^0L^{Mg-hcp} = -12\,476.8 + 7.49T;$ ${}^1L^{Mg-hcp} = -2\,724.6 + 2.4T;$ ${}^2L^{Mg-hcp} = -2\,788.2 + 2.0T;$	
Y-bcc (β)	${}^0L^{Y-bcc} = -28\,713.7 + 13.07T; {}^1L^{Y-bcc} = -2\,005.9 + 1.5T;$	
Mg ₄₈ Y ₁₀ (ϵ) (Mg%, Y) ₂₉ (Y%, Mg) ₁₀ (Mg) ₁₉	${}^0G_{Mg:Y:Mg}^\epsilon = -6\,179.0; {}^0G_{Mg:Mg:Mg}^\epsilon = 935.5 + 0.14T;$ ${}^0G_{Y:Y:Mg}^\epsilon = 8\,038.3; {}^0G_{Y:Mg:Mg}^\epsilon = 721.7$ (J/mole-atom)	
	${}^0G_{Mg:Y:Mg}^\delta = -9\,767.5 + 0.66T;$ ${}^0G_{Mg:Mg:Mg}^\delta = 3\,544.1 + 1.39T;$ ${}^0G_{Y:Y:Mg}^\delta = {}^0G_{Y:Mg:Mg}^\delta = 6\,976.3;$ ${}^0L_{Mg:Y:Y:Mg}^\delta = 641.8 + 11.86T;$ ${}^0L_{Mg,Y:Mg:Mg}^\delta = {}^0L_{Y,Y:Mg:Mg}^\delta = 9\,006.5 + 88.60T;$ ${}^0L_{Mg,Y,Mg:Mg}^\delta = -2\,096.2 + 0.05T$ (J/mole-atom)	
Mg ₂ Y (δ) (Mg%, Y) ₆ (Y%, Mg) ₄ (Mg) ₂	${}^0G_{Mg:Y}^\gamma = -10\,727.3 + 1.26T; {}^0G_{Mg:Va}^\gamma = -10\,464.5;$ ${}^0G_{Y:Y}^\gamma = {}^0G_{Y:Va}^\gamma = 13\,483.6;$ ${}^0L_{Mg,Y:Y}^\gamma = 15\,006.5 + 16T; {}^0L_{Mg,Y:Va}^\gamma = 15\,006.5 + 15T; {}^0L_{Mg,Y:Va}^\gamma = {}^0L_{Y:Y:Va}^\gamma = -5\,000.0 + 7T$ (J/mole-atom)	

TABLE 19: Enthalpy of formation of the Mg-Y intermetallic compounds.

Compound	Enthalpy of formation (kJ/mole-atom)	Entropy of formation (J/mole-atom-K)	Reference
Mg ₂₄ Y ₅ (ϵ)	-6.18	0	This work Cal. (<i>Calphad</i>)
	-7.5 \pm 0.84	0.4 \pm 0.3	[65] Exp.
	-6.1		[70] Exp.
	-5.84		[71] Cal. (<i>F.P.</i>)
Mg ₂ Y (δ)	-5.4		[162] (<i>F.P.</i>)
	-9.77	-0.66	This work Cal. (<i>Calphad</i>)
	-14.2 \pm 1.26	-1.3 \pm 0.4	[65] Exp.
	-12.0		[70] Exp.
MgY (γ)	-9.17		[71] (<i>F.P.</i>)
	-8.6		[162] (<i>F.P.</i>)
	-10.7	-1.26	This work Cal. (<i>Calphad</i>)
	-12.6 \pm 1.26	-0.3 \pm 0.4	[65] Exp.
MgY (γ)	-30.3		[70] Exp.
	-10.64		[71] (<i>F.P.</i>)
	-10.2		[162] (<i>F.P.</i>)

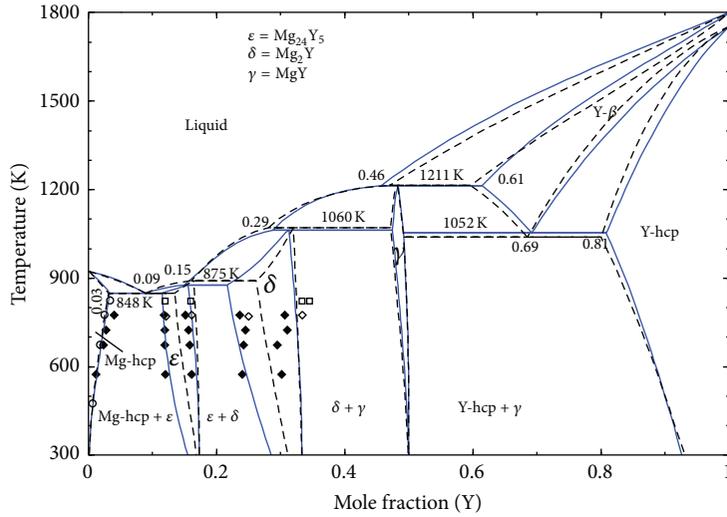


FIGURE 13: Calculated Mg-Y phase diagram (this work) compared with the literature solid solubility data: \blacklozenge : [62], \diamond : [63], \circ : [64], \square : [65]. Dotted line represents the previous assessment [66].

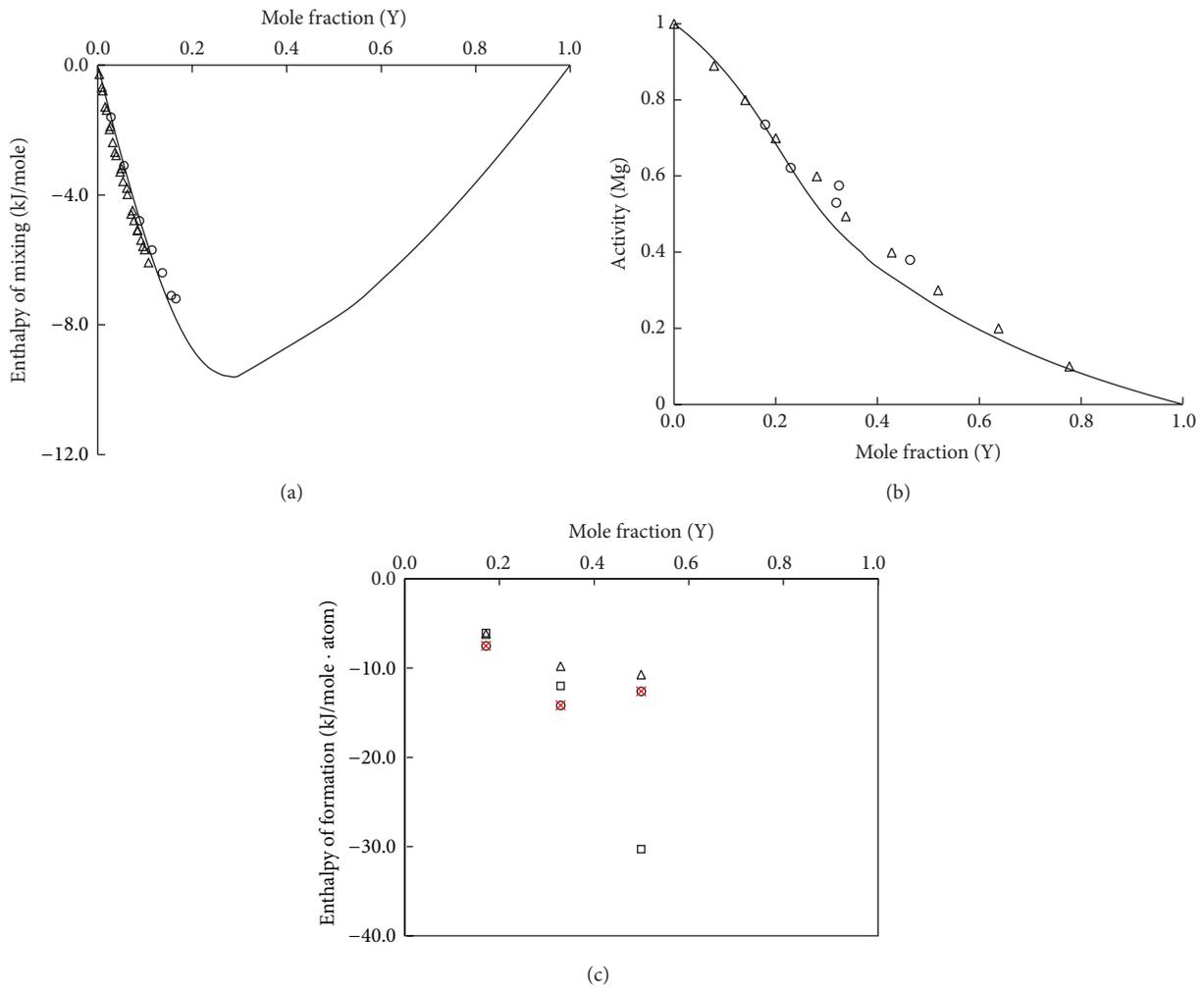


FIGURE 14: Calculated (a) enthalpy of mixing of liquid Mg-Y at 984 K: \triangle : [67] at 975 K, \circ : [67] at 984 K. (b) Activity of liquid Mg at 1173 K: \triangle : [68], \circ : [69]. (c) Enthalpy of formation of the intermetallic compounds: \triangle : [this work]; \square : [65]; \times : [71].

TABLE 20: Crystal structure data for Mg-Ni intermetallic compounds.

Phase	Prototype	Space group number	Space group	Lattice parameter (nm)			Reference
				<i>a</i>	<i>b</i>	<i>c</i>	
Mg ₂ Ni	Mg ₂ Ni	180	<i>P</i> 6 ₂ 22	0.5140	0.5140	1.3220	[163]
MgNi ₂	MgNi ₂	227	<i>P</i> 6 ₃ / <i>mmc</i>	0.4815	0.4815	1.5802	[164]

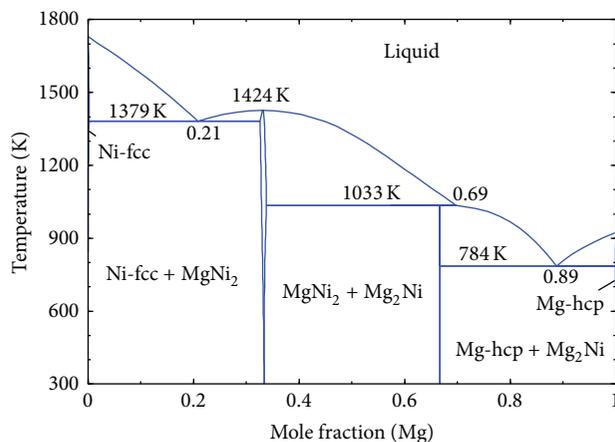


FIGURE 15: Mg-Ni phase diagram [45].

Mg₂Ni and MgNi₂, to 67.3 at.% Ni at the eutectic three phase equilibrium of liquid, Ni-fcc and MgNi₂.

Haughton and Payne [192] mentioned that the solid solubility of Ni in Mg is less than 0.04 at.% Ni at 773 K, whereas Merica and Waltenberg [194] reported that the solid solubility of Mg in Ni is less than 0.2 at.% Mg at 1373 K. Wollam and Wallace [195] and Buschow [163] disputed the ferromagnetic behavior of this system. They investigated the system by heat capacity and magnetic susceptibility measurements and did not find any anomaly in the behavior of MgNi₂ at any temperature.

Laves and Witte [164] determined the crystal structure of MgNi₂ to be hexagonal hP24-type with 8 molecules per unit cell, and the lattice parameters as $a = 0.48147$ nm and $c = 1.58019$ nm which are in good agreement with the reported values of Bagnoud and Feschotte [193] and Lieser and Witte [196]. The crystal structure of Mg₂Ni was determined by Schubert and Anderko [197] who reported a hexagonal, C16-type structure with 6 molecules per unit cell and lattice parameters of $a = 0.514$ nm and $c = 1.322$ nm which agree with the values reported by Buschow [163]. The crystal structures of the compounds are listed in Table 20.

Feufel and Sommer [16] measured the integral enthalpy of mixing by calorimetric method at 1002 K and 1008 K. Sryvalin et al. [72] measured the activity of Mg confirming the results of Micke and Ipsier [73] in the composition range $X_{Ni} \leq 0.30$. Sieben and Schmahl [74], also, measured the activity of Mg. Experimental data on the heat capacity of MgNi₂ is also available. Feufel and Sommer [16] measured the heat capacity from 343 until 803 K with 20 K step, whereas, Schubel [75] measured the same at about 100 K step from 474 to 867 K. Enthalpy of formation of the MgNi₂ and Mg₂Ni compounds was measured by [74, 76–78]. Also, enthalpies

of formation of the compounds were determined using first principle calculations by Zhang et al. [71]. All these data are in reasonable agreement among one another.

Thermodynamic calculations of this system were carried out by Nayeb-Hashemi and Clark [198], Jacobs and Spencer [199] and most recently by Islam and Medraj [43], Xiong et al. [200] and Mezbahul-Islam and Medraj [45]. All these assessments gradually improved the consistency of the phase diagram and thermodynamic properties with the experimental data over years. But with the exception of Mezbahul-Islam and Medraj [45], none of the modeling considered the short range ordering in the liquid. Hence, their assessed parameters are used here to calculate the phase diagram and thermodynamic properties of the Mg-Ni system as shown in Figures 15 and 16. However, in order to be consistent with the experimental Cp data of MgNi₂ of Feufel and Sommer [16], temperature dependant higher order terms are added during optimization of MgNi₂ in the current assessment. Hence, small adjustment of the optimized parameters of Mezbahul-Islam and Medraj [45] is made in the current work as shown in Table 21. The calculated enthalpy of formation of Mg₂Ni and MgNi₂ compared with the available experimental data is shown in Figure 16(d) and Table 22.

