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Review Article

Essential Magnesium Alloys Binary Phase Diagrams and Their Thermochemical Data

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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

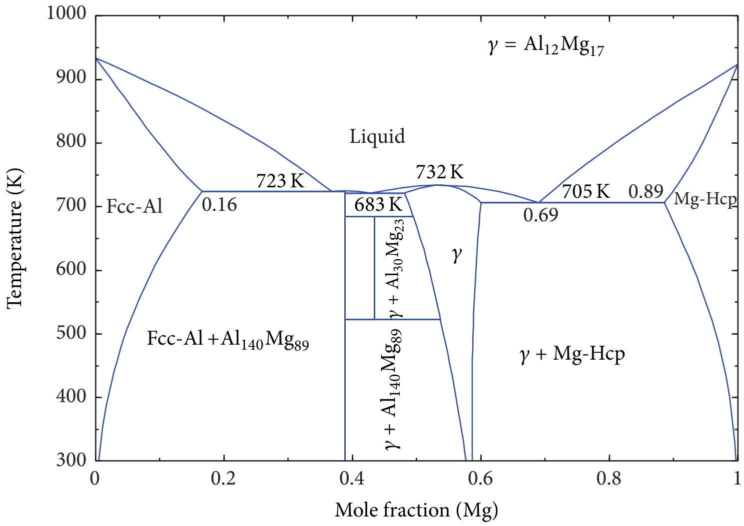


Figure 1: Mg-Al phase diagram.

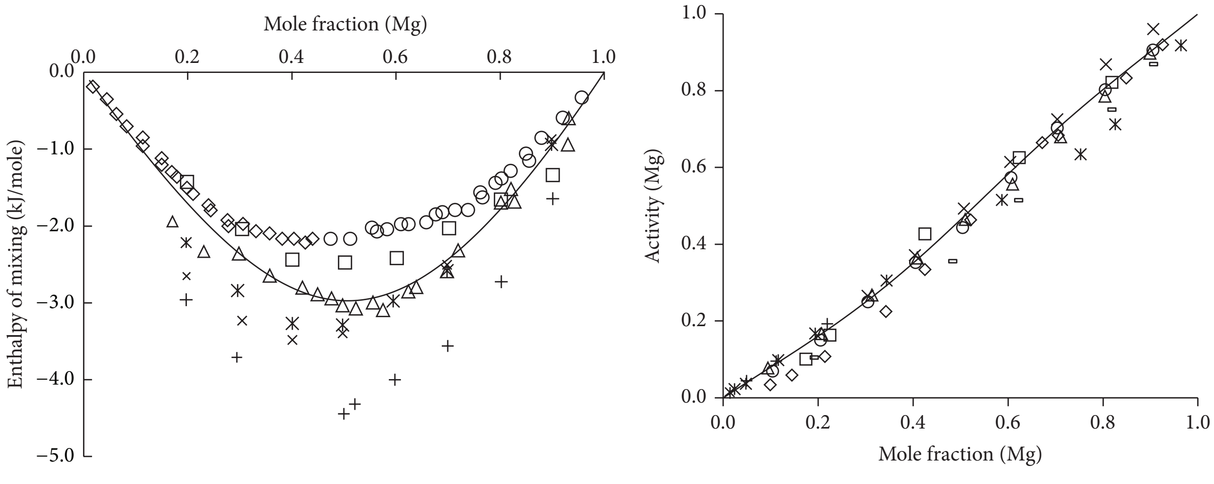
hexagonal crystal structure, γ-solid solution with the αMn structure type, R phase with rhombohedral structure at 42 at.% Mg, Al solid solution with a maximum solubility of 18.9 at.% Mg at 723 K, and Mg solid solution with a maximum solubility of 11.8 at.% Al at 710 K. In view of the relative atomic 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 $Al_{30}Mg_{23}(\varepsilon)$ and $Al_{12}Mg_{17}(\gamma)$ 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 Mg_2Zn_{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



(a) (b)

FIGURE 2: Calculated (a) enthalpy of mixing of liquid Mg-Al at 1073 K: ○: [10] at 948 K, ◊: [10] at 973 K, △: [11] at 1073 K, □: [12] at 1073 K, ×: [13] at 1073 K, +: [14] at 1073 K, ∗: [15] at 973 K, □: [16] at 1002 K, ○: [16] at 1008 K. (b) Activity of liquid Mg 1073 K: ○: [14] at 1073 K, △ [17] at 923 K, ×: [18] at 923 K, □: [19] at 1073 K, ◊: [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*	
$Al_{30}Mg_{23}$ (ε)	$Al_{30}Mg_{23}$	148	R $\bar{3}$ h	1.2825	1.2825	2.1748	[137]
$Al_{140}Mg_{89}$ (β)	$Al_{45}Mg_{28}$	227	F D $\bar{3}$ m	2.8300	2.8300	2.8300	[137]
$Al_{12}Mg_{17}$ (γ)	$Al_{12}Mg_{17}$	217	I 4 $\bar{3}$ 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, ${}^o\Delta H$ in J/mole·atom and ${}^o\Delta S$ in J/mole·atom·K
Liquid	$Z^{Mg}{}_{MgAl} = 6,\ Z^{Al}{}_{AlMg} = 4$ $\Delta g^{0}_{MgAl} = -4\,495.5 + 2.85T;\ \Delta g^{10}_{MgAl} = 436.8 + 0.42T;$ $\Delta g^{01}_{MgAl} = 732.5$
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	${}^0L^{\text{Al-fcc}} = 4973.1 - 3.5T;\ {}^1L^{\text{Al-fcc}} = 900.4 + 0.42T;$ ${}^2L^{\text{Al-fcc}} = 950.4$
$Al_{30}Mg_{23}$ (ε) $Al_{140}Mg_{89}$ (β)	${}^o\Delta H^{Al_{30}Mg_{23}}_{AlMg} = -991.8;\ {}^o\Delta S^{Al_{30}Mg_{23}}_{Al,Mg} = 3.27$ ${}^o\Delta H^{Al_{140}Mg_{89}}_{AlMg} = -1\ 075.0;\ {}^o\Delta S^{Al_{140}Mg_{89}}_{Al,Mg} = 2.95$
$Al_{12}Mg_{17}$ (γ) $(Mg)_5(Al, Mg)_{12}(Al, Mg)_{12}$	${}^0L^{\gamma}_{Mg:Al:Al,Mg} = 3901.7 - 0.50T;\ {}^0L^{\gamma}_{Mg:Mg:Al,Mg} = 3901.7 - 0.50T$

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 $Mg_7Zn_3 \leftrightarrows \alpha\text{-Mg} + MgZn$ at near 598 K. After careful crystal structure study, Higashi et al. [113] replaced the compound Mg_7Zn_3 by $Mg_{51}Zn_{20}$ 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 $Mg_{51}Zn_{20}$,

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*)
$Al_{140}Mg_{89}$ (β)	−2.47		[138] Exp.
	−1.22		[139] Exp.
	−1.08	2.95	[104] Cal. (*Calphad*)
$Al_{12}Mg_{17}$ (γ)	−3.80		[138] Exp.
	−1.01		[139] Exp.
	−3.60		[101] Cal. (*F.P.*)

$Mg_{12}Zn_{13}$, Mg_2Zn_3, $MgZn_2$, and Mg_2Zn_{11} 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 $MgZn_2$ 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 $L + (\alpha\text{-Mn}) \rightarrow Mg$ 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

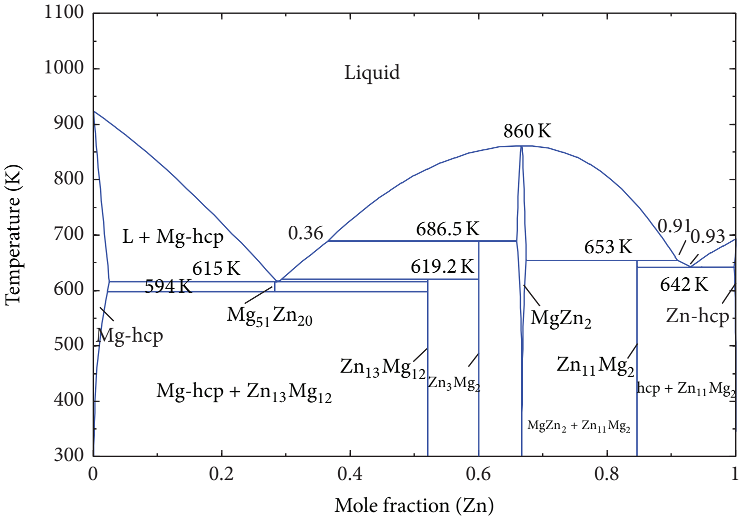


FIGURE 3: Mg-Zn phase diagram [22].