9. Mg-Ce (Magnesium-Cerium)

Using DTA, XRD, and metallography, Wood and Cramer [201] showed that the three compounds CeMg₁₂, Ce₂Mg₁₇, and CeMg_{8.25} in the Mg-rich corner were formed peritectically, and the eutectic between Mg and CeMg₁₂ occurred at 866 K and 4.2 at.% Ce. They [201] revealed the existence of CeMg_{8.25} but did not identify its crystal structure. Later, Johnson and Smith [202] determined the structure of this

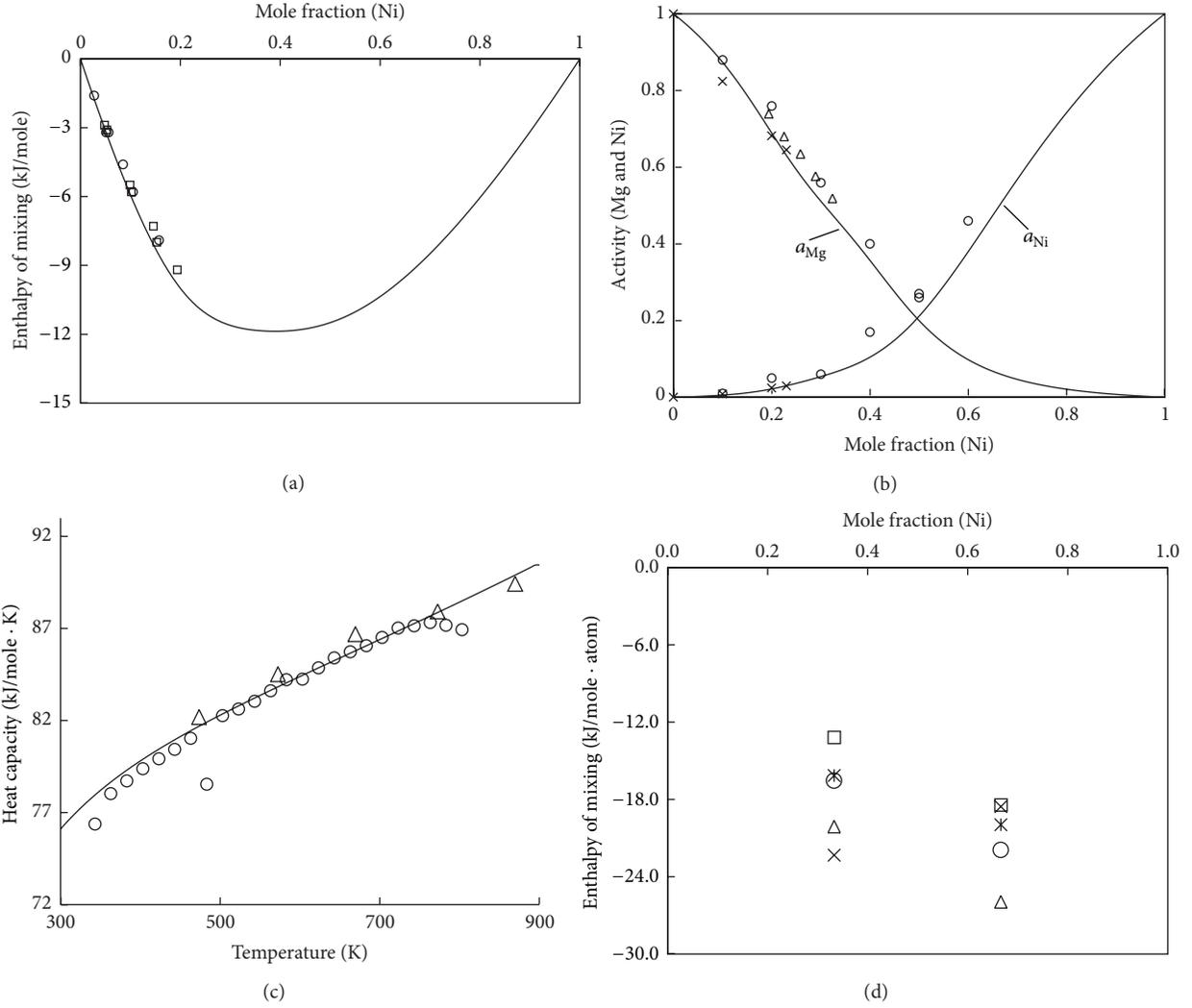


FIGURE 16: Calculated (a) enthalpy of mixing of liquid Mg-Ni at 1008 K: \square : [16] at 1002 K, \circ : [16] at 1008 K. (b) Activity of liquid Mg and Ni at 1100 K: \circ : [72] at 1100 K, \triangle : [73] at 1092 K, \times : [74] at 1100 K. (c) Heat capacity for the MgNi_2 : \circ : [16], \square : [75]. (d) Enthalpy of formation of Mg_2Ni and MgNi_2 : \circ : this work; \triangle : [74]; \times : [76]; \square : [77]; $*$: [78].

TABLE 21: Optimized model parameters of the Mg-Ni system [45].

Phase	Parameters Δg^0 and 0L in J/mole
Liquid	$Z_{\text{MgNi}}^{\text{Mg}} = 2, Z_{\text{NiMg}}^{\text{Ni}} = 4;$ $\Delta g_{\text{MgNi}}^0 = -16\,829.4 + 5.02T; \Delta g_{\text{MgNi}}^{10} = -15\,068.9 + 10.49T;$ $\Delta g_{\text{MgNi}}^{01} = -16345.6 + 1.26T$
Mg-hcp	${}^0L^{\text{Mg-hcp}} = 3767.2$
Ni-fcc	${}^0L^{\text{Ni-fcc}} = 36835.0$
Mg_2Ni^*	$\Delta G_f = -16075.7 + 4.66T$ (J/mole·atom)
MgNi_2^* (Mg%, Ni) ₁ (Mg, Ni%) ₂	${}^0G_{\text{Mg:Mg}}^{\text{MgNi}_2} = 8332.6 + 12.65T; {}^0G_{\text{Mg:Ni}}^{\text{MgNi}_2} =$ $-21\,431.0 + 25.24T - 9.39T \ln T + 22.17 \times 10^{-4}T^2 + 6.66 \times 10^4 T^{-1};$ ${}^0G_{\text{Ni:Mg}}^{\text{MgNi}_2} = 23\,343.37 + 4.66T; {}^0G_{\text{Ni:Ni}}^{\text{MgNi}_2} = 4\,908.55 + 7.0T$ (J/mole·atom)

* Modified in this work.

TABLE 22: Enthalpy and entropy of formation of the Mg-Ni intermetallic compounds.

Compound	Enthalpy of formation (kJ/mole-atom)	Entropy of formation (J/mole-atom-K)	Reference
Mg ₂ Ni	-16.07	-4.66	This work Cal. (<i>Calphad</i>)
	-22.33	-8.37 ± 4.05	[76] Exp.
	-20.09	-9.21	[121] Exp.
	-16.15	-4.96	[78] Exp.
	-13.19 ± 0.42		[77] Exp.
	-19.87		[71] Cal. (<i>F.P.</i>)
MgNi ₂	-12.1 ± 2.10		[16] Exp.
	-21.43	-25.24	This work Cal. (<i>Calphad</i>)
	-18.56	-0.84 ± 1.95	[76] Exp.
	-25.96	-10.89	[121] Exp.
	-19.97		[78] Exp.
	-18.42 ± 0.70	-0.83	[77] Exp.
	-25.85		[71] Cal. (<i>F.P.</i>)
-17.7 ± 3.30		[16] Exp.	

compound using single crystal X-ray diffraction technique. These authors [202] reported that CeMg_{8.25} has a body centered tetragonal (BCT) unit cell with $a = 14.78 \text{ \AA}$ and $c = 10.43 \text{ \AA}$ lattice parameters and $I4/m$ space group. Pahlman and Smith [169] studied the thermodynamics of the compound's formation in the Ce-Mg binary system in the temperature range of 650 K to 930 K. Pahlman and Smith [169] measured the vapour pressure of pure Mg over Ce-Mg alloys using the knudsen effusion method [151]. From the free energy function ($\Delta^\circ G = 7.98 - 9.04 \times 10^{-3} T \text{ kJ} \cdot \text{mol}^{-1}$), they [169] concluded that CeMg₂ should decompose eutectoidally at 875 K. They also reported the eutectoidal decomposition of δ -Ce solid solution at 783 K. Experimental measurement of the heat of formation of the intermetallic compounds was carried out by Nagarajan and Sommer [170], Biltz and Pieper [168] and Pahlman and Smith [169], while first principle calculations to determine the same for the compounds were performed by Tao et al. [162].

The Ce-Mg phase diagram was redrawn by Nayeb-Hashemi and Clark [203], considering six intermetallic compounds CeMg₁₂, Ce₅Mg₄₁, CeMg₃, CeMg, CeMg_{10.3}, and CeMg₂. With the exception of CeMg₃, which melts congruently, all other compounds were considered to be formed peritectically. Later, Saccone et al. [204] studied the Ce-rich and Mg-rich sides of the Ce-Mg phase diagram experimentally using XRD, EPMA/SEM, and metallography. Their [204] findings on the eutectoidal decomposition of CeMg_{10.3} at 886 K, the peritectic formation of CeMg₁₂ at 888 K, and the peritectic formation of CeMg_{10.3} at 896 K were in good agreement with the obtained results by Wood and Cramer [201]. Zhang et al. [205] recently suggested slightly shifted compositions for two compounds; CeMg₁₂ was redesignated as CeMg₁₁ and Ce₅Mg₄₁ as Ce₅Mg₃₉. On the other hand, they excluded the CeMg_{10.3} compound from their version of the phase diagram. More recently, Okamoto [165] put back the compounds former formulae and recommended that the shape of CeMg₃ phase field needs to

be reexamined. This is because the two-phase region field CeMg₂ + CeMg₃ in the phase diagram reported by Zhang et al. [205] increases with temperature, which violates the binary phase diagram rules addressed by Okamoto [206].

Thermodynamic modeling of this system has been carried out by Cacciamani et al. [207], Kang et al. [189], and Zhang et al. [208] and later by Ghosh and Medraj [42] using the CALPHAD approach. All these modelings sequentially improved quality of the thermodynamic description of the Mg-Ce system. In the present paper the optimized parameters published by Ghosh and Medraj [42] are used to calculate the phase diagram and thermodynamic properties as these authors provided the latest and most accurate understanding of this system. The calculated Mg-Ce phase diagram and thermodynamic properties of the liquid are shown in Figures 17, 18, and 19. The crystallographic data of the compounds and the thermodynamic parameter set are listed in Tables 23 and 24. Also, the enthalpies and entropies of formation of the intermetallic compounds collected from different sources are listed in Table 25.

10. Mg-Nd (Magnesium-Nyodymium)

The terminal solid solubility of Nd in Mg was determined by Park and Wyman [109] and Drits et al. [34] at the 819 K eutectic temperature as 0.1 at.% Nd. Later, Joseph and Gschneider [209] determined the maximum solid solubility of Mg in α -Nd as 8.2 at.% Mg at the 824 K eutectoidal decomposition of β -Nd. Iandelli and Palenzona [210] determined the crystal structure of the intermediate compound MgNd as cubic with $cP2$ -CsCl type. The Mg₂Nd was determined as $cF24$ -Cu₂Mg type, Mg₃Nd as $cF16$ -BiF₃ type, Mg₄₁Nd₅ as $tI92$ -Ce₅Mg₄₁ type, and Mg₁₂Nd as $tI26$ -ThMn₁₂ type structures [211]. Nayeb-Hashemi and Clark [212] constructed the Mg-Nd phase diagram based on the available data in the literature. According to their assessment, five intermetallic compounds, MgNd, Mg₂Nd, Mg₃Nd, Mg₄₁Nd₅ and Mg₁₂Nd,

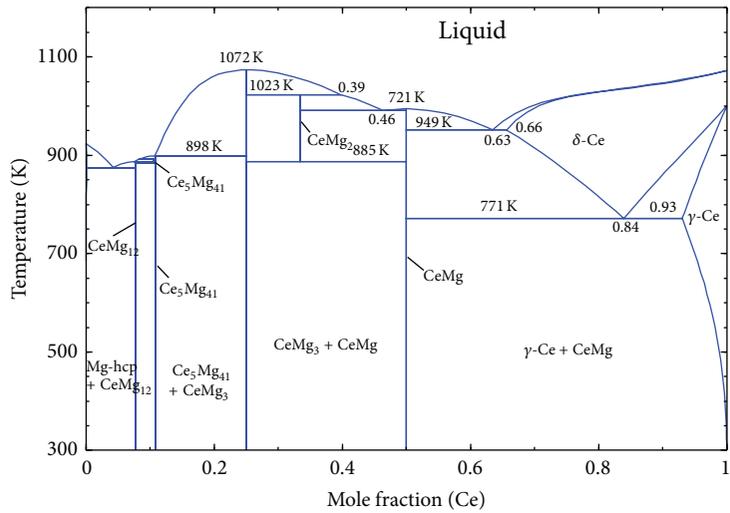


FIGURE 17: Mg-Ce phase diagram.

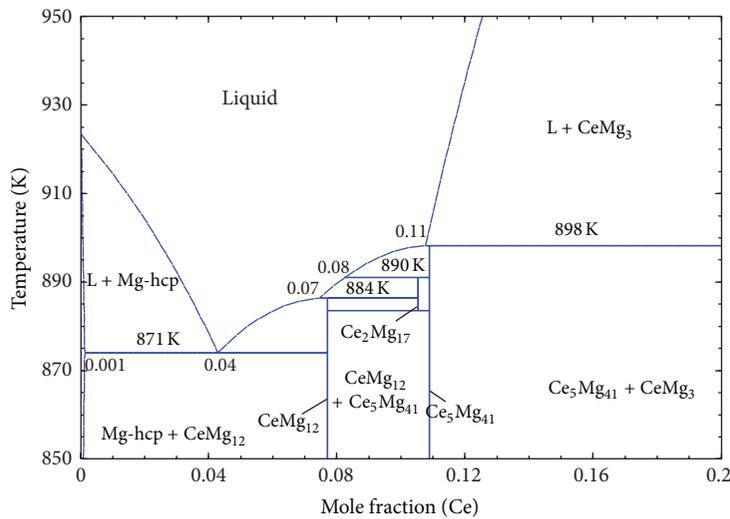


FIGURE 18: Magnified portion of the Mg-Ce phase diagram.

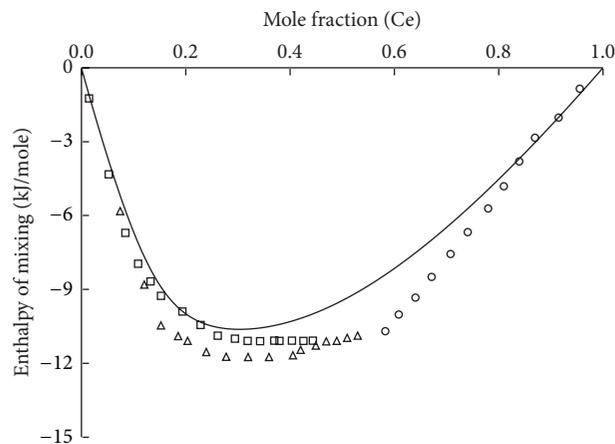


FIGURE 19: Calculated (a) enthalpy of mixing of liquid Mg-Ce at 1090 K: \square : [16] at 1002 K, \circ : [16] at 1008 K. (b) Activity of liquid Mg and Ni at 1100 K: \circ : [72] at 1100 K, \triangle : [73] at 1092 K, \times : [74] at 1100 K. (c) Heat capacity for the $MgNi_2$: \circ : [16], \square : [75]. (d) Enthalpy of formation of Mg_2Ni and $MgNi_2$: \triangle : [74]; \times : [76]; \square : [77]; $*$: [78].

TABLE 23: Crystal structure data for Mg-Ce intermetallic compounds.

Phase	Prototype	Space group number	Space group	Lattice parameter (nm)			Reference
				<i>a</i>	<i>b</i>	<i>c</i>	
(δ Ce)	W	229	$Im\bar{3}m$	0.4120			[141, 165]
(γ Ce)	Cu	225	$Fm\bar{3}m$	0.5160			[141, 165]
CeMg	CsCl	221	$Pm\bar{3}m$	0.3901			[141, 165]
CeMg ₂	Cu ₂ Mg	227	$Fd\bar{3}m$	0.8733			[141, 165]
CeMg ₃	BiF ₃	225	$Fm\bar{3}m$	0.7420			[141, 165]
Ce ₅ Mg ₄₁	Ce ₅ Mg ₄₁	87	$I4/m$	1.4540		1.0280	[141, 165]
CeMg _{10.3}	Ni ₁₇ Th ₂	194	$P6_3/mmc$	1.0350		1.0260	[141, 165]
CeMg ₁₂	Mn ₁₂ Th	139	$I4/mmm$	1.0330		0.5960	[141, 165]
Mg	Mg	194	$P6_3/mmc$	0.3207		0.5210	[141, 165]

TABLE 24: Optimized model parameters of the Mg-Ce system [42].

Phase	Parameters
	Δg^0 and 0L in J/mole, ${}^0\Delta H$ in J/mole-atom and ${}^0\Delta S$ in J/mole-atom-K
Liquid	$Z_{MgCe}^{Mg} = 2, Z_{CeMg}^{Ce} = 6;$ $\Delta g_{MgCe}^0 = -15\,914.4 + 7.44T;$ $\Delta g_{MgCe}^{10} = -9\,632.4 + 2.51T;$ $\Delta g_{MgCe}^{01} = -8\,371.8$
Mg-hcp	${}^0L^{Mg-hcp} = -24\,486.4$
δ -Ce	${}^0L^{\delta-Ce} = -15\,600.7 - 9.75T; {}^1L^{\delta-Ce} = -9003$
γ -Ce	${}^0L^{\gamma-Ce} = -9277.0T;$
CeMg	${}^0\Delta H_{Ce,Mg}^{CeMg} = -14300.0; {}^0\Delta S_{Ce,Mg}^{CeMg} = -2.52$
CeMg ₂	${}^0\Delta H_{Ce,Mg}^{CeMg_2} = -15816.3; {}^0\Delta S_{Ce,Mg}^{CeMg_2} = -3.43$
CeMg ₃	${}^0\Delta H_{Ce,Mg}^{CeMg_3} = -19000.0; {}^0\Delta S_{Ce,Mg}^{CeMg_3} = -6.62$
Ce ₅ Mg ₄₁	${}^0\Delta H_{Ce,Mg}^{Ce_5Mg_{41}} = -12521.8; {}^0\Delta S_{Ce,Mg}^{Ce_5Mg_{41}} = -6.50$
Ce ₂ Mg ₁₇	${}^0\Delta H_{Ce,Mg}^{Ce_2Mg_{17}} = -11363.5; {}^0\Delta S_{Ce,Mg}^{Ce_2Mg_{17}} = -5.40$
CeMg ₁₂	${}^0\Delta H_{Ce,Mg}^{CeMg_{12}} = -10931.1; {}^0\Delta S_{Ce,Mg}^{CeMg_{12}} = -6.65$

TABLE 25: Enthalpy of formation of the Mg-Ce intermetallic compounds.

Compound	Enthalpy of formation (kJ/mole-atom)	Entropy of formation (J/mole-atom·K)	Reference
CeMg	-27.20		[168] Exp.
	-13.08		[169] Exp.
	-12.00		[162] Cal. [F.P.]
	-14.30	-2.52	[42] Cal. (Calphad)
CeMg ₂	-11.38		[169] Exp.
	-11.20		[162] Cal. [F.P.]
	-15.82	-3.43	[42] Cal. (Calphad)
CeMg ₃	-17.78		[168] Exp.
	-18.9		[169] Exp.
	-14.93		[170]
	-12.80		[162] Cal. [F.P.]
	-19.0	-6.62	[42] Cal. (Calphad)
Ce ₅ Mg ₄₁	-18.13		[169] Exp.
	-7.00		[162] Cal. [F.P.]
	-12.52	-6.50	[42] Cal. (Calphad)
Ce ₂ Mg ₁₇	-11.36	-5.40	[42] Cal. (Calphad)
CeMg ₁₂	-14.09		[169] Exp.
	-10.93	-6.65	[42] Cal. (Calphad)

TABLE 26: Crystal structure data for Mg-Nd intermetallic compounds.

Phase	Prototype	Space group number	Space group	Lattice parameter (nm)			Reference
				<i>a</i>	<i>b</i>	<i>c</i>	
(Mg)	Mg	194	$P6_3/mmc$	0.3223		0.5219	[140, 141]
$Mg_{41}Nd_5$	Ce_5Mg_{41}	87	$I4/m$	1.4741		1.0390	[140, 141]
Mg_3Nd	BiF_3	225	$Fm\bar{3}m$	0.7399			[140, 141]
Mg_2Nd	Cu_2Mg	227	$Fd\bar{3}m$	0.8671			[140, 141]
MgNd	CsCl	221	$Pm\bar{3}m$	0.3869			[140, 141]
(β Nd)	W	229	$Im\bar{3}m$	0.4130			[140, 141]
(α Nd)	α La	194	$P6_3/mmc$	0.3659		1.1796	[140, 141]

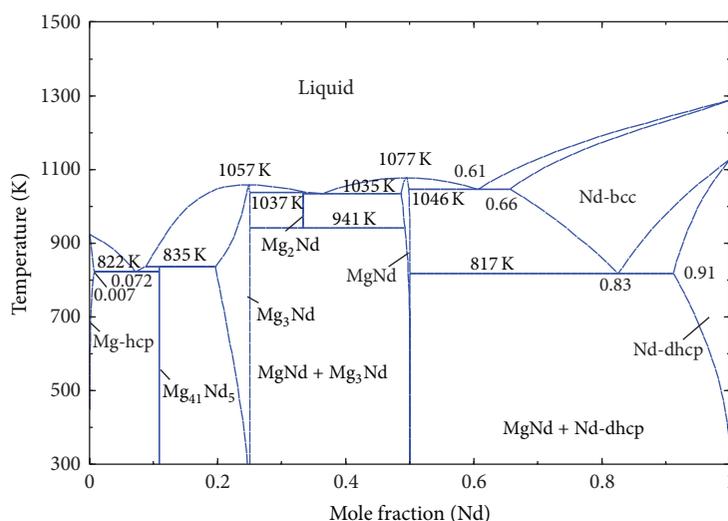


FIGURE 20: Mg-Nd phase diagram [116].

along with terminal solid solutions of Nd in Mg, Mg in α -Nd, and Mg in β -Nd exist in the Mg-Nd phase diagram. Afterwards, Delfino et al. [211] studied this system using X-ray, DTA, metallography, and SEM analysis. According to them [211], Mg_2Nd is a metastable compound because it was only observed in the samples quenched directly from liquid and not in the annealed ones. Later, Gorsse et al. [213] also reported Mg_2Nd as a metastable compound based on their microstructural analysis. $Mg_{41}Nd_5$ has been found as the Mg-richest stable phase by Delfino et al. [211]. They also suggested small solubility for MgNd. In addition they reported Mg_3Nd with maximum solubility of 6 at.% at 833 K extending towards the Mg-rich side. Pahlman and Smith [169] determined the vapor pressure of Mg in Mg-Nd alloys in the temperature range 650–930 K by the knudsen effusion technique. Ogren et al. [214] determined the enthalpy of formation of MgNd compound.

Thermodynamic modeling on the Mg-Nd system has been carried out by Gorsse et al. [213] who considered the Mg activities obtained from vapour pressure data of Pahlman and Smith [169]. However, in their assessment, the intermediate compounds MgNd, Mg_2Nd , Mg_3Nd , and $Mg_{41}Nd_5$ were treated as stoichiometric compounds. Guo and Du [215], Meng et al. [216], and Qi et al. [217] also made thermodynamic assessments on this system. Guo and Du

[215] used Sublattice models to reproduce the homogeneity range of the intermetallic compounds: MgNd, Mg_3Nd , and $Mg_{41}Nd_5$. Recently, Kang et al. [171] assessed all the previous optimizations and reoptimized this system using Modified quasichemical model. They [171] also employed first principle calculations to predict the heat of formation of the intermetallic compounds which are in fair agreement with the reported values by Tao et al. [162]. The crystallographic information of the intermetallic compounds is listed in Table 26. The phase diagram in Figure 20 has been calculated using the FTlight database [116]. The enthalpies and entropies of formation of the intermetallic compounds on the Mg-Nd system are listed in Table 27.

11. Mg-Cu (Magnesium-Copper)

Three very old assessments dating back to 1900s, on the Mg-Cu phase equilibria by Boudouard [218], Sahmen [219] and Urazov [220], could be found in the literature. The existence of two congruently melting compounds (Mg_2Cu and $MgCu_2$) and three eutectic points were reported in those works. But the most extensive work on the Mg-Cu system was done by Jones [221] in 1931 using both thermal and microscopic analyses. His reported data were not fully consistent with the previous authors [218–220]. Since he used

TABLE 27: Enthalpy and entropy of formation of the Mg-Nd intermetallic compounds.

Compound	Enthalpy of formation (kJ/mole-atom)	Entropy of formation (J/mole-atom·K)	Reference
Mg ₄₁ Nd ₅	-17.99 ± 1.34	5.86 ± 1.80	[169] Exp.
	-5.90		[162] Cal. (F.P.)
	-24.61		[171] Cal. (F.P.)
Mg ₃ Nd	-18.74 ± 1.42	5.15 ± 1.88	[169] Exp.
	-11.70		[162] Cal. (F.P.)
Mg ₂ Nd	-18.66 ± 1.42	6.32 ± 1.88	[169] Exp.
	-9.60		[162] Cal. (F.P.)
MgNd	-13.89 ± 1.55	4.02 ± 2.05	[169] Exp.
	-11.00		[162] Cal. (F.P.)

huge number of samples and extreme precautions during the sample preparations his data were more reliable.

Mg₂Cu does not have any solid solubility. However, MgCu₂ shows temperature dependent solubility range. Grime and Morris-Jones [222] reported a homogeneity range of 2 to 3 at.% on both sides of the MgCu₂ stoichiometry. Also, X-ray diffraction from Sederman [223] disclosed that the extension of solubility on both sides of MgCu₂ at 773 K should not exceed 2.55 at.% (from 64.55 to 67.20 at.% Cu) and considerably less at lower temperatures. However X-ray diffraction, microscopic, simple, and differential thermal analysis by Bagnoud and Feschotte [193] confirmed that the maximum solid solubilities at the eutectic temperatures on both sides of MgCu₂ are 64.7 and 69 at.% Cu.

Limited terminal solubility of Cu in Mg as well as Mg in Cu has been reported in different assessments. Hansen [224] showed that the solubility of Cu in Mg increases from about 0.1 at.% Cu at room temperature to about 0.4-0.5 at.% Cu at 758 K. However, elaborate metallographic analysis of Jones [221] showed that the solubility of Cu in Mg is only 0.007 at.% Cu at room temperature, increasing to about 0.012 at.% Cu near the eutectic temperature. These values are contradictory to those given by Hansen [224]. Later, Stepanov and Kornilov [225] revealed that the solubility is 0.2 at.% Cu at 573 K, 0.3 at.% Cu at 673 K, and 0.55 at.% Cu at 753 K. This is in considerable agreement with the metallographic work of Hansen [224]. However considering the accuracy of the analysis of Jones [221], it appears that the solubility limits given by [224, 225] are quite high. On the other hand, quite large solubility of Mg in Cu has been found. According to Grime and Morris-Jones [222], the maximum solubility is approximately 7.5 at.% Mg, whereas, Jones [221] reported that this solubility is about 5.3 at.% Mg at 773 K, increasing to about 6.3 at.% Mg at 1003 K. Stepanov and Kornilov [225], however, determined the maximum solid solubility of 10.4 at.% Mg using an electrical resistance method. Bagnoud and Feschotte [193] placed the maximum solubility at 6.94 at.% Mg. With the exception of Stepanov and Kornilov [225] most of these data [193, 221, 222] are in close agreement with each other.

The vapor pressures of Mg over Mg-Cu liquid were measured by Garg et al. [120], Schmahl and Sieben [121], Juneja et al. [119], and Hino et al. [122]. All these results are in close agreement with each other. Enthalpy of mixing

for the Mg-Cu liquid was measured by Sommer et al. [117] and Batalin et al. [118] using calorimetric method. King and Kleppa [77] determined the enthalpies of formation of MgCu₂ and Mg₂Cu by calorimetric method. Similar values have been determined by Eremenko et al. [123] using EMF measurements. The vapor pressure measurements of Smith and Christian [76] showed discrepancy with the other results. Due to different measurement techniques, the reported values are contradictory to one another.

Several thermodynamic assessments on the Mg-Cu system have been carried out by Nayeb-Hashemi and Clark [226], Coughanowr et al. [227], Zuo and Chang [228]. The latest assessment on this system was published by Mezbahul-Islam et al. [66] who considered the presence of short range ordering in the liquid. The Mg-Cu phase diagram and some of the thermodynamic properties have been calculated as shown in Figures 21 and 22, based on their optimized parameters as listed in Table 29. Also, the crystallographic data of the Mg-Cu intermetallics are listed in Table 28. Mashovets and Puchkov [59] used modified quasichemical model for describing the liquid and also their phase diagram and thermodynamic properties showed very good agreement with the available experimental data. The enthalpies and entropies of formation of Mg₂Cu and MgCu₂ are listed in Table 30.

12. Mg-Sn (Magnesium-Tin)

The Mg-Sn phase diagram has been studied by many researchers. The liquid near the Mg-rich side of the Mg-Sn system has been investigated by Grube [229], Kurnakow and Stepanow [230], Hume-Rothery [231] and Raynor [232] using thermal analysis. Nayak and Olsen [233, 234] also measured the same using a calorimetric analysis. These results are fairly in agreement with each other. The liquidus curve near Mg₂Sn was determined by several researchers [229-236] and the melting point of Mg₂Sn was reported as 1043 K ± (8 to 25). The Sn-rich liquidus curve was first measured by Heycock and Neville [237] and later on by other investigators [229, 231, 233, 234, 238, 239]. Hume-Rothery [231] reported a hump in this side of the liquidus curve and interpreted it as a slight

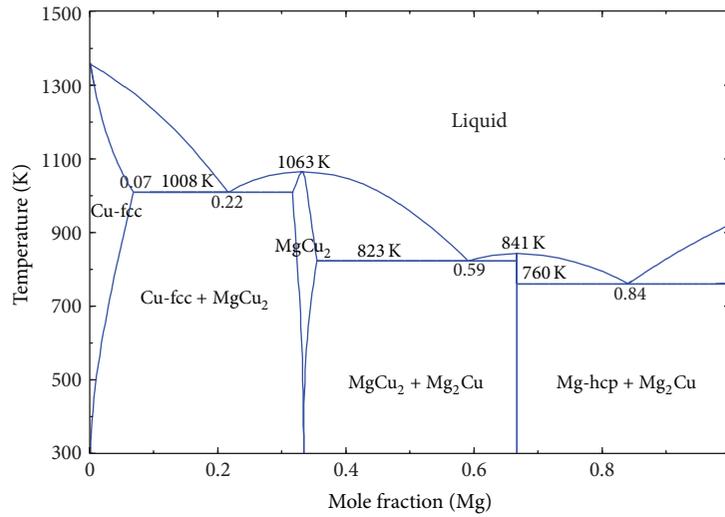


FIGURE 21: Mg-Cu phase diagram [66].