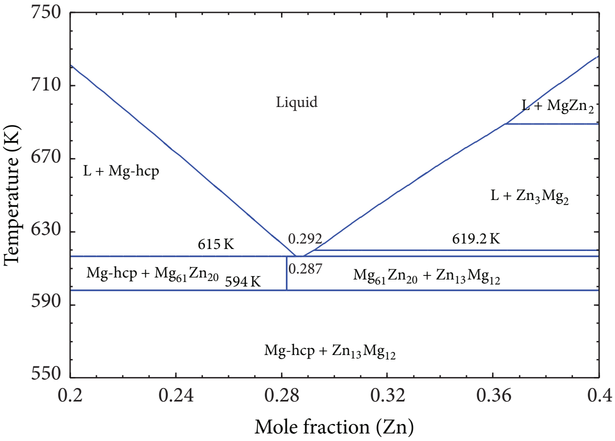
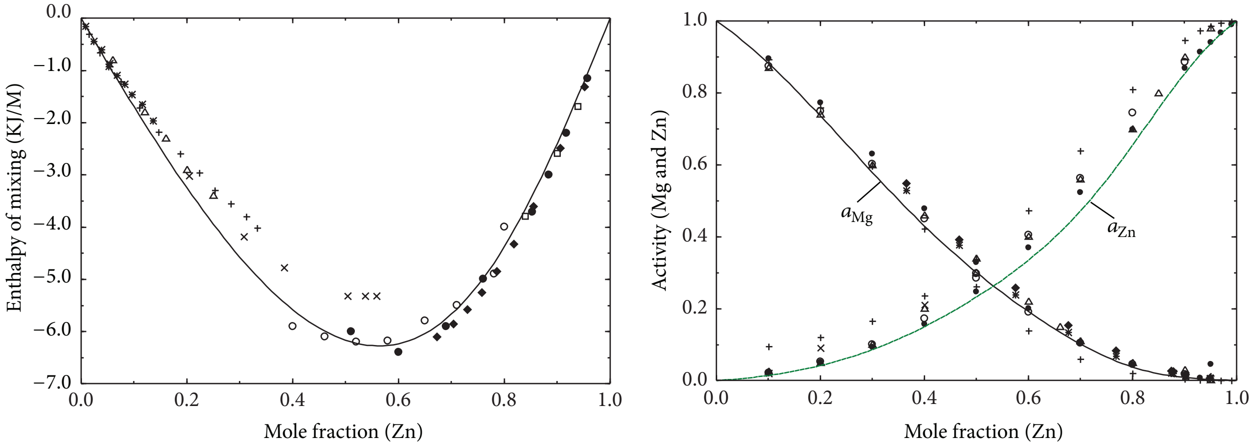


FIGURE 4: Magnified part of the Mg-Zn phase diagram [22].



(a)

(b)

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
				a	*b*	*c*	
$Mg_{51}Zn_{20}$		71	*Immm*	1.4025			[140, 141]
$Mg_{21}Zn_{25}$		167	$R\bar{3}ch$	2.5776		0.8762	[140, 141]
Mg_4Zn_7		12	*C12/m1*	2.5960	0.5240	1.4280	[140, 141]
$MgZn_2$	$MgZn_2$	164	$P6_3/mmc$	0.5220		0.8566	[140, 141]
Mg_2Zn_{11}	Mg_2Zn_{11}	200	$Pm\bar{3}$	0.8552			[140, 141]

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

Phase	Parameters Δg^0 and ${}^0L$ in J/mole, ${}^o\Delta H$ in J/mole·atom and ${}^o\Delta S$ in J/mole·atom·K
Liquid	$Z^{Mg}{}_{MgZn} = 6$, $Z^{Zn}{}_{ZnMg} = 4$; $\Delta g^{0}_{MgZn} = -8\,326.2 + 3.19T$; $\Delta g^{10}_{MgZn} = -4\,602.4 - 3.26T$; $\Delta g^{01}_{MgZn} = -62.8 - 3.76T$ (J/mole)
Mg-hcp (Mg in Zn-hcp, Zn in Mg-hcp)	${}^0L^{\text{Mg-hcp}} = -3502.5 + 5.64T$; ${}^1L^{\text{Mg-hcp}} = -6129.9 + 5.66T$;
Mg_2Zn_{11}	${}^o\Delta H^{Mg_2Zn_{11}}_{Mg,Zn} = -6\,601.2$; ${}^o\Delta S^{Mg_2Zn_{11}}_{Mg,Zn} = -1.82$
Mg_2Zn_3	${}^o\Delta \mathrm{H}^{Mg_2Zn_3}_{Mg,Zn} = -10\,989.9$; ${}^o\Delta S^{Mg_2Zn_3}_{Mg,Zn} = -1.3$
$Mg_{12}Zn_{13}$	${}^o\Delta H^{Mg_{12}Zn_{13}}_{Mg,Zn} = -10\,019.9$; ${}^o\Delta S^{Mg_{12}Zn_{13}}_{Mg,Zn} = -1.92$
$Mg_{51}Zn_{20}$	${}^o\Delta H^{Mg_{51}Zn_{20}}_{Mg,Zn} = -4\,718.3$; ${}^o\Delta S^{Mg_{51}Zn_{20}}_{Mg,Zn} = 0.16$
$MgZn_2$ (Mg%, Zn) $(Mg, Zn\%)_2$	${}^0G^{MgZn_2}_{Mg:Mg} = 43\,508.7$; ${}^0G^{MgZn_2}_{Mg:Zn} = -55\,979.2 + 380.9T - 74T\ln T + 0.00085T^2 - 3.333 \times 10^{-6}\,T^3$; ${}^o\Delta H^{MgZn_2} = -33815$; ${}^oS^{MgZn_2} = 115.005$; $c_p = 70 - 0.0017T + 2 \times 10^{-5}\,T^2$ ${}^0G^{MgZn_2}_{Zn:Mg} = 30\,012.9$; ${}^0G^{MgZn_2}_{Zn:Zn} = 20\,008.6$; ${}^0L^{MgZn_2}_{Mg,Zn:Mg} = {}^0L^{MgZn_2}_{Mg,Zn:Zn} = {}^0L^{MgZn_2}_{Mg:Mg,Zn} = {}^0L^{MgZn_2}_{Zn:Mg,Zn} = 1.0$

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)
$Mg_{12}Zn_{13}$	−10.5 ± 3.1		[142] Exp.
	−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_2Zn_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)
	−10.4 ± 1.5		[143] Exp.
Mg_2Zn_{11}	−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
				a	*b*	*c*	
(Mg)	Mg	194	$P6_3/mmc$	0.31997		0.51969	[134]
(αMn)	αMn	217	$I\bar{4}3m$	0.89219			[134]
(βMn)	βMn	213	$P4_132$	0.63152			[134]
(γMn)	Cu	225	$Fm\bar{3}m$	0.38624			[134]
(δMn)	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	$Z^{\mathrm{Mg}}_{\mathrm{MgMn}} = 4$, $Z^{\mathrm{Mg}}_{\mathrm{MnMg}} = 6$; $\Delta g^0_{\mathrm{MgMn}} = -22\,973.4 + 0.81T$; $\Delta g^{10}_{\mathrm{MgMn}} = -11\,995.2$;
Mg-hcp	${}^0L^{\mathrm{Mn\text{-}fcc}} = 4\,785.2 - 8.83T$; ${}^1L^{\mathrm{Mg\text{-}hcp}} = -3\,323.5$
Mn-fcc	${}^0L^{\mathrm{Mn\text{-}fcc}} = 83\,716.0$
δ-fcc	${}^0L^{\delta\text{-}\mathrm{Mn}} = 83\,716.0$

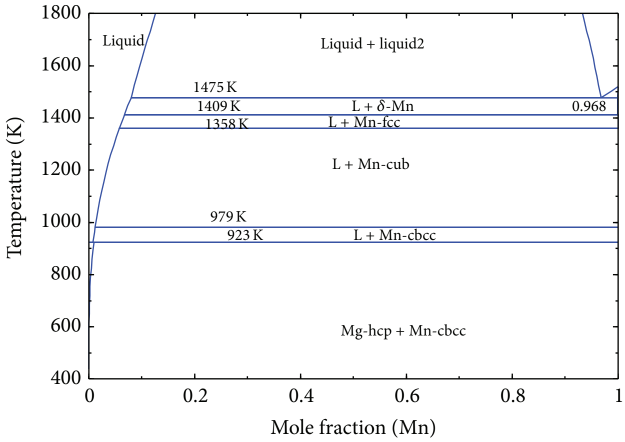


FIGURE 6: Mg-Mn phase diagram [32].

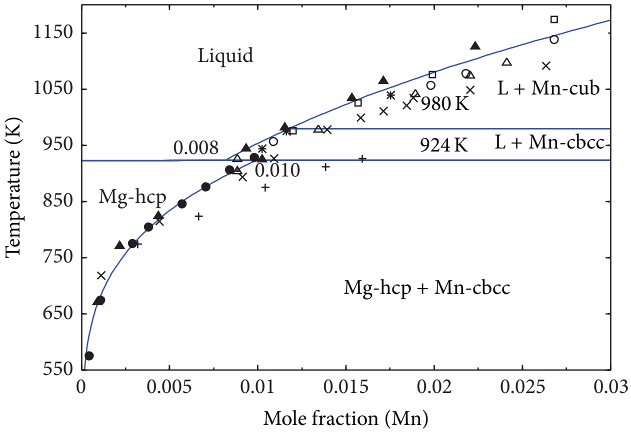


FIGURE 7: Mg-rich side of the Mg-Mn phase diagram [32]. ○: [33], ▲: [34], □: [35], △: [36], ∗: [37], ×: [38], ●: [39], +: [40].