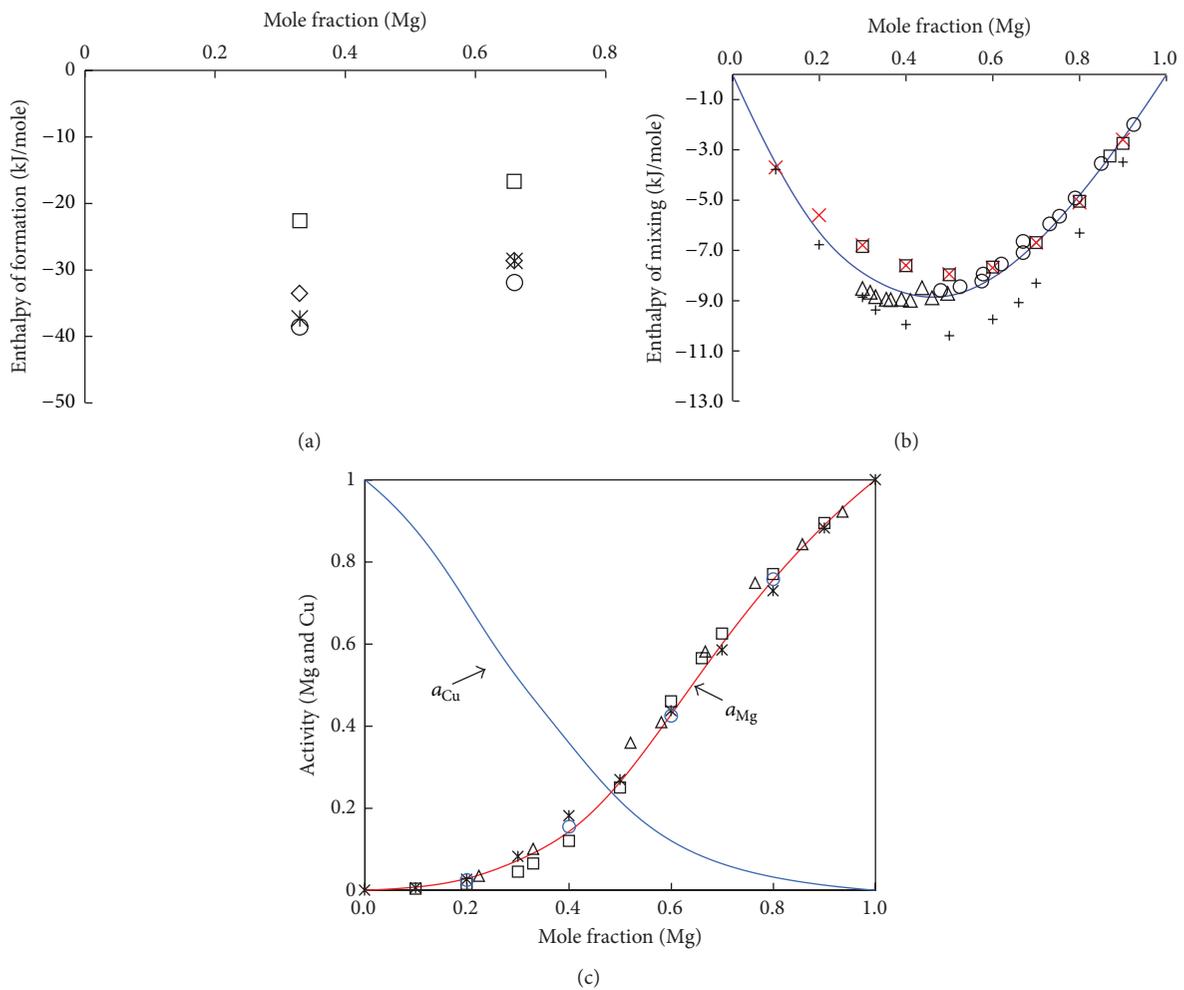


FIGURE 22: (a) Calculated enthalpy of mixing of Mg-Cu liquid at 1400 K [66]: \square : [117] at 1100 K, \triangle : [117] at 1120 K, \circ : [117] at 1125 K, \times : [118] at 1100 K, $+$: [119] at 1100 K. (b) Activity of Mg in the Mg-Cu liquid at 1123 K: $*$: [120] at 1100 K, \triangle : [121] at 1123 K, \square : [119] at 1100 K, \circ : [122] at 1100 K. (c) Heat of formation of the stoichiometric compounds: $*$: [66], \diamond : [77], \circ : [123], \square : [76].

TABLE 28: Crystal structure data for Mg-Cu intermetallic compounds.

Phase	Prototype	Space group number	Space group	Lattice parameter (nm)			Reference
				<i>a</i>	<i>b</i>	<i>c</i>	
Mg ₂ Cu	Mg ₂ Cu	70	<i>Fddd</i>	0.5283	0.9062	1.8351	[137]
MgCu ₂	MgCu ₂	227	<i>Fd$\bar{3}m$</i>	0.7031	0.7031	0.7031	[137]

TABLE 29: Optimized model parameters for the Mg-Cu system [66].

Phase	Parameters
Liquid	$Z_{\text{MgCu}}^{\text{Mg}}=4, Z_{\text{CuMg}}^{\text{Cu}}=2;$
	$\Delta g_{\text{MgCu}}^0 = -12975.95;$
	$\Delta g_{\text{MgCu}}^{10} = -6153.13 + 1.26T;$
	$\Delta g_{\text{MgCu}}^{01} = -13528.50$
Mg-hcp	${}^0L^{\text{Mg-hcp}} = 8371.60$
Cu-fcc	${}^0L^{\text{Cu-fcc}} = -21923.39 + 5.37T$
Mg ₂ Cu	$\Delta G_f = -28620.0 + 0.03T$
MgCu ₂ (Mg%, Cu) (Cu%, Mg) ₂	${}^0G_{\text{Cu:Cu}}^{\text{MgCu}_2} = 16743.20; {}^0G_{\text{Mg:Cu}}^{\text{MgCu}_2} = -37684.26;$ ${}^0G_{\text{Cu:Mg}}^{\text{MgCu}_2} = 0; {}^0G_{\text{Mg:Mg}}^{\text{MgCu}_2} = 6278.7;$ ${}^0L_{\text{Mg,Cu:Cu}}^{\text{MgCu}_2} = {}^0L_{\text{Mg,Cu:Mg}}^{\text{MgCu}_2} = 13011.35;$ ${}^0L_{\text{Cu:Mg,Cu}}^{\text{MgCu}_2} = {}^0L_{\text{Mg:Mg,Cu}}^{\text{MgCu}_2} = 6599.45;$

liquid immiscibility. However, the other investigators [230, 233, 234, 237–239] did not confirm this phenomenon.

The (Mg) solidus curve was determined by Grube and Vosskuhler [240] and Vosskuhler [241] using resistivity technique, by Raynor [232] using metallography and by Nayak and Oelsen [234] using calorimeter. The solid solubility of Sn in Mg was reported by Stepanow [242] and Gann [243] and later by Grube and Vosskuhler [240], Vosskuhler [241], Raynor [232], Nayak and Oelsen [234] and Nishinura and Tanaka [244] by different methods. According to Nayeb-Hashemi and Clark [239] the solid solubility of Mg in Sn is infinitesimally small. Eldridge et al. [245] and Caulfield and Hudson [246] reported a very narrow solid solubility range of Mg and Sn in Mg₂Sn at high temperature (few tenth of a percent [245] to 0.5 at% [246]).

Kawakami [25], Sommer [172] and Nayak and Oelsen [173, 247] measured the heat of mixing of the Mg-Sn liquid using calorimetric method, whereas Eremenko and Lukashenko [248], Steiner et al. [235], Eldridge et al. [245] and Sharma [127] calculated it from the EMF measurement. The heat of formation of the Mg-Sn solid was determined by Kubaschewski [249], Nayak and Oelsen [173], Sharma [127], Beardmore et al. [174], kBiltz and Holverscheit [250], Ashtakala and Pidgeon [251] and Borsese et al. [175], whereas Dobovisek and Paulin [176] calculated heat of formation of the Mg₂Sn compound using the Pauling's rule. The heat capacity of the Mg₂Sn compound was determined by Jelinek et al. [252] at low temperature (up to 300 K), whereas Chen et al. [253] determined the same at much higher temperature (300–700 K).

The phase equilibrium and experimental phase diagram data are reviewed by Nayeb-Hashemi and Clark [239]. Higher

negative heat of formation values of Mg₂Sn were reported by Sharma [127], Eldridge et al. [245] and Biltz and Holverscheit [250] than those by Nayeb-Hashemi and Clark [239]. Nayeb-Hashemi and Clark [239] along with others like Egan [254], Eckert et al. [255], Pavlova and Poyarkov [256] optimized the phase diagram using measured thermodynamic data. Very recently, Jung and Kim [257], Meng et al. [258] and Kang and Pelton [259] optimized the same system and modeled the liquid phase by the MQM. They considered the thermodynamic data reviewed by Nayeb-Hashemi and Clark [239]. The most recent optimization has been performed by Ghosh et al. [22] who critically reviewed all the work done prior to them and reported a more accurate description of the Mg-Sn system. The crystal structure information and thermodynamic modeling parameters are listed in Tables 31 and 32. Figures 23 and 24 show the Mg-Sn phase diagram as well as some of the thermodynamic properties of the liquid. The enthalpy and entropy of formation of Mg₂Sn are listed in Table 33.

13. Summary

Eleven essential Mg-based binary systems have been reviewed in this paper. All the available experimental data has been summarized and assessed critically to provide detailed understanding of each system. The phase diagrams are calculated based on the most up-to-date optimized parameters. Critical information of the phase diagram both as composition and temperature is shown on the figures. All the binary systems have been modeled using the modified quasichemical model which is the only scientific model that accounts for the short range ordering

TABLE 30: Enthalpy and entropy of formation of the Mg-Cu intermetallic compounds.

Compound	Enthalpy of formation (kJ/mole-atom)	Entropy of formation (J/mole-atom·K)	Reference
Mg ₂ Cu	-9.54	-0.01	[66] Cal. (<i>Calphad</i>)
	-5.58 ± 2.51	9.49 ± 5.02	[76] Exp.
	-10.63 ± 1.09	-1.49 ± 1.38	[123] Exp.
	-9.55 ± 0.42		[77] Exp.
	-9.8 ± 1.8		[16] Exp.
MgCu ₂	-12.56	0.0	[66] Cal. (<i>Calphad</i>)
	-7.5 ± 1.53	3.91 ± 2.09	[76] Exp.
	-12.85 ± 0.67	0.42 ± 0.84	[123] Exp.
	-11.18 ± 0.42		[77] Exp.
	-4.75		[71] Cal. (<i>F.P.</i>)
	-12.7 ± 2.0		[16] Exp.

TABLE 31: Crystal structure data for Mg-Sn intermetallic compound.

Phase	Prototype	Space group number	Space group	Lattice parameter (nm)			Reference
				<i>a</i>	<i>b</i>	<i>c</i>	
Mg ₂ Sn	CF ₂	225	<i>Fm</i> $\bar{3}$ <i>m</i>	0.6760	0.6760	0.6760	[137]

TABLE 32: Optimized model parameters for the Mg-Sn system [22].

Phase	Parameters Δg^0 and 0L in J/mole, ${}^\circ\Delta H$ in J/mole-atom and ${}^\circ\Delta S$ in J/mole-atom·K
Liquid	$Z_{MgSn}^{Mg} = 3, Z_{SnMg}^{Sn} = 6;$ $\Delta g_{MgSn}^0 = -17\,819.7 - 4.10T; \Delta g_{MgSn}^{10} = 1\,171.5;$ $\Delta g_{MgSn}^{01} = -41\,840 - 2.09T$
Mg-hcp	${}^0L_{Mg-hcp} = -62\,000$ $[{}^\circ G_{Sn-hcp} = {}^\circ G_{Sn-bct} + 5000]$
Cu-fcc	${}^0L_{Sn-bct} = -20\,000$ $[{}^\circ G_{Mg-bct} = {}^\circ G_{Mg-hcp} + 8360]$
Mg ₂ Sn	${}^\circ\Delta H_{Sn,Mg}^{SnMg_2} = -28\,332.9; {}^\circ\Delta S_{Sn,Mg}^{SnMg_2} = -1.59$

TABLE 33: Enthalpy and entropy of formation of Mg₂Sn.

Enthalpy of formation (kJ/mole-atom)	Entropy of formation (J/mole-atom·K)	Reference
-28.33	-1.59	[22] Cal. (<i>Calphad</i>)
-8.47		[172] Exp.
-7.40		[173] Exp.
-9.30		[127] Exp.
-8.97		[174] Exp.
-8.17		[175] Exp.
-10.75		[176] Exp.

in the liquid. Reoptimization of the Mg-Y system has been performed to comply with the recent experimental data on the homogeneity range of the intermetallic compounds. The Mg-Nd phase diagram has been calculated using the FTlight database and its thermodynamic parameters are

not available. The thermodynamic model parameters for all other systems have been summarized. These parameters are important for further development of the alloys into the multicomponent systems. The available thermodynamic properties for these binary systems have been calculated

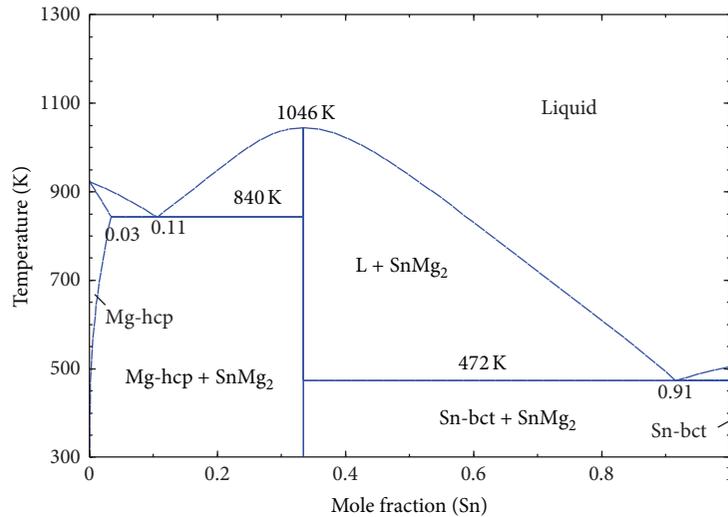


FIGURE 23: Mg-Sn phase diagram [22].

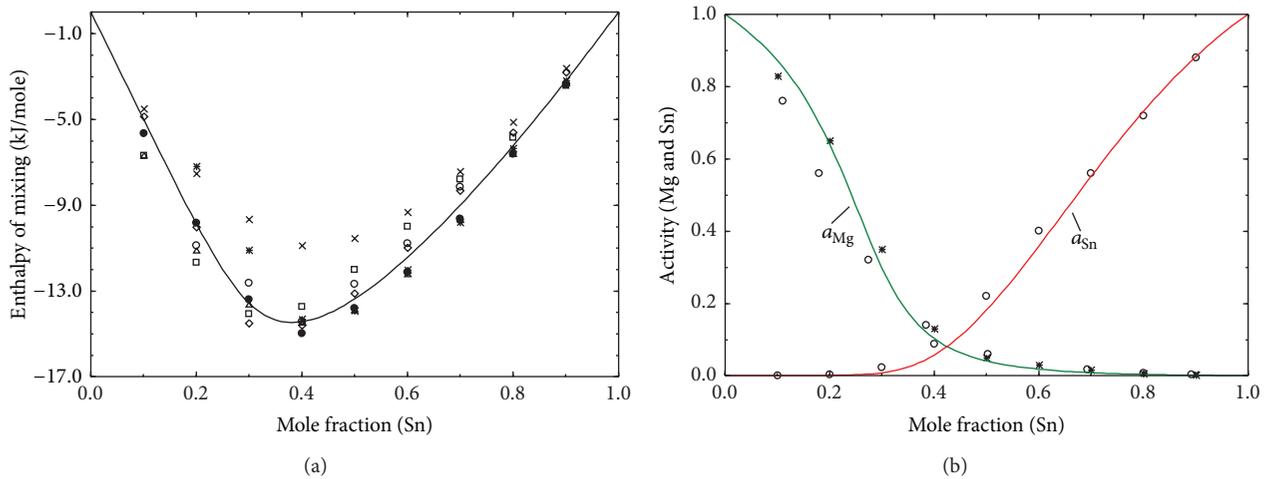


FIGURE 24: (a) Calculated enthalpy of mixing of Mg and Sn in the Mg-Sn liquid at 1073 K: o: [25], □: [124], △: [125], ●: [126], *: [127], ×: [128], ◇: [61]; (b) calculated activities of liquid Mg and Sn at 1073 K: o: [127], *: [124].

and compared with the experimental data for better understanding. The crystallographic data which is one of the primary requirements for Sublattice modeling is also provided in detail for all the binary systems. In addition heat of formation of the intermetallic compounds for each system obtained from experimental, first principle calculations and CALPHAD optimizations are provided. This paper will provide a much needed summarization of all the essential Mg alloys.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

References

- [1] R. Gradinger and P. Stolfig, "Magnesium wrought alloys for automotive applications," in *Proceedings of the Minerals, Metals & Materials Society*, pp. 231–236, March 2003.
- [2] M. O. Pekguleryuz, E. Baril, P. Labelle, and D. Argo, "Creep resistant Mg-Al-Sr alloys," *Journal of Advanced Materials*, vol. 35, no. 3, pp. 32–38, 2003.
- [3] H. Mao, J. Brevick, C. Mobley et al., "Microstructural characteristics of die cast AZ91D and AM60 magnesium alloys," SAE Technical Paper, 1999.
- [4] B. Zberg, P. J. Uggowitzer, and J. F. Löffler, "MgZnCa glasses without clinically observable hydrogen evolution for biodegradable implants," *Nature Materials*, vol. 8, no. 11, pp. 887–891, 2009.

- [5] E. Ma and J. Xu, "Biodegradable alloys: the glass window of opportunities," *Nature Materials*, vol. 8, no. 11, pp. 855–857, 2009.
- [6] E. Aghion, B. Bronfin, F. von Buch, S. Schumann, and H. Friedrich, "Dead sea magnesium alloys newly developed for high temperature applications," in *Proceedings of the Minerals, Metals & Materials Society*, pp. 177–182, March 2003.
- [7] B. Mark, "Remarkable magnesium: the 21st century structural alloy for small components," White Paper, FisherCast Global Corporation, 2013.
- [8] A. Boby, U. Pillai, B. Pillai, and B. Pai, "Developments in magnesium alloys for transport applications—an overview," *Indian Foundry Journal*, vol. 57, pp. 29–37, 2011.
- [9] Z. Yanga, J. X. Zhang, G. W. Lorimer, and J. Robson, "Review on research and development of magnesium alloys," *Acta Metallurgica Sinica (English Letters)*, vol. 21, pp. 313–328, 2008.
- [10] R. Agarwal and F. Sommer, "Calorimetric measurements of liquid aluminum-magnesium alloys," *Zeitschrift für Metallkunde*, vol. 82, pp. 118–120, 1991.
- [11] Z. Moser, W. Zakulski, K. Rzyman et al., "New thermodynamic data for liquid Aluminum-Magnesium alloys from emf, vapor pressures, and calorimetric studies," *Journal of Phase Equilibria*, vol. 19, no. 1, pp. 38–47, 1998.
- [12] Y. J. Bhatt and S. P. Garg, "Thermodynamic study of liquid aluminum-magnesium alloys by vapor pressure measurements," *Metallurgical Transactions B*, vol. 7, no. 2, pp. 271–275, 1976.
- [13] G. R. Belton and Y. K. Rao, "Galvanic cell study of activities in magnesium-aluminum liquid alloys," *Transactions of the AIME*, vol. 245, no. 10, pp. 2189–2193, 1969.
- [14] J. M. Juneja, K. P. Abraham, and G. N. K. Iyengar, "Thermodynamic study of liquid magnesium-aluminum alloys by vapour pressure measurement using the boiling point method," *Scripta Metallurgica*, vol. 20, no. 2, pp. 177–180, 1986.
- [15] V. P. Kazimirov and G. I. Batalin, "Calculation of thermodynamic properties of aluminum-magnesium melts by the pseudopotential method," *Ukrainskii Khimicheskii Zhurnal*, vol. 49, no. 8, pp. 887–888, 1983.
- [16] H. Feufel and F. Sommer, "Thermodynamic investigations of binary liquid and solid CuMg and MgNi alloys and ternary liquid CuMgNi alloys," *Journal of Alloys and Compounds*, vol. 224, no. 1, pp. 42–54, 1995.
- [17] E. E. Lukashenko and A. M. Pogodaev, "Thermodynamics of magnesium-aluminum molten alloys," *Izvestiya Akademii Nauk SSSR, Metall*, pp. 91–96, 1971.
- [18] V. N. Eremenko and G. M. Lukashenko, "Thermodynamic properties of liquid solutions in the magnesium-aluminum system," *Ukrainskii Khimicheskii Zhurnal (Russian Edition)*, vol. 28, pp. 462–466, 1962.
- [19] A. Schneider and E. K. Stoll, "Metal vapor pressure. I. Vapor pressure of magnesium over aluminum-magnesium alloys," *Zeitschrift für Angewandte Physik Und Chemie*, vol. 47, pp. 519–526, 1941.
- [20] M. Y. Vyazner, A. G. Morachevskii, and A. Y. U. Taits, "Thermodynamic properties of magnesium-aluminum system molten alloys," *Zhurnal Prikladnoi Khimii*, vol. 44, no. 5, pp. 722–726, 1971.
- [21] B. L. Tiwari, "Thermodynamic properties of liquid aluminum-magnesium alloys measured by the emf method," *Metallurgical and Materials Transactions A*, vol. 18, pp. 1645–1651, 1987.
- [22] P. Ghosh, M. Mezbahul-Islam, and M. Medraj, "Critical assessment and thermodynamic modeling of Mg-Zn, Mg-Sn, Sn-Zn and Mg-Sn-Zn systems," *Calphad*, vol. 36, pp. 28–43, 2012.
- [23] Magnesium overview, 2013, <http://www.intlmag.org/index.cfm>.
- [24] H. Pyka, *Untersuchungen zur thermodynamik glasbildender ternärer Legierungen [Ph.D. thesis]*, University Stuttgart, Stuttgart, Germany, 1984.
- [25] M. Kawakami, *Scientific Reports of Reserch Institute Tohoku University*, vol. 19, 1930.
- [26] R. Agarwal, S. G. Fries, H. L. Lukas et al., "Assessment of the Mg-Zn system," *Zeitschrift für Metallkunde*, vol. 83, pp. 216–223, 1992.
- [27] A. M. Pogodaev and E. E. Lukashenko, "Thermodynamic study of molten magnesium and zinc alloys," *Zhurnal Fizicheskoi Khimii*, vol. 46, pp. 337–339, 1972.
- [28] Z. Moser, "Thermodynamic properties of dilute solutions of magnesium in zinc," *Metallurgical and Materials Transactions*, vol. 5, no. 6, pp. 1445–1450, 1974.
- [29] P. Chiotti and E. P. Stevens, "Thermodynamic properties of Mg-Zn alloys," *Transactions of the American Society for Metals*, vol. 233, pp. 198–203, 1965.
- [30] J. Terpilowski, "Thermodynamic properties of liquid zinc-magnesium solutions," *Bulletin de l'Academie Polonaise des Sciences, Serie des Sciences Chimiques*, vol. 10, pp. 221–225, 1962.
- [31] Z. Kozuka, J. Moriyama, and I. Kushima, "Activities of the component metals in fused binary alloys (Zn-Al system and Zn-Mg system)," *Denki Kagaku*, vol. 28, pp. 523–526, 1960.
- [32] M. Asgar-Khan and M. Medraj, "Thermodynamic description of the Mg-Mn, Al-Mn and Mg-Al-Mn systems using the modified quasichemical model for the liquid phases," *Materials Transactions*, vol. 50, no. 5, pp. 1113–1122, 2009.
- [33] M. V. Chukhov, "On the solubility of Mn in liquid Mg," *Doklady Akademii Nauk SSSR*, vol. 1, pp. 302–305, 1958.
- [34] M. Drits, E. Padezhnova, and N. Miklina, "The combined solubility of neodymium and zinc in solid magnesium," *Russian Metallurgy*, vol. 3, pp. 143–146, 1974.
- [35] A. Schneider and S. Hennistobbe, "Structure and technical preparation of corrosion-resistant magnesium-manganese alloys," *Metall*, vol. 4, pp. 178–183, 1950.
- [36] G. Siebel, "The solubility of iron, manganese, and zirconium in magnesium and magnesium alloys," *Zeitschrift für Metallkunde*, vol. 39, pp. 22–27, 1948.
- [37] N. Tiner, "The solubility of manganese in liquid magnesium," *Metals Technology*, pp. 1–7, 1945.
- [38] J. D. Grogan and J. L. Haughton, "Alloys of Mg. XIV. The constitution of the Mg-rich alloys of Mg and Mn," *Journal of the Institute of Metals*, vol. 69, pp. 241–248, 1943.
- [39] M. E. Drits, Z. A. Sviderskaya, and L. L. Rokhlin, "Alloys of the system magnesium-neodymium-manganese in the region close to the magnesium corner," *Zhurnal Neorganicheskoi Khimii*, vol. 7, pp. 2771–2777, 1962.
- [40] E. Schmid and G. Siebel, "Determination of solid solubility of Mn in Mg by x-ray analysis," *Metallwirtschaft*, vol. 10, pp. 923–925, 1931.
- [41] M. Aljarrah and M. Medraj, "Thermodynamic modelling of the Mg-Ca, Mg-Sr, Ca-Sr and Mg-Ca-Sr systems using the modified quasichemical model," *Calphad*, vol. 32, no. 2, pp. 240–251, 2008.

- [42] P. Ghosh and M. Medraj, "Thermodynamic calculation of the Mg-Mn-Zn and Mg-Mn-Ce systems and re-optimization of their constitutive binaries," *Calphad*, vol. 41, pp. 89–107, 2013.
- [43] F. Islam and M. Medraj, "The phase equilibria in the Mg-Ni-Ca system," *Calphad*, vol. 29, no. 4, pp. 289–302, 2005.
- [44] M. Mezbahul-Islam, E. Essadiqi, and M. Medraj, "A differential scanning calorimetric study of the Mg-Cu-Y system," *Materials Science Forum*, vol. 706–709, pp. 1215–1220, 2012.
- [45] M. Mezbahul-Islam and M. Medraj, "A critical thermodynamic assessment of the Mg-Ni, Ni-Y binary and Mg-Ni-Y ternary systems," *Calphad*, vol. 33, no. 3, pp. 478–486, 2009.
- [46] M. Mezbahul-Islam and M. Medraj, "Thermodynamic modeling of the Mg-Cu-Ni ternary system using the modified quasichemical model," in *Proceedings of the Conference of Metallurgists (COM '11)*, pp. 241–253, Montreal, Canada, 2011.
- [47] S. Wasiur-Rahman and M. Medraj, "Critical assessment and thermodynamic modeling of the binary Mg-Zn, Ca-Zn and ternary Mg-Ca-Zn systems," *Intermetallics*, vol. 17, no. 10, pp. 847–864, 2009.
- [48] M. A. Parvez, M. Medraj, E. Essadiqi, A. Muntasar, and G. Dénès, "Experimental study of the ternary magnesium-aluminium-strontium system," *Journal of Alloys and Compounds*, vol. 402, no. 1–2, pp. 170–185, 2005.
- [49] T. Balakumar and M. Medraj, "Thermodynamic modeling of the Mg-Al-Sb system," *Calphad*, vol. 29, no. 1, pp. 24–36, 2005.
- [50] F. Islam and M. Medraj, "Thermodynamic modelling of the Mg-Al-Ca system," *Canadian Metallurgical Quarterly*, vol. 44, no. 4, pp. 523–536, 2005.
- [51] F. Islam, A. K. Thykadavil, and M. Medraj, "A computational thermodynamic model of the Mg-Al-Ge system," *Journal of Alloys and Compounds*, vol. 425, no. 1–2, pp. 129–139, 2006.
- [52] S. Al Shakhshir and M. Medraj, "Computational thermodynamic model for the Mg-Al-Y system," *Journal of Phase Equilibria and Diffusion*, vol. 27, no. 3, pp. 231–244, 2006.
- [53] M. Aljarrah, U. Aghaulor, and M. Medraj, "Thermodynamic assessment of the Mg-Zn-Sr system," *Intermetallics*, vol. 15, no. 2, pp. 93–97, 2007.
- [54] M. Aljarrah, M. Medraj, J. Li, and E. Essadiqi, "Phase equilibria of the constituent ternaries of the Mg-Al-Ca-Sr system," *JOM*, vol. 61, no. 5, pp. 68–74, 2009.
- [55] Y.-N. Zhang, D. Kevorkov, J. Li, E. Essadiqi, and M. Medraj, "Determination of the solubility range and crystal structure of the Mg-rich ternary compound in the Ca-Mg-Zn system," *Intermetallics*, vol. 18, no. 12, pp. 2404–2411, 2010.
- [56] Y. N. Zhang, D. Kevorkov, F. Bridier, and M. Medraj, "Experimental study of the Ca-Mg-Zn system using diffusion couples and key alloys," *Science and Technology of Advanced Materials*, vol. 12, no. 2.
- [57] M. Mezbahul-Islam and M. Medraj, "Phase equilibrium in Mg-Cu-Y," *Scientific Reports*, vol. 3, article 3033, 2013.
- [58] F. Sommer, B. Predel, and D. Assman, "Thermodynamic investigation of liquid alloys in the systems Mg-Ca, Mg-Sr, and Mg-Ba," *Zeitschrift für Metallkunde*, vol. 68, pp. 347–349, 1977.
- [59] V. P. Mashovets and L. V. Puchkov, "Vapour pressure over molten alloys in the system Mg-Ca," *Zhurnal Prikladnoi Khimii*, vol. 35, pp. 1009–1014, 1965.
- [60] F. Sommer, "Thermodynamic activities of liquid alloys in the system Ca-Mg using a modified ruff method," *Zeitschrift für Metallkunde*, vol. 70, no. 8, pp. 545–547, 1979.
- [61] F. Sommer, "Determination of thermodynamic activities of liquid alloys in the systems Mg-Sr and Ba-Mg," *Zeitschrift für Metallkunde*, vol. 71, pp. 434–437, 1980.
- [62] H. D. Zhao, G. W. Qin, Y. P. Ren, W. L. Pei, D. Chen, and Y. Guo, "The maximum solubility of γ in α -Mg and composition ranges of $Mg_{24}Y_{5-x}$ and Mg_2Y_{1-x} intermetallic phases in Mg-Y binary system," *Journal of Alloys and Compounds*, vol. 509, no. 3, pp. 627–631, 2011.
- [63] H. Flandorfer, M. Giovannini, A. Saccone, P. Rogl, and R. Ferro, "The Ce-Mg-Y system," *Metallurgical and Materials Transactions A*, vol. 28, no. 2, pp. 265–276, 1997.
- [64] Z. A. Sviderskaya and E. M. Padezhnova, "Phase equilibria in magnesium-yttrium and magnesium-yttrium-manganese systems," *Izvestiya Akademii Nauk SSSR, Metallurgy*, pp. 183–190, 1968.
- [65] J. F. Smith, D. M. Bailey, D. B. Novotny, and J. E. Davison, "Thermodynamics of formation of yttrium-magnesium intermediate phases," *Acta Metallurgica*, vol. 13, no. 8, pp. 889–895, 1965.
- [66] M. Mezbahul-Islam, D. Kevorkov, and M. Medraj, "The equilibrium phase diagram of the magnesium-copper-yttrium system," *The Journal of Chemical Thermodynamics*, vol. 40, no. 7, pp. 1064–1076, 2008.
- [67] R. Agarwal, H. Feufel, and F. Sommer, "Calorimetric measurements of liquid LaMg, MgYb and MgY alloys," *Journal of Alloys and Compounds*, vol. 217, no. 1, pp. 59–64, 1995.
- [68] V. Ganesan, F. Schuller, H. Feufel, F. Sommer, and H. Ipser, "Thermodynamic properties of ternary liquid Cu-Mg-Y alloys," *Zeitschrift für Metallkunde*, vol. 88, no. 9, pp. 701–710, 1997.
- [69] V. Ganesan and H. Ipser, "Thermodynamic properties of liquid magnesium-yttrium alloys," *Journal de Chimie Physique et de Physico-Chimie Biologique*, vol. 94, no. 5, pp. 986–991, 1997.
- [70] I. N. Pyagai, A. V. Vakhobov, N. G. Shmidt, O. V. Zhikhareva, and M. I. Numanov, "Heats of formation of magnesium intermetallic compounds with yttrium, lanthanum, and neodymium," *Doklady Akademii Nauk Tadzhikshoi SSR*, vol. 32, pp. 605–607, 1989.
- [71] H. Zhang, S. Shang, J. E. Saal et al., "Enthalpies of formation of magnesium compounds from first-principles calculations," *Intermetallics*, vol. 17, no. 11, pp. 878–885, 2009.
- [72] I. T. Sryvalin, O. A. Esin, and B. M. Lepinskikh, "Thermodynamic properties of solutions of magnesium in nickel, lead, and silicon," *Zhurnal Fizicheskoi Khimii*, vol. 38, pp. 637–641, 1964.
- [73] K. Micke and H. Ipser, "Thermodynamic properties of liquid magnesium-nickel alloys," *Monatshefte für Chemie*, vol. 127, no. 1, pp. 7–13, 1996.
- [74] P. Sieben and N. G. Schmahl, "Vapor pressure and activity of magnesium in the binary alloy systems with nickel and copper and vapor pressures of some pure metals," *Giesserei, Technisch-Wissenschaftliche Beihefte, Giessereiwesen und Metallkunde*, vol. 18, pp. 197–211, 1966.
- [75] P. Schubel, "The heat capacity of metals and metallic compounds between 18 and 600°," *Zeitschrift für Anorganische Chemie*, vol. 87, pp. 81–119, 1914.
- [76] J. F. Smith and J. L. Christian, "Thermodynamics of formation of coppermagnesium and nickelmagnesium compounds from vapor pressure measurements," *Acta Metallurgica*, vol. 8, no. 4, pp. 249–255, 1960.
- [77] R. C. King and O. J. Kleppa, "A thermochemical study of some selected laves phases," *Acta Metallurgica*, vol. 12, no. 1, pp. 87–97, 1964.
- [78] G. M. Lukashenko and V. N. Eremenko, "Thermodynamic properties of alloys in the system magnesium-nickel in the solid state," *Zvestiya Akademii Nauk SSSR, Metallurgy*, pp. 161–164, 1966.
- [79] A. D. Pelton, S. A. Degterov, G. Eriksson, C. Robelin, and Y. Dessureault, "The modified quasichemical model I—binary