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

Phase	Prototype	Space group number	Space group	Lattice parameter (nm) *a*	*b*	*c*	Reference
Mg_2Ca	$MgZn_2$	194	$P6_3/mmc$	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, ${}^o\Delta H$ in J/mole·atom and ${}^o\Delta S$ in J/mole·atom·K
Liquid	$Z^{Mg}{}_{MgCa} = 5$, $Z^{Ca}{}_{CaMg} = 4$; $\Delta g^{0}_{MgCa} = -13\,206.20 + 9.37T$; $\Delta g^{10}_{MgCa} = 6918.14 - 21.03T$; $\Delta g^{01}_{MgCa} = 8911.57 - 15.11$
Mg-hcp	${}^0L^{\text{Mg-hcp}} = 7153.98 - 9.41T$
Mg_2Ca	${}^o\Delta H^{Mg_2Ca}_{Mg,Ca} = -13\,468.63$; ${}^o\Delta S^{Mg_2Ca}_{Mg,Ca} = -1.93$

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 Mg_2Ca 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 Mg_2Ca [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 Mg_2Ca 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 Mg_2Ca which were then used as input data in the optimization process. Their results are in good agreement with those form 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 11. 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 Mg_2Ca 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 Mg_2Sr. 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.

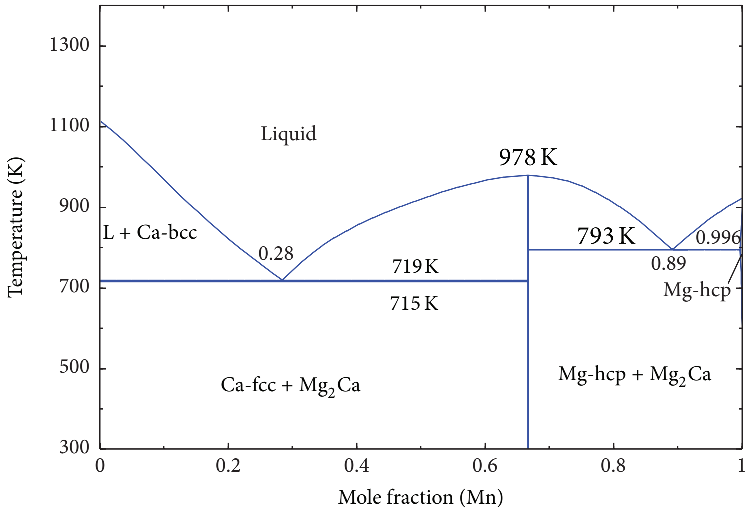
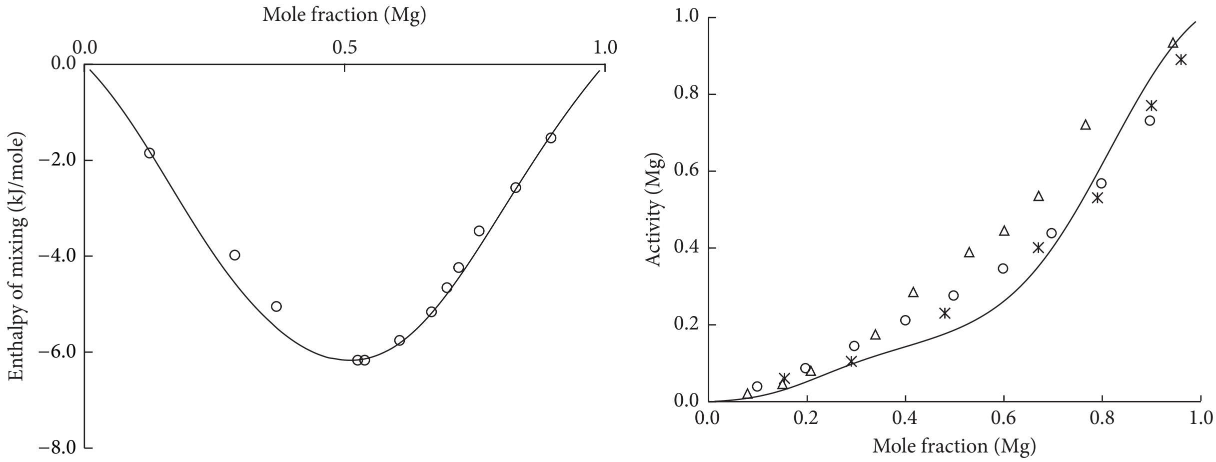


Figure 8: Mg-Ca phase diagram [41].



(a)

(b)

Figure 9: Calculated (a) enthalpy of mixing of liquid Mg-Ca at 1150 K: ○: [58]. (b) Activity of liquid Mg at 1100 K: △: [59] at 1200 K, ⋆: [59] at 1080 K, ○: [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. (*Calphad*)
−11.72 ± 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. (*F.P.*)
−12.14		[71] Cal. (*F.P.*)
−12.85		[157] Cal. (*F.P.*)

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

Phase	Prototype	Space group number	Space group	Lattice parameter (nm) *a*	*b*	*c*	Reference
Mg_2Sr	$MgZn_2$	194	$P6_3/mmc$	0.6475	0.6475	1.0433	[137]
$Mg_{38}Sr_9$	$Mg_{38}Sr_9$	194	$P6_3/mmc$	1.0500	1.0500	2.8251	[137]
$Mg_{23}Sr6$	Th_6Mn_{23}	225	$Fm\bar{3}m$	1.5000	1.5000	1.5000	[137]
$Mg_{17}Sr_2$	Th_2Ni_{17}	194	$P6_3/mmc$	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, $^{o}\Delta H$ in J/mole·atom and $^{o}\Delta S$ in J/mole·atom·K
Liquid	$Z^{Mg}{}_{MgSr} = 4, Z^{Sr}{}_{SrMg} = 6;$ $\Delta g^{0}_{MgSr} = -7\,425.6 + 2.59T;$ $\Delta g^{10}_{MgSr} = -1\,417.3 + 0.54T;$ $\Delta g^{01}_{MgSr} = 1\,938.0$
Mg_2Sr	$^{o}\Delta H^{Mg_2Sr}_{Mg,Sr} = -10\,300.0; {}^{o}\Delta S^{Mg_2Sr}_{Mg,Sr} = -1.88$
$Mg_{38}Sr_9$	$^{o}\Delta H^{Mg_{38}Sr_9}_{Mg,Sr} = -6\,038.\,3; {}^{o}\Delta S^{Mg_{38}Sr_9}_{Mg,Sr} = -0.25$
$Mg_{23}Sr_6$	$^{o}\Delta H^{Mg_{23}Sr_6}_{Mg,Sr} = -6\,496.5; {}^{o}\Delta S^{Mg_{23}Sr_6}_{Mg,Sr} = -0.39$
$Mg_{17}Sr_2$	$^{o}\Delta H^{Mg_{17}Sr_2}_{Mg,Sr} = -3\,631.6; {}^{o}\Delta S^{Mg_{17}Sr_2}_{Mg,Sr} = 0.01$

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 $MgY(\gamma)$, $Mg_2Y(\delta)$, and $Mg_{24}Y_5(\varepsilon)$ intermediate phases. The crystallographic data of the compounds are listed in Table 17. Smith et al. [65] also reported the homogeneity ranges of $Mg_{24}Y_5(\varepsilon)$ and $MgY(\gamma)$. The $Mg_2Y(\delta)$ 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 $Mg_{24}Y_5(\varepsilon)$ and $Mg_2Y(\delta)$ are listed in Table 16. These measurements by [62] showed significantly different solubility ranges especially for $Mg_2Y(\delta)$ 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 $MgY(\gamma)$, 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. (*F.P.*)
	−10.3	−1.88	[41] Cal. (*Calphad*)
	−11.34		[157] Cal. (*F.P*)
$Mg_{38}Sr_9$	−6.27		[158] Cal. (*F.P.*)
	−6.74		[157] Cal. (*F.P*)
	−6.04	−0.25	[41] Cal. (*Calphad*)
$Mg_{23}Sr_6$	−7.74		[158] Cal. (*F.P.*)
	−8.52		[157] Cal. (*F.P*)
	−6.50	−0.39	[41] Cal. (*Calphad*)
$Mg_{17}Sr_2$	−4.80		[158] Cal. (*F.P.*)
	−5.60		[157] Cal. (*F.P*)
	−3.63	0.01	[41] Cal. (*Calphad*)

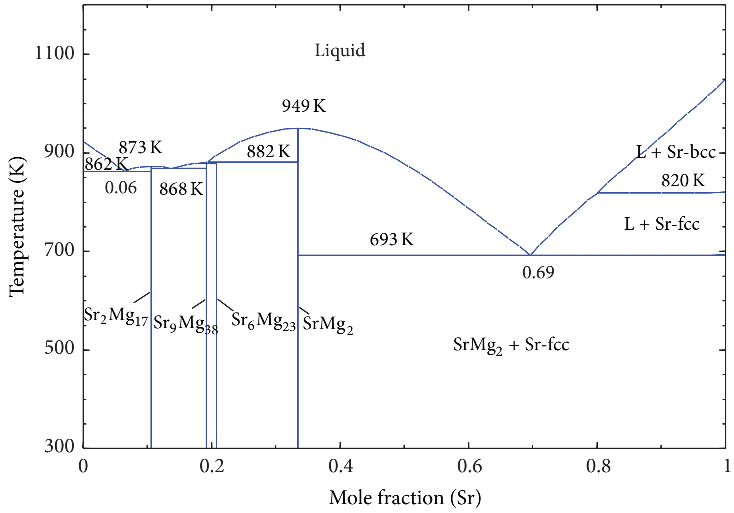


Figure 10: Mg-Sr phase diagram.