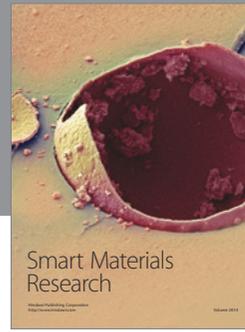
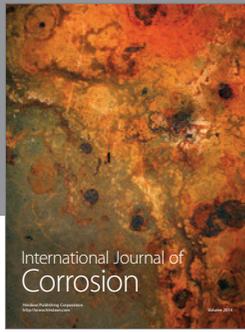
- solutions," *Metallurgical and Materials Transactions B*, vol. 31, no. 4, pp. 651–659, 2000.
- [80] M. Hillert, "The compound energy formalism," *Journal of Alloys and Compounds*, vol. 320, no. 2, pp. 161–176, 2001.
- [81] M. Kawakami, "Equilibrium diagram of aluminum-magnesium system," *Science Reports of the Tohoku Imperial University series I*, pp. 727–747, 1936.
- [82] G. Siebel and H. Vosskuhler, "The determination of the solubility of magnesium in aluminum," *Zeitschrift für Metallkunde*, vol. 31, pp. 359–362, 1939.
- [83] N. S. Kurnakov and V. I. Mikheeva, "Transformations in the middle part of the system aluminum-magnesium," *Doklady Akademii Nauk SSSR*, vol. 13, pp. 209–224, 1940.
- [84] N. S. Kurnakov and V. I. Mikheeva, "Properties of solid solutions of magnesium and aluminum in the system aluminum-magnesium," *Doklady Akademii Nauk SSSR*, vol. 13, pp. 201–208, 1940.
- [85] E. Butchers and W. Hume-Rothery, "Constitution of aluminum-magnesium-manganese-zinc alloys: the solidus," *Journal of the Institute of Metals*, vol. 71, pp. 291–311, 1945.
- [86] W. Stiller and H. Hoffmeister, "Determination of liquid-solid phase equilibria of aluminum-magnesium-zinc alloy," *Zeitschrift für Metallkunde*, vol. 70, pp. 167–172, 1979.
- [87] E. Schuermann and H. J. Voss, "Melting equilibria of magnesium-lithium-aluminum alloys. Part 4. Melting equilibria of the aluminum-magnesium binary system," *Giessereiforschung*, vol. 33, pp. 43–46, 1981.
- [88] N. C. Goel, J. R. Cahoon, and B. Mikkelsen, "An experimental technique for the rapid determination of binary phase diagrams: the Al-Mg system," *Metallurgical Transactions A*, vol. 20, no. 2, pp. 197–203, 1989.
- [89] E. Schuermann and A. Fischer, "Melting equilibria in the ternary aluminum magnesium silicon system—1. Binary aluminum magnesium alloys," *Giessereiforschung*, vol. 29, no. 3, pp. 107–111, 1977.
- [90] E. Schuermann and I. K. Geissler, "Phase equilibria in the solid condition of the aluminum- resp. the magnesium-rich corner of the ternary system of aluminum-lithium-magnesium. Part 3. Phase equilibria in the solid condition of the binary system of aluminium-magnesium," *Giessereiforschung*, vol. 32, pp. 167–170, 1980.
- [91] P. Liang, H. L. Su, P. Donnadiou, M. Harmelin, and A. Quivy, "Experimental investigation and thermodynamic calculation of the central part of the Mg-Al phase diagram," *Zeitschrift für Metallkunde*, vol. 89, pp. 536–540, 1998.
- [92] D. Hanson and M. L. Gayler, "The constitution of the alloys of aluminum and magnesium," *Journal of Institute of Metals*, vol. 24, pp. 201–232, 1920.
- [93] W. Hume-Rothery and G. V. Raynor, "The constitution of the magnesium-rich alloys in the systems aluminum-magnesium, gallium-magnesium, indium-magnesium, and thallium-magnesium," *Journal of the Institute of Metals*, vol. 63, pp. 201–226, 1938.
- [94] E. S. Makarkov, "Crystal structure of the gamma phase of the systems Al-Mg and Tl-Bi," *Doklady Akademii Nauk SSSR*, vol. 74, pp. 935–938, 1950.
- [95] J. L. Murray, "The Al-Mg (Aluminum-Magnesium) system," *Bulletin of Alloy Phase Diagrams*, vol. 3, no. 1, pp. 60–74, 1982.
- [96] P. Chartrand and A. D. Pelton, "Critical evaluation and optimization of the thermodynamic properties and phase diagrams of the Al-Mg, Al-Sr, Mg-Sr, and Al-Mg-Sr systems," *Journal of Phase Equilibria*, vol. 15, no. 6, pp. 591–605, 1994.
- [97] N. Saunders, "A review and thermodynamic assessment of the aluminum-magnesium and magnesium-lithium systems," *Calphad*, vol. 14, pp. 61–70, 1990.
- [98] T. Czeppe, W. Zakulski, and E. Bielańska, "Study of the thermal stability of phases in the Mg-Al system," *Journal of Phase Equilibria*, vol. 24, no. 3, pp. 249–254, 2003.
- [99] Y. Zuo and Y. A. Chang, "Thermodynamic calculation of the AlMg phase diagram," *Calphad*, vol. 17, no. 2, pp. 161–174, 1993.
- [100] K. Ozturk, Z.-K. Liu, and A. A. Luo, "Phase identification and microanalysis in the Mg-Al-Ca alloy system," in *Proceedings of the Magnesium Technology*, pp. 195–200, March 2003.
- [101] Y. Zhong, M. Yang, and Z.-K. Liu, "Contribution of first-principles energetics to Al-Mg thermodynamic modeling," *Calphad*, vol. 29, no. 4, pp. 303–311, 2005.
- [102] G. I. Batalin, V. E. Sokol'skii, and T. B. Shimanskaya, "Enthalpies of mixing liquid alloys of aluminum with magnesium and antimony," *Ukrainskii Khimicheskii Zhurnal*, vol. 37, p. 397, 1971.
- [103] N. M. Tsyplakova and K. L. Strelets, "Thermodynamic properties of a magnesium-aluminum system studied by an emf method," *Zhurnal Prikladnoi Khimii*, vol. 42, no. 11, pp. 2498–2503, 1969.
- [104] M. Aljarrah, *Thermodynamic modeling and experimental investigation of the Mg-Al-Ca-Sr system [Ph.D. thesis]*, Mechanical and Industrial Engineering, Concordia University, Montreal, Canada, 2008.
- [105] O. Boudouard, "Alloys of zinc and magnesium," *Proceedings of the National Academy of Sciences*, vol. 139, pp. 424–426, 1904.
- [106] G. Grube, "Alloys of magnesium with cadmium, zinc, bismuth and antimony," *The Journal of Physical Chemistry*, vol. 10, pp. 587–592, 1906.
- [107] R. J. Chadwick, "The constitution of the alloys of magnesium and zinc," *Journal of the Institute of Metals*, vol. 449, pp. 285–299, 1928.
- [108] S. Samson, "The crystal structure of Mg_2Zn_{11} : isomorphism between Mg_2Zn_{11} and $Mg_2Cu_6Al_5$," *Acta Chemica Scandinavica*, vol. 3, pp. 835–843, 1949.
- [109] J. J. Park and L. L. Wyman, "Phase relationships in magnesium alloys," WADC Technical Report: Astia Document AD142110 57-504, 1957.
- [110] E. D. R. W. Hume-Rothery, "The system magnesium-zinc," *Journal of the Institute of Metals*, vol. 41, pp. 119–138, 1929.
- [111] F. Laves, "Zur konstitution der magnesium-zink-legierungen," *Die Naturwissenschaften*, vol. 27, no. 26, pp. 454–455, 1939.
- [112] J. Clark and F. Rhins, "Central region of the Mg-Zn phase diagram," *Journal of Metals*, vol. 9, pp. 425–430, 1957.
- [113] I. Higashi, N. Shiotani, M. Uda, T. Mizoguchi, and H. Katoh, "The crystal structure of $Mg_{51}Zn_{20}$," *Journal of Solid State Chemistry*, vol. 36, no. 2, pp. 225–233, 1981.
- [114] J. B. Clark, L. Zabdyr, and Z. Moser, *Phase Diagrams of Binary Magnesium Alloys*, ASM INTERNATIONAL, Metals Park, Ohio, USA, 1988.
- [115] P. Liang, T. Tarfa, J. A. Robinson et al., "Experimental investigation and thermodynamic calculation of the Al-Mg-Zn system," *Thermochimica Acta*, vol. 314, no. 1-2, pp. 87–110, 1998.
- [116] C. W. Bale, P. Chartrand, S. A. Degterov et al., *FTlight Thermochemical Database*, CRCT, Montreal, Canada, 2013.
- [117] F. Sommer, J. J. Lee, and B. Predel, "Calorimetric investigations of liquid alkaline earth metal alloys," *Berichte der Bunsengesellschaft für Physikalische Chemie*, vol. 87, pp. 792–797, 1983.