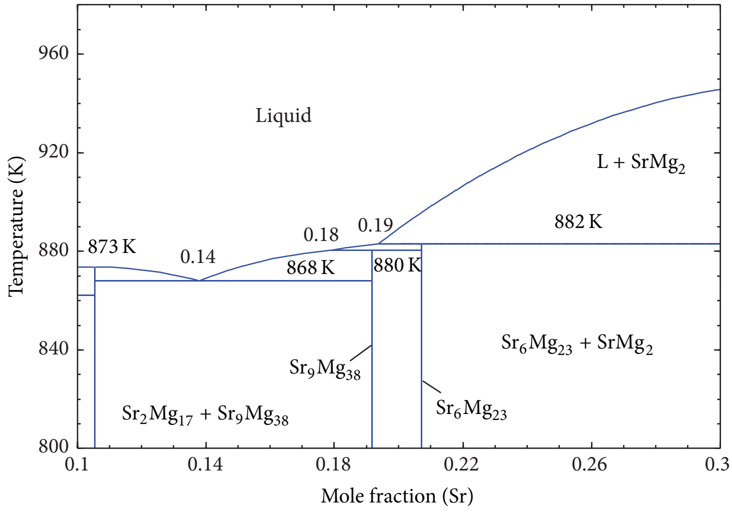


Figure 11: Magnified portion of the Mg-Sr phase diagram.

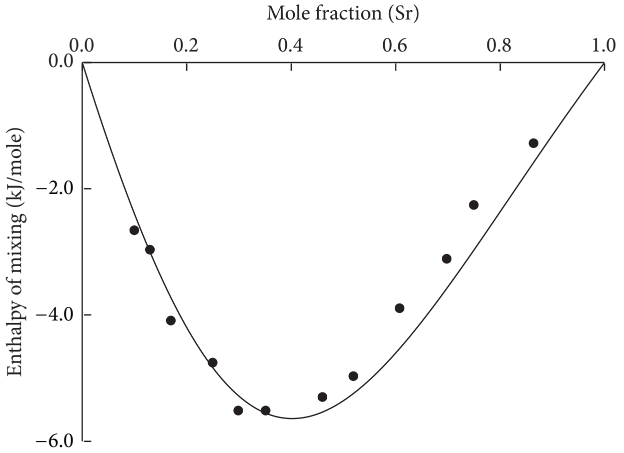


Figure 12: Calculated enthalpy of mixing of liquid Mg-Sr at 1080 K: ●: [61].

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 $Mg_{24}Y_5(\varepsilon)$ and $Mg_2Y(\delta)$ 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 staring 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, $Mg_{24}Y_5(\varepsilon)$, and $Mg_2Y(\delta)$ 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 $Mg_{24}Y_5(\varepsilon)$ and $Mg_2Y(\delta)$ 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 (L $\leftrightarrow$ Mg-hcp + $Mg_{24}Y_5(\varepsilon)$) 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 $0.04 < X_{Ni} < 0.98$. 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 ($0 \leq X_{Ni} \leq 0.34$) by thermal analysis using high purity elements. Bagnoud and Feschotte [193] investigated the system using XRD, metallography, EPMA and DTA. Micke and Ipser [73] determined the activity of magnesium over the Mg-Ni liquid in the $X_{Mg} > 0.65$ composition range by the isopiestic method. They also obtained the liquidus between $0.30 < X_{Ni} < 0.40$. 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
				a	b	c	
$Mg_{24}Y_5$ (ε)	Ti_5Re_{24}	217	$I\bar{4}3m$	1.1278	1.1278	1.1278	[137]
Mg_2Y (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, ${}^o\Delta H$ in J/mole·atom and ${}^o\Delta S$ in J/mole·atom·K
Liquid	$Z^{Mg}{}_{MgY} = 2, Z^{Y}{}_{YMg} = 4;$ $\Delta g^{0}_{MgY} = -13\,980.6 + 6.45T; \Delta g^{10}_{MgY} = -15\,445.6 + 8.87T;$ $\Delta g^{01}_{MgY} = 5\,274.1 + 2.09T;$
Mg-hcp	${}^0L^{\text{Mg-hcp}} = -12\,476.8 + 7.49T;$ ${}^1L^{\text{Mg-hcp}} = -2\,724.6 + 2.4T;$ ${}^2L^{\text{Mg-hcp}} = -2\,788.2 + 2.0T;$
Y-bcc (β)	${}^0L^{\text{Y-bcc}} = -28\,713.7 + 13.07T; {}^1L^{\text{Y-bcc}} = -2\,005.9 + 1.5T;$
$Mg_{48}Y_{10}$ (ε) $(Mg\%, Y)_{29}$ $(Y\%, Mg)_{10}$ $(Mg)_{19}$	${}^0G^{\varepsilon}_{Mg:Y:Mg} = -6\,179.0; {}^0G^{\varepsilon}_{Mg:Mg:Mg} = 935.5 + 0.14T;$ ${}^0G^{\varepsilon}_{Y:Y:Mg} = 8\,038.3; {}^0G^{\varepsilon}_{Y:Mg:Mg} = 721.7$ (J/mole·atom)
Mg_2Y(δ) $(Mg\%, Y)_6$ $(Y\%, Mg)_4$ $(Mg)_2$	${}^0G^{\delta}_{Mg:Y:Mg} = -9\,767.5 + 0.66T;$ ${}^0G^{\delta}_{Mg:Mg:Mg} = 3\,544.1 + 1.39T;$ ${}^0G^{\delta}_{Y:Y:Mg} = {}^0G^{\delta}_{Y:Mg:Mg} = 6\,976.3;$ ${}^0L^{\delta}_{Mg,Y:Y:Mg} = 641.8 + 11.86T;$ ${}^0L^{\delta}_{Mg,Y:Mg:Mg} = {}^0L^{\delta}_{Y:Y,Mg:Mg} = 9\,006.5 + 88.60T;$ ${}^0L^{\delta}_{Mg:Y,Mg:Mg} = -2\,096.2 + 0.05T$ (J/mole·atom)
MgY (γ) (Mg%, Y) (Y%, Va)	${}^0G^{\gamma}_{Mg:Y} = -10\,727.3 + 1.26T; {}^0G^{\gamma}_{Mg:Va} = -10\,464.5;$ ${}^0G^{\gamma}_{Y:Y} ={}^0 G^{\gamma}_{Y:Va} = 13\,483.6;$ ${}^0L^{\gamma}_{Mg,Y:Y} = 15\,006.5 + 16T; {}^0L^{\gamma}_{Mg,Y:Va} = 15\,006.5 + 15T; {}^0L^{\gamma}_{Mg,Y:Va} = {}^0L_{Y:Y,Va} = -5$ $000.0 + 7T$ (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. (*Calphad*)
	−7.5 ± 0.84	0.4 ± 0.3	[65] Exp.
	−6.1		[70] Exp.
	−5.84		[71] Cal. (*F.P.*)
	−5.4		[162] (*F.P.*)
Mg_2Y (δ)	−9.77	−0.66	This work Cal. (*Calphad*)
	−14.2 ± 1.26	−1.3 ± 0.4	[65] Exp.
	−12.0		[70] Exp.
	−9.17		[71] (*F.P.*)
	−8.6		[162] (*F.P.*)
MgY (γ)	−10.7	−1.26	This work Cal. (*Calphad*)
	−12.6 ± 1.26	−0.3 ± 4.0	[65] Exp.
	−30.3		[70] Exp.
	−10.64		[71] (*F.P.*)
	−10.2		[162] (*F.P.*)

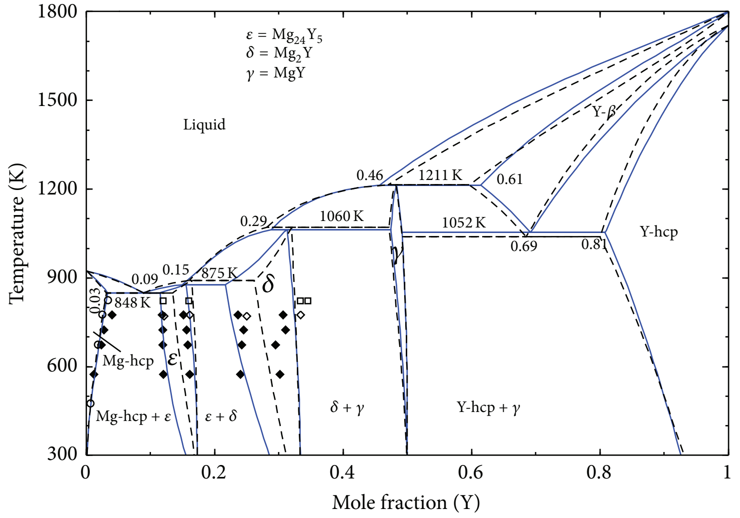
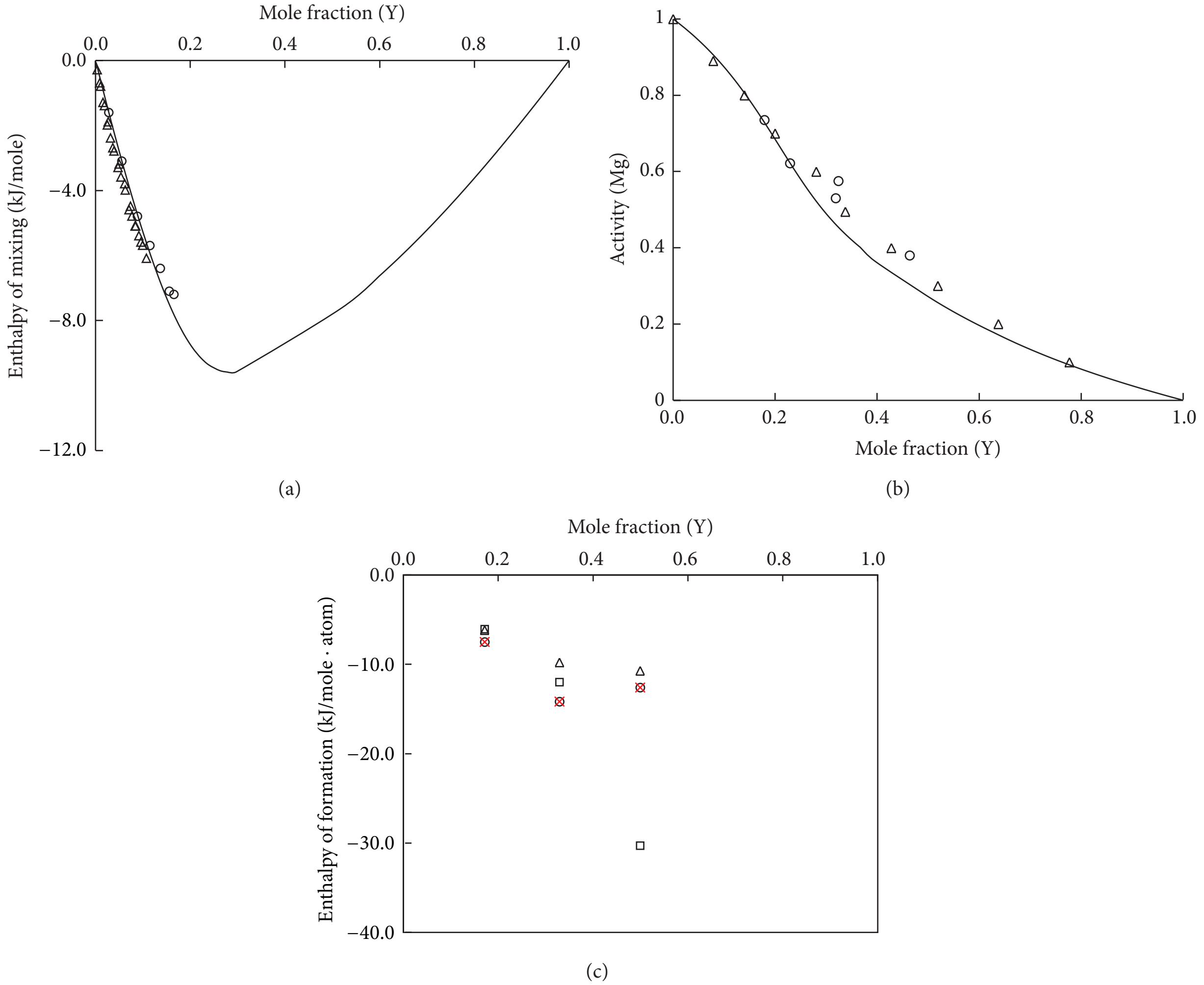


FIGURE 13: Calculated Mg-Y phase diagram (this work) compared with the literature solid solubility data: ♦: [62], ◊: [63], o: [64], □: [65]. Dotted line represents the previous assessment [66].



(a)

(b)

(c)

FIGURE 14: Calculated (a) enthalpy of mixing of liquid Mg-Y at 984 K: △: [67] at 975 K, ○: [67] at 984 K. (b) Activity of liquid Mg at 1173 K: △: [68], ○: [69]. (c) Enthalpy of formation of the intermetallic compounds: △: [this work]; ○: [65]; □: [70]; ×: [71].

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

Phase	Prototype	Space group number	Space group	Lattice parameter (nm)			Reference
				a	b	c	
Mg_2Ni	Mg_2Ni	180	$P6_222$	0.5140	0.5140	1.3220	[163]
$MgNi_2$	$MgNi_2$	227	$P6_3/mmc$	0.4815	0.4815	1.5802	[164]

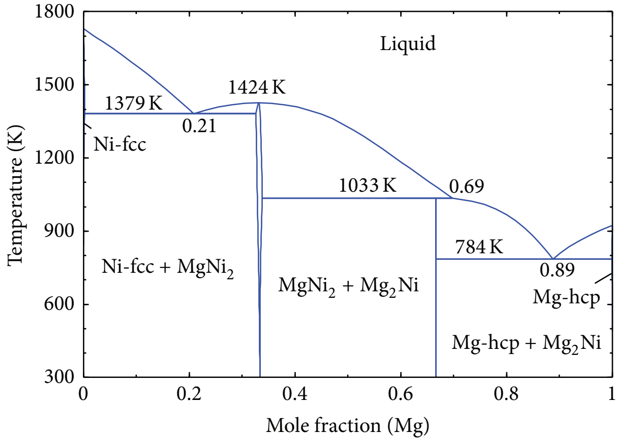


Figure 15: Mg-Ni phase diagram [45].

Mg_2Ni and $MgNi_2$, to 67.3 at.% Ni at the eutectic three phase equilibrium of liquid, Ni-fcc and $MgNi_2$.

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 $MgNi_2$ at any temperature.

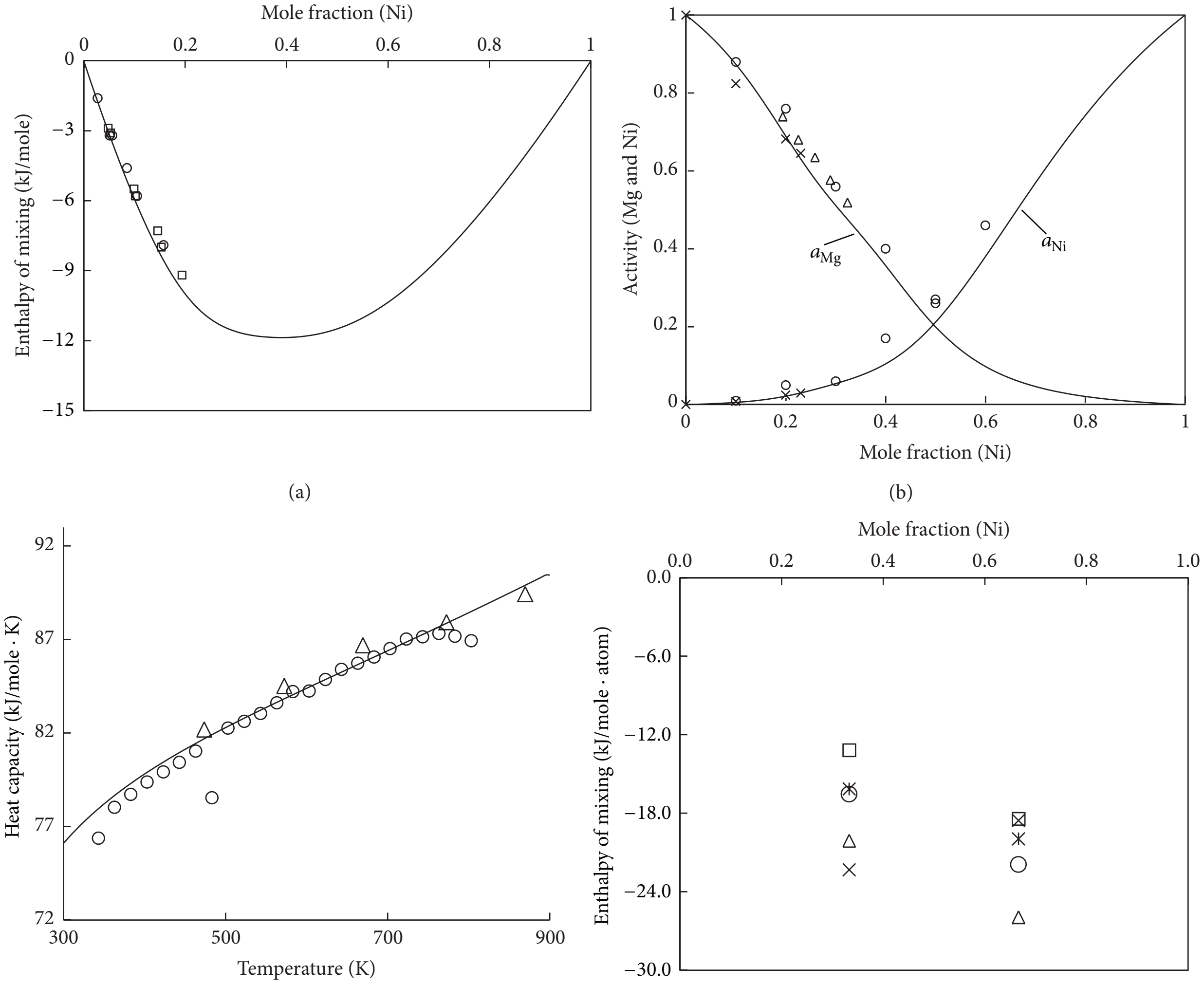
Laves and Witte [164] determined the crystal structure of $MgNi_2$ to be hexagonal hP24-type with 8 molecules per unit cell, and the lattice parameters as $a = 0.48147$ nm and $c = 1.58019$ nm which are in good agreement with the reported values of Bagnoud and Feschotte [193] and Lieser and Witte [196]. The crystal structure of Mg_2Ni 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 Ipser [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 $MgNi_2$ 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 $MgNi_2$ and Mg_2Ni 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 $MgNi_2$ of Feufel and Sommer [16], temperature dependant higher order terms are added during optimization of $MgNi_2$ 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 Mg_2Ni and $MgNi_2$ 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 $CeMg_{12}$, Ce_2Mg_{17}, and $CeMg_{8.25}$ in the Mg-rich corner were formed peritectically, and the eutectic between Mg and $CeMg_{12}$ 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