- [118] A. V. Volkovich, A. V. Krivopushkin, and I. F. Nichkov, "Thermodynamic properties of zinc-strontium alloys," *Izv Vyssh Uchebn Zaved Tsvetn Metall*, pp. 29–31, 1987.
- [119] J. M. Juneja, G. N. K. Iyengar, and K. P. Abraham, "Thermodynamic properties of liquid (magnesium + copper) alloys by vapour-pressure measurements made by a boiling-temperature method," *The Journal of Chemical Thermodynamics*, vol. 18, no. 11, pp. 1025–1035, 1986.
- [120] S. P. Garg, Y. J. Bhatt, and C. V. Sundaram, "Thermodynamic study of liquid Cu-Mg alloys by vapor pressure measurements," *Metallurgical Transactions*, vol. 4, no. 1, pp. 283–289, 1973.
- [121] N. G. Schmahl and P. Sieben, "Vapor pressures of magnesium in its binary alloys with copper, nickel, and lead and their thermodynamic evaluation," *Physical Chemistry of Metallic Solutions and Intermetallic Compounds, Symposium*, vol. 1, pp. 268–282, 1960.
- [122] M. Hino, T. Nagasaka, and R. Takehama, "Activity measurement of the constituents in liquid Cu-Mg and Cu-Ca alloys with mass spectrometry," *Metallurgical and Materials Transactions B*, vol. 31, pp. 927–935, 2000.
- [123] V. N. Eremenko, G. M. Lukashenko, and R. I. Polotskaya, "Thermodynamic properties of magnesium-copper compounds," *Izvestiya Akademii Nauk SSSR, Metall*, pp. 210–212, 1968.
- [124] V. N. Eremenko and G. M. Lukashenko, "Thermodynamic properties of Mg-Pb system," *Ukrainskii Khimicheskii Zhurnal*, vol. 29, pp. 896–900, 1963.
- [125] A. Steiner, E. Miller, and K. L. Komarek, "Magnesium-tin phase diagram and thermodynamic properties of liquid magnesium-tin alloys," *Transactions of Metals Society AIME*, vol. 230, pp. 1361–1367, 1964.
- [126] J. M. Eldridge, E. Miller, and K. L. Komarek, *Transactions of the Metals Society AIME*, vol. 239, pp. 775–781, 1967.
- [127] R. A. Sharma, "Thermodynamic properties of liquid Mg+Pb and Mg+Sn Alloys by e.m.f. measurements," *The Journal of Chemical Thermodynamics*, vol. 2, no. 3, pp. 373–389, 1970.
- [128] A. K. Nayak and W. Oelsen, "Determination of the heats of formation of the solid and liquid Mg-Sn alloys at 20° and 800°C respectively and the heat content of the alloys at 800°C," *Transactions of the Indian Institute of Metals*, vol. 24, no. 2, pp. 66–73, 1971.
- [129] M. Morishita, K. Koyama, S. Shikata, and M. Kusumoto, "Standard gibbs energy of formation of Mg₄₈Zn₅₂ determined by solution calorimetry and measurement of heat Capacity from near absolute zero kelvin," *Metallurgical and Materials Transactions B*, vol. 35, no. 5, pp. 891–895, 2004.
- [130] M. Morishita, H. Yamamoto, S. Shikada, M. Kusumoto, and Y. Matsumoto, "Thermodynamics of the formation of magnesium-zinc intermetallic compounds in the temperature range from absolute zero to high temperature," *Acta Materialia*, vol. 54, no. 11, pp. 3151–3159, 2006.
- [131] M. Morishita, K. Koyama, S. Shikada, and M. Kusumoto, "Calorimetric study of Mg₂Zn₃," *Zeitschrift für Metallkunde*, vol. 96, no. 1, pp. 32–37, 2005.
- [132] M. Morishita and K. Koyama, "Calorimetric study of MgZn₂ and Mg₂Zn₁₁," *Zeitschrift für Metallkunde*, vol. 94, no. 9, pp. 967–971, 2003.
- [133] D. A. Petrov, M. S. Mirgalovskaya, I. A. Strelnikova, and E. M. Komova, *The Constitution Diagram For the Magnesium-Manganese System*, vol. 1, Institute of Materials Science, Academy of Sciences of the Ukrainian SSR, 1958.
- [134] A. A. Nayeb-Hashemi and J. B. Clark, "The Mg-Mn (Magnesium-Manganese) system," *Bulletin of Alloy Phase Diagrams*, vol. 6, no. 2, pp. 160–164, 1985.
- [135] J. Gröbner, D. Mirkovic, M. Ohno, and R. Schmid-Fetzer, "Experimental investigation and thermodynamic calculation of binary Mg-Mn Phase equilibria," *Journal of Phase Equilibria and Diffusion*, vol. 26, no. 3, pp. 234–239, 2005.
- [136] Y.-B. Kang, A. D. Pelton, P. Chartrand, P. Spencer, and C. D. Fuerst, "Thermodynamic database development of the Mg-Ce-Mn-Y system for Mg alloy design," *Metallurgical and Materials Transactions A*, vol. 38, no. 6, pp. 1231–1243, 2007.
- [137] P. Villars and K. Cenzual, *Pearson's Crystal Data—Crystal Structure Database for Inorganic Compounds (on CD-ROM)*, ASM International, Materials Park, Ohio, USA, 2009.
- [138] J. A. Brown and J. N. Pratt, "The thermodynamic properties of solid Al-Mg alloys," *Metallurgical Transactions*, vol. 1, no. 10, pp. 2743–2750, 1970.
- [139] B. Predel and K. Hulse, "Thermodynamic properties of aluminum-magnesium alloys," *Zeitschrift für Metallkunde*, vol. 69, no. 10, pp. 661–666, 1978.
- [140] H. Okamoto, "Supplemental literature review of binary phase diagrams: Cs-In, Cs-K, Cs-Rb, Eu-In, Ho-Mn, K-Rb, Li-Mg, Mg-Nd, Mg-Zn, Mn-Sm, O-Sb, and Si-Sr," *Journal of Phase Equilibria and Diffusion*, vol. 34, pp. 251–263, 2013.
- [141] P. Villars and L. Calvert, "K. Pearson's Crystal Data, Crystal Structure Database for Inorganic Compounds, CD-ROM software version 1.3," OH, 2009.
- [142] A. Schneider, H. Klotz, J. Stendel, and G. Strauss, "Thermochemistry of alloys," *Pure and Applied Chemistry*, vol. 2, pp. 13–16, 1961.
- [143] A. Berche, C. Drescher, J. Rogez, M.-C. Record, S. Brühne, and W. Assmus, "Thermodynamic measurements in the Mg-Zn system," *Journal of Alloys and Compounds*, vol. 503, no. 1, pp. 44–49, 2010.
- [144] W. Biltz and G. Hohorst, "Contributions to the systematic study of affinity. XV. The heats of formation of the compounds of metallic magnesium with metallic zinc, cadmium, aluminium and calcium," *Zeitschrift für Anorganische und Allgemeine Chemie*, vol. 121, pp. 1–24, 1922.
- [145] N. Baar, "On the alloys of molybdenum with nickel, manganese with thallium, and calcium with magnesium, thallium, lead, copper, and silver," *Zeitschrift für Anorganische und Allgemeine Chemie*, vol. 70, pp. 362–366, 1911.
- [146] M. W. Chase, "Heat of transition of the elements," *Bulletin of Alloy Phase Diagrams*, vol. 4, pp. 123–124, 1983.
- [147] R. Paris, "Contribution on the ternary alloys," *Ministère de L'Air: Publications Scientifiques et Techniques du Ministère de L'Air*, vol. 45, pp. 39–41, 1934.
- [148] J. L. Haughton, "Alloys of magnesium. Part 6—the construction of the magnesium-rich alloys of magnesium and calcium," *Journal of Institute of Metals*, vol. 61, pp. 241–246, 1937.
- [149] H. Vosskübler, "The Phase diagram of magnesium-rich Mg-Ca alloys," *Zeitschrift für Metallkunde*, vol. 29, pp. 236–237, 1937.
- [150] W. Klemm and F. Dinkelacker, "On the behavior of magnesium with calcium, strontium, and barium," *Zeitschrift für Anorganische und Allgemeine Chemie*, vol. 255, pp. 2–12, 1947.
- [151] J. F. Smith and R. L. Smythe, "Vapor pressure measurements over calcium, magnesium and their alloys and the thermodynamics of formation of CaMg₂," *Acta Metallurgica*, vol. 7, no. 4, pp. 261–267, 1959.

- [152] P. Chiotti, R. W. Curtis, and P. F. Woerner, "Metal hydride reactions. II. Reaction of hydrogen with CaMg₂ and CaCu₂ and thermodynamic properties of the compounds," *Journal of The Less-Common Metals*, vol. 7, no. 2, pp. 120–126, 1964.
- [153] J. E. Davison and J. F. Smith, "Enthalpy of formation of CaMg₂," *Transactions of the Metallurgical Society of AIME*, vol. 242, pp. 2045–2049, 1968.
- [154] G. J. Gartner, *Application of an Adiabatic Calorimeter to the Determination of the Heats of Fusion And Heats of Formation of Several Metallic Compounds*, Iowa State University, Ames, Iowa, USA, 1965.
- [155] I. N. Pyagai and A. V. Vakhobov, "Heats of formation of intermetallic compounds in the systems magnesium-calcium (strontium, barium)," *Zhurnal Fizicheskoi Khimii*, vol. 64, pp. 2788–2789, 1990.
- [156] Y. Zhong, K. Ozturk, J. O. Sofo, and Z.-K. Liu, "Contribution of first-principles energetics to the Ca-Mg thermodynamic modeling," *Journal of Alloys and Compounds*, vol. 420, no. 1-2, pp. 98–106, 2006.
- [157] Z. Yang, J. Du, C. Hu, R. Melnik et al., "First principles studies on the structural, elastic, electronic properties and heats of formation of Mg-AE (AE = Ca, Sr, Ba) intermetallics," *Intermetallics*, vol. 32, pp. 156–161, 2013.
- [158] Y. Zhong, J. O. Sofo, A. A. Luo, and Z. Liu, "Thermodynamics modeling of the Mg-Sr and Ca-Mg-Sr systems," *Journal of Alloys and Compounds*, vol. 421, pp. 172–178, 2006.
- [159] H. Nowotny, E. Wormnes, and E. Mohrnhelm, "Investigation on the Al-Ca, Mg-Ca, and Mg-Zr systems," *Zeitschrift für Metallkunde*, vol. 32, pp. 39–42, 1940.
- [160] E. C. Burke, "Solid solubility of calcium in magnesium," *Journal of Metals Transactions of AIME*, vol. 203, pp. 285–286, 1955.
- [161] E. F. W. Bulian, "Solubility of calcium in magnesium," *Metallforschung*, vol. 1, p. 70, 1946.
- [162] X. Tao, Y. Ouyang, H. Liu et al., "Phase stability of magnesium-rare earth binary systems from first-principles calculations," *Journal of Alloys and Compounds*, vol. 509, no. 24, pp. 6899–6907, 2011.
- [163] K. H. J. Buschow, "Magnetic properties of MgCo₂, MgNi₂ and Mg₂Ni," *Solid State Communications*, vol. 17, no. 7, pp. 891–893, 1975.
- [164] F. Laves and H. Witte, "X-ray determination of structure of MgNi₂," *Metallwirtschaft, Metallwissenschaft, Metalltechnik*, vol. 14, p. 1002, 1935.
- [165] H. Okamoto, "Ce-Mg (Cerium-Magnesium)," *Journal of Phase Equilibria and Diffusion*, vol. 32, pp. 265–266, 2011.
- [166] R. Agarwal, J. J. Lee, H. L. Lukas, and F. Sommer, "Calorimetric measurements and thermodynamic optimization of the Ca-Mg system," *Zeitschrift für Metallkunde*, vol. 86, no. 2, pp. 103–108, 1995.
- [167] B. P. Burylev, "Thermodynamic properties of calcium based alloys," in *Termodin Termokhin Konstanty Izd. Nauka*, K. V. Astakhov, Ed., pp. 32–39, USSR, Moscow, Russia, 1970.
- [168] W. Biltz and H. Pieper, "Contributions to the systematic affinity principle. XXVII. The heats of formation of intermetallic compounds. IV. Cerium alloys," *Zeitschrift Für Anorganische und Allgemeine Chemie.*, vol. 134, pp. 13–24, 1924.
- [169] J. Pahlman and J. Smith, "Thermodynamics of formation of compounds in the Ce-Mg, Nd-Mg, Gd-Mg, Dy-Mg, Er-Mg, and Lu-Mg binary systems in the temperature range 650 to 930K," *Metallurgical and Materials Transactions B*, vol. 3, pp. 2423–2432, 1972.
- [170] K. Nagarajan and F. Sommer, "Calorimetric investigations of CeMg liquid alloys," *Journal of The Less-Common Metals*, vol. 142, pp. 319–328, 1988.
- [171] Y. B. Kang, L. Jin, P. Chartrand, A. E. Gheribi, K. Bai, and P. Wu, "Thermodynamic evaluations and optimizations of binary Mg-light Rare Earth (La, Ce, Pr, Nd, Sm) systems," *Calphad*, vol. 38, pp. 100–116, 2012.
- [172] F. Sommer, J. J. Lee, and B. Predel, "Temperaturabhängigkeit der Mischungsenthalpien flüssiger Magnesium-Blei und Magnesium-Zinn Legierungen," *MetaUkd*, vol. 71, pp. 818–821, 1980.
- [173] A. K. Nayak and W. Oelsen, "Determination of the heats of formation of the solid and liquid Mg-Sn alloys at 20° and 800°C respectively and the heat content of the alloys at 800°C," *Transactions of the Indian Institute of Metals*, vol. 24, no. 2, pp. 66–73, 1971.
- [174] P. Beardmore, B. W. Howlett, Lichter, B. D et al., "Thermodynamic properties of compounds of magnesium and group IVB elements," *Transactions of Metals Society AIME*, vol. 236, pp. 102–108, 1966.
- [175] A. Borsese, G. Borzone, R. Ferro, and R. Capelli, "Heat of formation of magnesium-tin alloys," *Zeitschrift für Metallkunde*, vol. 66, no. 4, pp. 226–227, 1975.
- [176] B. Dobovisek and A. Paulin, "Influence of the structure of intermetallic compounds on thermodynamic properties of metallic systems," *Rudarsko Metals of Zbornik*, vol. 1, pp. 37–49, 1966.
- [177] A. A. Nayeb-Hashemi and J. B. Clark, "The Ca-Mg (calcium-magnesium) system," *Bulletin of Alloy Phase Diagrams*, vol. 8, no. 1, pp. 58–65, 1987.
- [178] A. A. Nayeb-Hashemi and J. B. Clark, "The Mg-Sr (Magnesium-Strontium) system," *Bulletin of Alloy Phase Diagrams*, vol. 7, no. 2, pp. 149–156, 1986.
- [179] H. Vosskuehler, "The structure of the magnesium-rich alloys of magnesium and strontium," *Metallwirtschaft*, vol. 18, pp. 377–378, 1939.
- [180] J. W. Brown, *The strontium-magnesium phase system [Ph.D. thesis]*, Syracuse University, Syracuse, NY, USA, 1973.
- [181] J. P. Ray, *The strontium-magnesium equilibrium diagram [Ph.D. thesis]*, Syracuse University, Syracuse, NY, USA, 1947.
- [182] H. Vosskuhler, "The structure of the magnesium-rich magnesium-strontium alloys," *Metallwirtsch, Metallwiss, Metalltech*, vol. 18, pp. 377–378, 1939.
- [183] E. D. Gibson and O. N. Carlson, "The yttrium-magnesium alloy system," *Transactions of the American Society For Metals*, vol. 52, pp. 1084–1096, 1960.
- [184] D. Mizer and J. B. Clark, "Magnesium-rich region of the magnesium-yttrium phase diagram," *Transactions of the American Institute of Mining, Metallurgical and Petroleum Engineers*, vol. 221, pp. 207–208, 1961.
- [185] Q. Ran, H. L. Lukas, G. Effenberg, and G. Petzow, "Thermodynamic optimization of the Mg-Y system," *Calphad*, vol. 12, no. 4, pp. 375–381, 1988.
- [186] O. B. Fabrichnaya, H. L. Lukas, G. Effenberg, and F. Aldinger, "Thermodynamic optimization in the Mg-Y system," *Intermetallics*, vol. 11, no. 11-12, pp. 1183–1188, 2003.
- [187] F. G. Meng, J. Wang, H. S. Liu, L. B. Liu, and Z. P. Jin, "Experimental investigation and thermodynamic calculation of phase relations in the Mg-Nd-Y ternary system," *Materials Science and Engineering A*, vol. 454-455, pp. 266–273, 2007.