(a) (b) (c) (d)

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

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

Phase	Parameters Δg^0 and ^0L in J/mole
Liquid	$Z^{Mg}{}_{MgNi} = 2, Z^{Ni}{}_{NiMg} = 4;$ $\Delta g^0_{MgNi} = -16\,829.4 + 5.02T; \Delta g^{10}_{MgNi} = -15\,068.9 + 10.49T;$ $\Delta g^{01}_{MgNi} = -16345.6 + 1.26T$
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)
$MgNi_2{}^*$ $(Mg\%, Ni)_1$ $(Mg, Ni\%)_2$	$^oG^{MgNi_2}_{Mg:Mg} = 8332.6 + 12.65T; {}^oG^{MgNi_2}_{Mg:Ni} =$ $-21\,431.0 + 25.24T - 9.39T\ln T + 22.17 \times 10^{-4}T^2 + 6.66 \times 10^4 T^{-1};$ $^oG^{MgNi_2}_{Ni:Mg} = 23\,343.37 + 4.66T; {}^oG^{MgNi_2}_{Ni:Ni} = 4\,908.55 + 7.0T$ (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_2Ni	−16.07	−4.66	This work Cal. (*Calphad*)
	−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. (*F.P.*)
	−12.1 ± 2.10		[16] Exp.
$MgNi_2$	−21.43	−25.24	This work Cal. (*Calphad*)
	−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. (*F.P.*)
	−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 $a = 14.78$ Å and $c = 10.43$ Å 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 ($\Delta^{\circ}G = 7.98\text{–}9.04 \times 10^{-3}\,\mathrm{T\,kJ\cdot mol^{-1}}$), they [169] concluded that $CeMg_2$ 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 $CeMg_{12}$, Ce_5Mg_{41}, $CeMg_3$, CeMg, $CeMg_{10.3}$, and $CeMg_2$. With the exception of $CeMg_3$, 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 $CeMg_{12}$ 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; $CeMg_{12}$ was redesignated as $CeMg_{11}$ and Ce_5Mg_{41} as Ce_5Mg_{39}. 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 $CeMg_3$ phase field needs to be reexamined. This is because the two-phase region field $CeMg_2$ + $CeMg_3$ 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 Mg_2Nd was determined as $cF24$-Cu_2Mg type, Mg_3Nd as $cF16$-BiF_3 type, $Mg_{41}Nd_5$ as $tI92$-Ce_5Mg_{41} type, and $Mg_{12}Nd$ as $tI26$-$ThMn_{12}$ 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, Mg_2Nd, Mg_3Nd, $Mg_{41}Nd_5$ and $Mg_{12}Nd$,

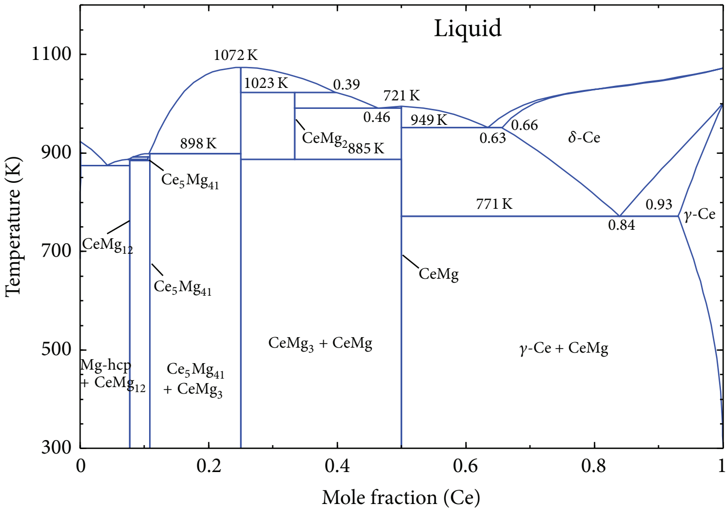


FIGURE 17: Mg-Ce phase diagram.

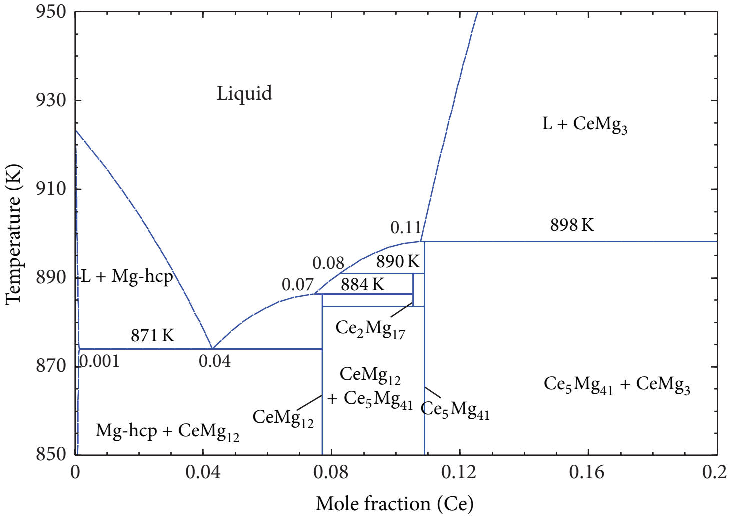


FIGURE 18: Magnified portion of the Mg-Ce phase diagram.

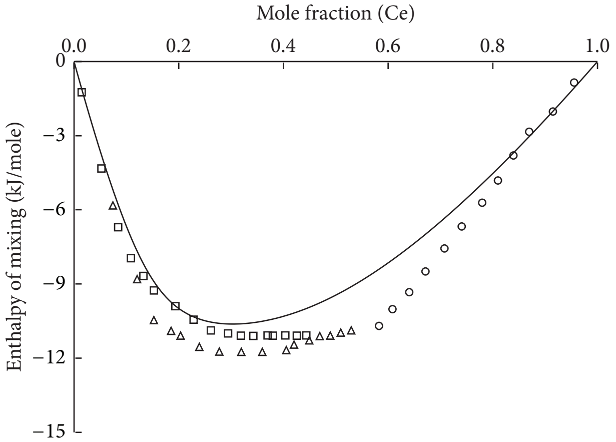


FIGURE 19: Calculated (a) enthalpy of mixing of liquid Mg-Ce at 1090 K: □: [16] at 1002 K, ○: [16] at 1008 K. (b) Activity of liquid Mg and Ni at 1100 K: ○: [72] at 1100 K, △: [73] at 1092 K, ×: [74] at 1100 K. (c) Heat capacity for the MgNi$_2$: ○: [16], □: [75]. (d) Enthalpy of formation of Mg$_2$Ni and MgNi$_2$: △: [74]; ×: [76]; □: [77]; ∗: [78].

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

Phase	Prototype	Space group number	Space group	Lattice parameter (nm)			Reference
				a	*b*	*c*	
(δCe)	W	229	$Im\bar{3}m$	0.4120			[141, 165]
(γCe)	Cu	225	$Fm\bar{3}m$	0.5160			[141, 165]
CeMg	CsCl	221	$Pm\bar{3}m$	0.3901			[141, 165]
$CeMg_2$	Cu_2Mg	227	$Fd\bar{3}m$	0.8733			[141, 165]
$CeMg_3$	BiF_3	225	$Fm\bar{3}m$	0.7420			[141, 165]
Ce_5Mg_{41}	Ce_5Mg_{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, ${}^{o}\Delta H$ in J/mole·atom and ${}^{o}\Delta S$ in J/mole·atom·K
Liquid	$Z^{Mg}_{MgCe} = 2, Z^{Ce}_{CeMg} = 6;$ $\Delta g^{0}_{MgCe} = -15\,914.4 + 7.44T;$ $\Delta g^{10}_{MgCe} = -9\,632.4 + 2.51T;$ $\Delta g^{01}_{MgCe} = -8\,371.8$
Mg-hcp	${}^{0}L^{\text{Mg-hcp}} = -24\,486.4$
δ-Ce	${}^{0}L^{\delta\text{-Ce}} = -15\,600.7 - 9.75T;\ {}^{1}L^{\delta\text{-Ce}} = -9003$
γ-Ce	${}^{0}L^{\gamma\text{-Ce}} = -9277.0T;$
CeMg	${}^{o}\Delta H^{CeMg}_{Ce,Mg} = -14300.0;\ {}^{o}\Delta S^{CeMg}_{Ce,Mg} = -2.52$
$CeMg_2$	${}^{o}\Delta H^{CeMg_2}_{Ce,Mg} = -15816.3;\ {}^{o}\Delta S^{CeMg_2}_{Ce,Mg} = -3.43$
$CeMg_3$	${}^{o}\Delta H^{CeMg_3}_{Ce,Mg} = -19000.0;\ {}^{o}\Delta S^{CeMg_3}_{Ce,Mg} = -6.62$
Ce_5Mg_{41}	${}^{o}\Delta H^{Ce_5Mg_{41}}_{Ce,Mg} = -12521.8;\ {}^{o}\Delta S^{Ce_5Mg_{41}}_{Ce,Mg} = -6.50$
Ce_2Mg_{17}	${}^{o}\Delta H^{Ce_2Mg_{17}}_{Ce,Mg} = -11363.5;\ {}^{o}\Delta S^{Ce_2Mg_{17}}_{Ce,Mg} = -5.40$
$CeMg_{12}$	${}^{o}\Delta H^{CeMg_{12}}_{Ce,Mg} = -10931.1;\ {}^{o}\Delta S^{CeMg_{12}}_{Ce,Mg} = -6.65$

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_5Mg_{41}	−18.13		[169] Exp.
	−7.00		[162] Cal. [*F.P.*]
	−12.52	−6.50	[42] Cal. (*Calphad*)
Ce_2Mg_{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
				a	*b*	*c*	
(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]
(βNd)	W	229	$Im\bar{3}m$	0.4130			[140, 141]
(αNd)	αLa	194	$P6_3/mmc$	0.3659		1.1796	[140, 141]

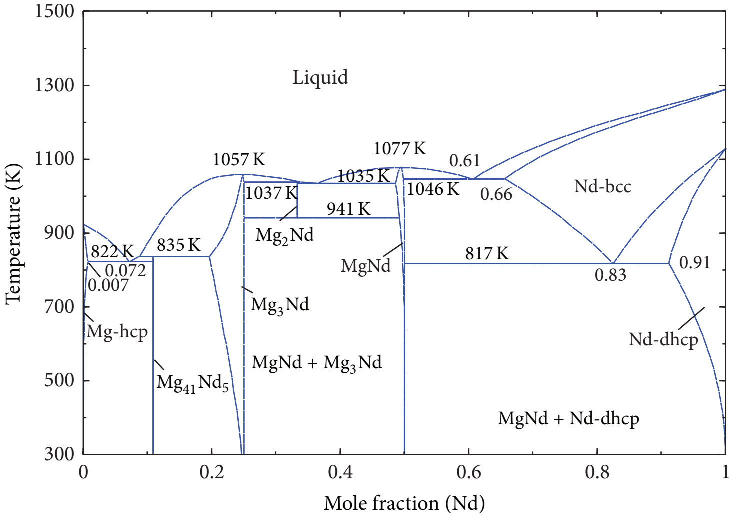


Figure 20: Mg-Nd phase diagram [116].

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_3Nd	−18.74 ± 1.42	5.15 ± 1.88	[169] Exp.
	−11.70		[162] Cal. (*F.P.*)
Mg_2Nd	−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.

Mg_2Cu does not have any solid solubility. However, $MgCu_2$ shows temperature dependent solubility range. Grime and Morris-Jones [222] reported a homogeneity range of 2 to 3 at.% on both sides of the $MgCu_2$ stoichiometry. Also, X-ray diffraction from Sederman [223] disclosed that the extension of solubility on both sides of $MgCu_2$ 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 $MgCu_2$ 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 $MgCu_2$ and Mg_2Cu 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 Mg_2Cu and $MgCu_2$ 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 Oelsen [233, 234] also measured the same using a calorimetric analysis. These results are fairly in agreement with each other. The liquidus curve near Mg_2Sn was determined by several researchers [229–236] and the melting point of Mg_2Sn 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

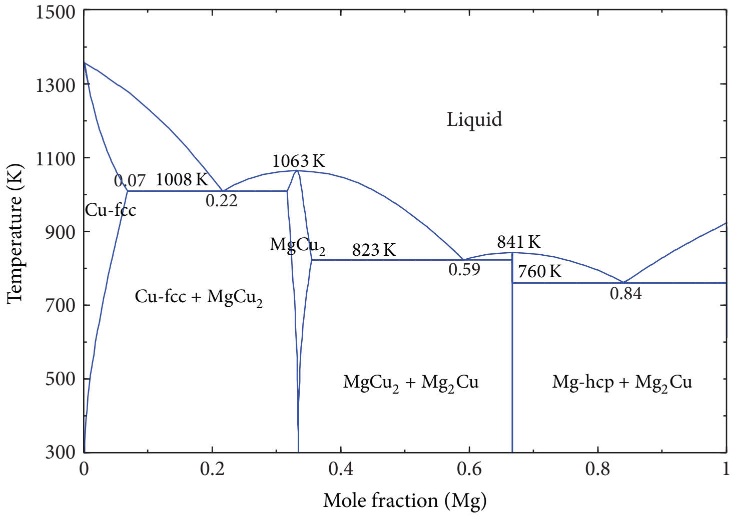
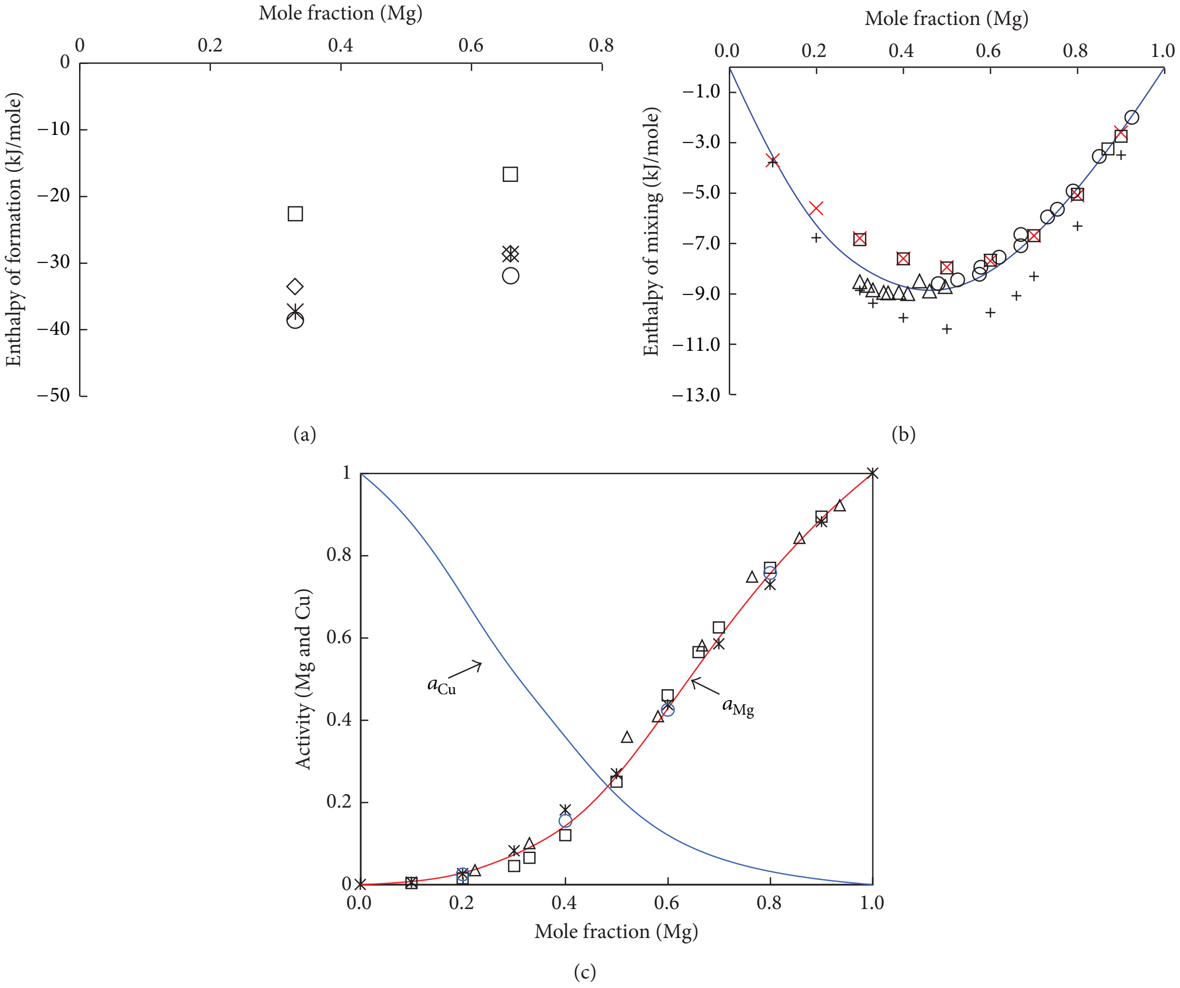


FIGURE 21: Mg-Cu phase diagram [66].



(a)

(b)

(c)

FIGURE 22: (a) Calculated enthalpy of mixing of Mg-Cu liquid at 1400 K [66]: □: [117] at 1100 K, △: [117] at 1120 K, ○: [117] at 1125 K, ×: [118] at 1100 K, +: [119] at 1100 K. (b) Activity of Mg in the Mg-Cu liquid at 1123 K: ∗: [120] at 1100 K, △: [121] at 1123 K, □: [119] at 1100 K, ○: [122] at 1100 K. (c) Heat of formation of the stoichiometric compounds: ∗: [66], ◊: [77], ○: [123], □: [76].