- [188] C. Guo, Z. Du, and C. Li, "A thermodynamic description of the Gd-Mg-Y system," *Calphad*, vol. 31, no. 1, pp. 75–88, 2007.
- [189] Y.-B. Kang, A. D. Pelton, P. Chartrand, P. Spencer, and C. D. Fuerst, "Critical evaluation and thermodynamic optimization of the binary systems in the Mg-Ce-Mn-Y system," *Journal of Phase Equilibria and Diffusion*, vol. 28, no. 4, pp. 342–354, 2007.
- [190] H. Okamoto, "Mg-Y (magnesium-yttrium)," *Journal of Phase Equilibria and Diffusion*, vol. 31, no. 2, p. 199, 2010.
- [191] G. Voss, "Alloys of nickel with tin, lead, thallium, bismuth, chromium, magnesium, zinc, and cadmium," *Zeitschrift für Anorganische Chemie*, vol. 57, pp. 34–71, 1908.
- [192] J. L. Haughton and R. J. M. Payne, "Alloys of magnesium research. I. The constitution of the magnesium-rich alloys of magnesium and nickel," *Journal of the Institute of Metals*, vol. 54, pp. 275–284, 1934.
- [193] P. Bagnoud and P. Feschotte, "Binary systems of magnesium-copper and magnesium-nickel, especially the nonstoichiometry of the $MgCu_2$ and $MgNi_2$ laves phases," *Zeitschrift für Metallkunde*, vol. 69, no. 2, pp. 114–120, 1978.
- [194] P. D. Merica and R. G. Waltenberg, "Malleability and metallography of nickel," Tech. Paper National Bureau of Standards (U.S) 19, 1925.
- [195] J. S. Wollam and W. E. Wallace, "Magnetic susceptibility, heat capacity and third-law entropy of $MgNi_2$," *Journal of Physics and Chemistry of Solids*, vol. 13, no. 3-4, pp. 212–220, 1960.
- [196] K. H. Lieser and H. Witte, "The ternary systems Mg-Cu-Zn, Mg-Ni-Zn, Mg-Cu-Ni," *Zeitschrift für Metallkunde*, vol. 43, pp. 396–401, 1952.
- [197] K. Schubert and K. Anderko, "Crystal structure of $NiMg_2$, $CuMg_2$ and $AuMg_3$," *Zeitschrift für Metallkunde*, vol. 42, pp. 321–324, 1951.
- [198] A. A. Nayeb-Hashemi and J. B. Clark, "The Mg-Ni (Magnesium-Nickel) system," *Bulletin of Alloy Phase Diagrams*, vol. 6, no. 3, pp. 238–244, 1985.
- [199] M. H. G. Jacobs and P. J. Spencer, "A critical thermodynamic evaluation of the system MG-NI," *Calphad*, vol. 22, no. 4, pp. 513–525, 1998.
- [200] W. Xiong, Y. Du, W.-W. Zhang, W.-H. Sun, X.-G. Lu, and F.-S. Pan, "Thermodynamic reassessment of the Cu-Mg-Ni system with brief comments on the thermodynamic modeling of the sub-systems," *Calphad*, vol. 32, no. 4, pp. 675–685, 2008.
- [201] D. H. Wood and E. M. Cramer, "Phase relations in the magnesium-rich portion of the cerium-magnesium system," *Journal of The Less-Common Metals*, vol. 9, no. 5, pp. 321–337, 1965.
- [202] Q. Johnson and G. Smith, "The crystal structure of Ce_5Mg_{42} ," *Acta Crystallographica*, vol. 22, pp. 360–365, 1967.
- [203] A. A. Nayeb-Hashemi and J. B. Clark, "The Ce-Mg (Cerium-Magnesium) system," *Journal of Phase Equilibria*, vol. 9, no. 2, pp. 162–172, 1988.
- [204] A. Saccone, D. Macciò, S. Delfino, F. H. Hayes, and R. Ferro, "Mg-Ce alloys. Experimental investigation by smith thermal analysis," *Journal of Thermal Analysis and Calorimetry*, vol. 66, no. 1, pp. 47–57, 2001.
- [205] X. Zhang, D. Kevorkov, and M. Pekguleryuz, "Stoichiometry study on the binary compounds in the Mg-Ce system-Part I," *Journal of Alloys and Compounds*, vol. 475, no. 1-2, pp. 361–367, 2009.
- [206] H. Okamoto and T. B. Massalski, "Thermodynamically improbable phase diagrams," *Journal of Phase Equilibria*, vol. 12, no. 2, pp. 148–168, 1991.
- [207] G. Cacciamani, G. Borzone, and R. Ferro, "System Ce-Mg," in *COST 507-Thermochemical Databases for Light Metal Alloys*, I. Ansara, A. T. Dinsdale, and M. H. Rand, Eds., vol. 2, pp. 137–140, European Commission, 1998.
- [208] H. Zhang, Y. Wang, S. Shang, L.-Q. Chen, and Z.-K. Liu, "Thermodynamic modeling of Mg-Ca-Ce system by combining first-principles and CALPHAD method," *Journal of Alloys and Compounds*, vol. 463, no. 1-2, pp. 294–301, 2008.
- [209] R. Joseph and K. A. Gschneidner, "Solid solubility of magnesium in some lanthanide metals," *Transactions of AIME*, vol. 233, pp. 2063–2069, 1965.
- [210] A. Iandelli and A. Palenzona, "Atomic size of rare earths in intermetallic compounds. MX compounds of CsCl type," *Journal of the Less-Common Metals*, vol. 9, no. 1, pp. 1–6, 1965.
- [211] S. Delfino, A. Saccone, and R. Ferro, "Phase relationships in the neodymium-magnesium alloy system," *Metallurgical Transactions A*, vol. 21, no. 8, pp. 2109–2114, 1990.
- [212] A. A. Nayeb-Hashemi and J. B. Clark, "The Mg-Nd system (Magnesium-Neodymium)," *Bulletin of Alloy Phase Diagrams*, vol. 9, no. 5, pp. 618–623, 1988.
- [213] S. Gorsse, C. R. Hutchinson, B. Chevalier, and J.-F. Nie, "A thermodynamic assessment of the Mg-Nd binary system using random solution and associate models for the liquid phase," *Journal of Alloys and Compounds*, vol. 392, no. 1-2, pp. 253–262, 2005.
- [214] J. R. Ogren, N. J. Magnani, and J. F. Smith, "Thermodynamics of formation of binary rare earth-magnesium phases with cesium chloride-type structures," *Transactions of the Metallurgical Society of AIME*, vol. 239, pp. 766–771, 1967.
- [215] C. Guo and Z. Du, "Thermodynamic assessment of the Mg-Nd system," *Zeitschrift für Metallkunde*, vol. 97, pp. 130–135, 2006.
- [216] F.-G. Meng, H.-S. Liu, L.-B. Liu, and Z.-P. Jin, "Thermodynamic optimization of Mg-Nd system," *Transactions of Nonferrous Metals Society of China (English Edition)*, vol. 17, no. 1, pp. 77–81, 2007.
- [217] H. Y. Qi, G. X. Huang, H. Bo, G. L. Xu, L. B. Liu, and Z. P. Jin, "Thermodynamic description of the Mg-Nd-Zn ternary system," *Journal of Alloys and Compounds*, vol. 509, no. 7, pp. 3274–3281, 2011.
- [218] M. O. Boudouard, "Les Alliages de Duirre et de Magnesium (The Binary Alloys of Magnesium)," *Bulletin de la Société d'Encouragement pour l'Industrie Nationale*, vol. 102, p. 200, 1903.
- [219] R. Sahmen, "Alloys of copper with cobalt, iron, manganese and magnesium," *Zeitschrift für Anorganische und Allgemeine Chemie*, vol. 57, pp. 1–33, 1908.
- [220] G. G. Urazov, "Alloys of copper and magnesium," *Zhurnal Russkogo Fiziko-Khimicheskogo Obschestva*, vol. 39, pp. 1556–1581, 1907.
- [221] W. R. D. Jones, "Copper-magnesium alloys. IV. Equilibrium diagram," *Journal of the Institute of Metals*, no. 574, p. 25, 1931.
- [222] G. Grime and W. Morris-Jones, "An x-ray investigation of the copper-magnesium alloys," *Philosophical Magazine Series*, vol. 7, pp. 1113–1134, 1929.
- [223] V. G. Sederman, "Cu₂Mg phase in the copper-magnesium system," *Philosophical Magazine Series*, vol. 18, pp. 343–352, 1934.
- [224] M. Hansen, "Note on the magnesium-rich magnesium copper alloys," *Journal of the Institute of Metals*, no. 428, p. 8, 1927.
- [225] N. I. Stepanov and I. I. Kornilov, "Solubility of copper in magnesium in the solid state," *Akademii Nauk SSSR*, vol. 7, pp. 89–98, 1935.

- [226] A. A. Nayeb-Hashemi and J. B. Clark, "The Cu-Mg (Copper-Magnesium) system," *Bulletin of Alloy Phase Diagrams*, vol. 5, no. 1, pp. 36–43, 1984.
- [227] C. A. Coughanowr, I. Ansara, R. Luoma, M. Hamalainen, and H. L. Lukas, "Assessment of the copper-magnesium system," *Zeitschrift für Metallkunde*, vol. 82, pp. 574–581, 1991.
- [228] Y. Zuo and Y. A. Chang, "Thermodynamic calculation of magnesium-copper phase diagram," *Zeitschrift für Metallkunde*, vol. 84, pp. 662–667, 1993.
- [229] G. Grube, "On the alloys of magnesium with tin and thallium," *Zeitschrift Fur Anorganische Chemie*, vol. 46, pp. 76–84, 1905.
- [230] N. S. Kurnakow and N. J. Stepanow, "On the alloys of magnesium with tin and thallium," *Zeitschrift Fur Anorganische Chemie*, vol. 46, pp. 177–192, 1905.
- [231] W. Hume-Rothery, "The system magnesium-tin and the compound Mg_4Sn_2 ," *Journal of the Institute of Metals*, vol. 35, pp. 336–347, 1926.
- [232] G. V. Raynor, "The constitution of the magnesium-rich alloys in the systems magnesium-lead, magnesium-tin, magnesium-germanium, and magnesium-silicon," *Journal of the Institute of Metals*, vol. 6, pp. 403–426, 1940.
- [233] A. K. Nayak and W. Oelsen, "Thermal analysis of Mg-Sn alloys by calorimetric measurements for determination of the liquidus curve part I," *Transactions on Indian Institute of Metals*, pp. 15–20, 1968.
- [234] A. K. Nayak and W. Oelsen, "Quatitative thermal analysis of magnesium-tin alloys by calorimetric measurement for the determination of solidus and liquidus curves," *Transactions on Indian Institute of Metals*, pp. 53–58, 1969.
- [235] A. Steiner, E. Miller, and K. L. Komarek, "Magnesium-tin phase diagram and thermodynamic properties of liquid magnesium-tin alloys," *Transactions of Metals Society AIME*, vol. 230, pp. 1361–1367, 1964.
- [236] P. Beardmore, B. W. Howlett, B. D. Lichter, and M. B. Bever, "Thermodynamic properties of compounds of magnesium and group IVB elements," *Transactions of Metals Society AIME*, vol. 236, pp. 102–108, 1966.
- [237] C. T. Heycock and F. H. Neville, "XXVII.—The molecular weights of metals when in solution," *Journal of the Chemical Society, Transactions*, vol. 57, pp. 376–393, 1890.
- [238] J. Ellmer, K. E. Hall, R. W. Kamphefner, J. T. Pfeifer, V. Stamboni, and C. D. Graham Jr., "On the liquidus in tin-rich Sn–Mg alloys," *Metallurgical Transactions*, vol. 4, no. 3, pp. 889–891, 1973.
- [239] A. A. Nayeb-Hashemi and J. B. Clark, *Phase Diagram of Binary Magnesium Alloys*, ASM International, Materials Park, Ohio, USA, 1988.
- [240] G. Grube and H. Vosskuhler, "Electrical conductivity and binary alloys phase diagram," *Zeitschrift Electrochemistry*, vol. 40, pp. 566–570, 1934.
- [241] H. Vosskuhler, "Solubility of tin in magnesium," *Metallwirtschaft*, vol. 20, pp. 805–808, 1941.
- [242] N. J. Stepanow, "Über die elektrische Leitfähigkeit der Metallegierungen," *Zeitschrift fur Anorganische Chemie*, vol. 78, pp. 1–32, 1912.
- [243] J. A. Gann, "Treatment and structure of magnesium alloys," *Transactions of the Metals Society AIME*, vol. 83, pp. 309–332, 1929.
- [244] H. Nishinura and K. Tanaka, "Age hardening of magnesium-rich magnesium-aluminum-tin alloys," *Transactions of the Institution of Mining and Metallurgy Alumni Association*, vol. 10, pp. 343–350, 1940.
- [245] J. M. Eldridge, E. Miller, and K. L. Komarek, "Thermodynamic properties of liquid magnesium-silicon alloys, discussion of the Mg-Group IVB systems," *Transactions of the Metals Society AIME*, vol. 239, pp. 775–781, 1967.
- [246] H. J. Caulfield and D. E. Hudson, "Sublimation in the intermetallic series Mg_2Si , Mg_2Ge , Mg_2Sn and Mg_2Pb ," *Solid State Communications*, vol. 4, no. 6, pp. 299–301, 1966.
- [247] A. K. Nayak and W. Oelsen, "Thermodynamic analysis of magnesium-tin alloys," *Transaction of the Indian Institute of Metals*, vol. 24, no. 2, pp. 22–28, 1971.
- [248] V. N. Eremenko and G. M. Lukashenko, "Thermodynamic properties of Mg-Pb system," *Ukrainskii Khimicheskii Zhurnal*, vol. 29, pp. 896–900, 1963.
- [249] O. Kubaschewski and A. Walter-Stuttgart, "Results of investigations of alloys by high-temperature calorimetry?" *Zeitschrift Für Elektrochemie*, vol. 45, pp. 732–740, 1939.
- [250] W. Biltz and W. Holverscheit, "Systematic affinity principle XLVII, the relation of mercury to a few metals," *Zeitschrift fur Anorganische Chemie*, vol. 176, p. 23, 1928.
- [251] S. Ashtakala and L. M. Pidgeon, "Determination of the activities of magnesium in liquid magnesium-tin alloys by vapor pressure measurements," *Canadian Journal of Chemistry*, vol. 40, pp. 718–728, 1962.
- [252] F. J. Jelinek, W. D. Shickell, and B. C. Gerstein, "Thermal study of group II-IV semiconductors, II. Heat capacity of Mg_2Sn in the range 5–300 K," *Journal of Physics and Chemistry of Solids*, vol. 28, no. 2, pp. 267–270, 1967.
- [253] H. Y. Chen, N. Savvides, T. Dasgupta, C. Stiewe, and E. Mueller, "Electronic and thermal transport properties of Mg_2Sn crystals containing finely dispersed eutectic structures," *Physica Status Solidi A*, vol. 207, no. 11, pp. 2523–2531, 2010.
- [254] J. J. Egan, "Thermodynamics of liquid magnesium alloys using CaF_2 solid electrolytes," *Journal of Nuclear Materials*, vol. 51, no. 1, pp. 30–35, 1974.
- [255] C. A. Eckert, J. S. Smith, R. B. Irwin, and K. R. Cox, "A chemical theory for the thermodynamics of highly-solvated liquid metal mixtures," *AICHE Journal*, vol. 28, no. 2, pp. 325–332, 1982.
- [256] L. M. Pavlova and K. B. Poyarkov, "Nature of the dissociation of Mg stannide and thermodynamic properties of Mg-Sn melts," *Zhurnal Fizicheskoi Khimii*, vol. 56, pp. 295–299, 1982.
- [257] I.-H. Jung and J. Kim, "Thermodynamic modeling of the Mg-Ge-Si, Mg-Ge-Sn, Mg-Pb-Si and Mg-Pb-Sn systems," *Journal of Alloys and Compounds*, vol. 494, no. 1-2, pp. 137–147, 2010.
- [258] F. G. Meng, J. Wang, L. B. Liu, and Z. P. Jin, "Thermodynamic modeling of the Mg-Sn-Zn ternary system," *Journal of Alloys and Compounds*, vol. 508, no. 2, pp. 570–581, 2010.
- [259] Y.-B. Kang and A. D. Pelton, "Modeling short-range ordering in liquids: the Mg-Al-Sn system," *Calphad*, vol. 34, no. 2, pp. 180–188, 2010.



Hindawi

Submit your manuscripts at
<http://www.hindawi.com>