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

Phase	Prototype	Space group number	Space group	Lattice parameter (nm) *a*	*b*	*c*	Reference
Mg_2Cu	Mg_2Cu	70	*Fddd*	0.5283	0.9062	1.8351	[137]
$MgCu_2$	$MgCu_2$	227	$Fd\bar{3}m$	0.7031	0.7031	0.7031	[137]

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

Phase	Parameters Δg^0 and ${}^0L$ in J/mole
Liquid	$Z^{Mg}{}_{MgCu}=4, Z^{Cu}{}_{CuMg} = 2;$ $\Delta g^{0}_{MgCu} = -12975.95;$ $\Delta g^{10}_{MgCu} = -6153.13 + 1.26T;$ $\Delta g^{01}_{MgCu} = -13528.50$
Mg-hcp	${}^0L^{\text{Mg-hcp}} = 8371.60$
Cu-fcc	${}^0L^{\text{Cu-fcc}} = -21923.39 + 5.37T$
Mg_2Cu	$\Delta G_f = -28620.0 + 0.03T$
$MgCu_2$ (Mg%, Cu) $(Cu\%, Mg)_2$	${}^0G^{MgCu_2}_{Cu:Cu} = 16743.20; {}^0G^{MgCu_2}_{Mg:Cu} = -37684.26;$ ${}^0G^{MgCu_2}_{Cu:Mg} = 0; {}^0G^{MgCu_2}_{Mg:Mg} = 6278.7;$ ${}^0L^{MgCu_2}_{Mg,Cu:Cu} = {}^0L^{MgCu_2}_{Mg,Cu:Mg} = 13011.35;$ ${}^0L^{MgCu_2}_{Cu:Mg,Cu} = {}^0L^{MgCu_2}_{Mg:Mg,Cu} = 6599.45;$

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 Mg_2Sn 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 Mg_2Sn compound using the Pauling's rule. The heat capacity of the Mg_2Sn 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 Mg_2Sn 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 Mg_2Sn 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_2Cu	−9.54	−0.01	[66] Cal. (*Calphad*)
	−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. (*Calphad*)
	−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. (*F.P.*)
	−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
				a	*b*	*c*	
Mg_2Sn	CF_2	225	$Fm\bar{3}m$	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, ${}^o\Delta H$ in J/mole·atom and ${}^o\Delta S$ in J/mole·atom·K
Liquid	$Z^{Mg}{}_{MgSn} = 3, Z^{Sn}{}_{SnMg} = 6;$ $\Delta g^0_{MgSn} = -17\,819.7 - 4.10T; \Delta g^{10}_{MgSn} = 1\,171.5;$ $\Delta g^{01}_{MgSn} = -41\,84.0 - 2.09T$
Mg-hcp	${}^0L^{Mg\text{-}hcp} = -62\,000$ $[{}^\circ G^{Sn\text{-}hcp} = {}^\circ G^{Sn\text{-}bct} + 5000]$
Cu-fcc	${}^0L^{Sn\text{-}bct} = -20\,000$ $[{}^\circ G^{Mg\text{-}bct} = {}^\circ G^{Mg\text{-}hcp} + 8360]$
Mg_2Sn	${}^o\Delta H^{SnMg_2}_{Sn,Mg} = -28\,332.9; {}^o\Delta S^{SnMg_2}_{Sn,Mg} = -1.59$

TABLE 33: Enthalpy and entropy of formation of Mg_2Sn.

Enthalpy of formation (kJ/mole·atom)	Entropy of formation (J/mole·atom·K)	Reference
−28.33	−1.59	[22] Cal. (*Calphad*)
−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

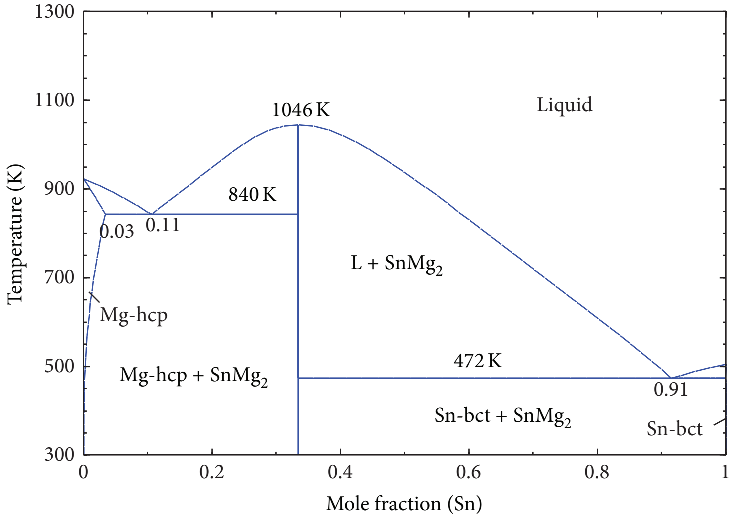
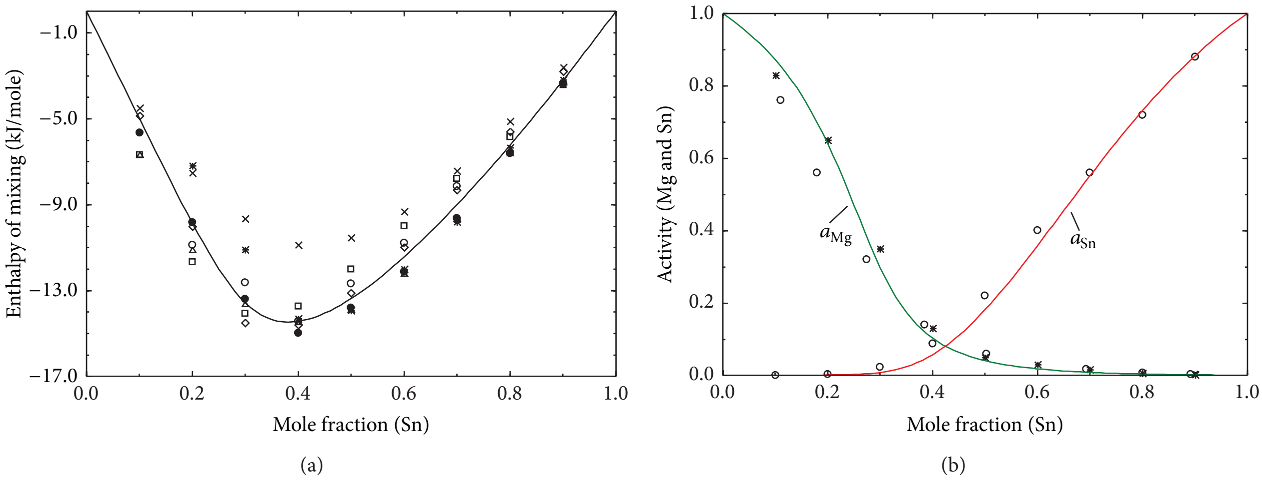


FIGURE 23: Mg-Sn phase diagram [22].



(a)

(b)

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.

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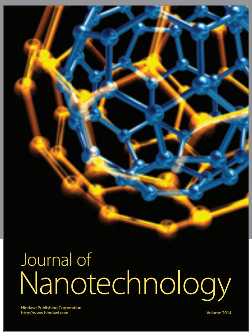
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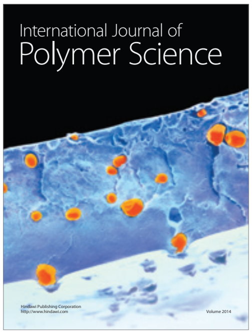
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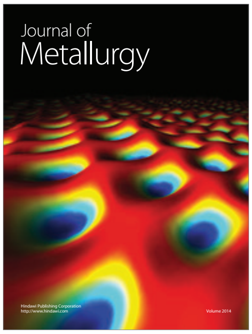
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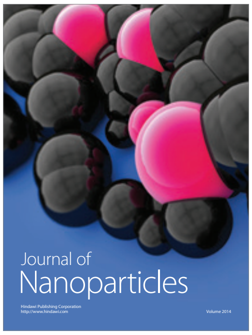
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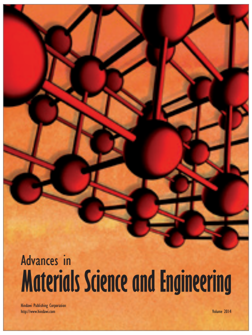
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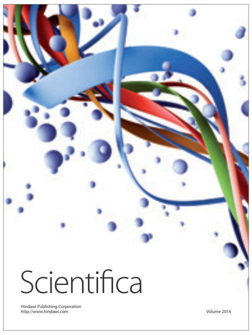
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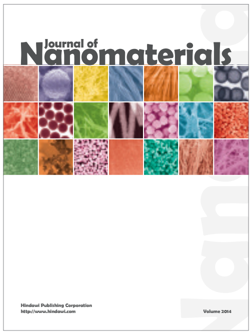
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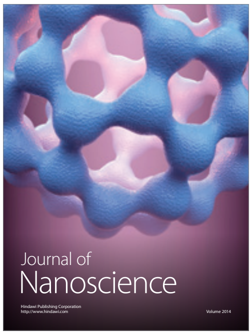
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