THERMODYNAMIC MODELLING OF THE Mg-Al-Ca SYSTEM

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Abstract — In this study, the ternary Mg-Al-Ca phase diagram was constructed by combining the three constituent binary systems of Mg-Al, Al-Ca and Mg-Ca. The Mg-Al system is taken from COST 507 database. The thermodynamic descriptions of the Mg-Ca and Al-Ca systems are obtained by modelling the Gibbs energy of all phases as a function of composition and temperature. The model parameters were optimized by minimizing Gibbs energy considering phase equilibria and thermodynamic data available in the literature. A self-consistent thermodynamic database was constructed with the optimized parameters of the three subsystems. The binary phase diagrams, their thermodynamic properties, the ternary phase diagram and the critical points were calculated from this database and compared with experimental results from the literature.

Résumé — Dans cette étude, on a construit le diagramme de phase ternaire Mg-Al-Ca en combinant les trois systèmes binaires constituants de Mg-Al, Al-Ca et Mg-Ca. Le système Mg-Al provient de la base de données COST 507. On a obtenu les descriptions thermodynamiques des systèmes Mg-Ca et Al-Ca en modélisant l'énergie de Gibbs de toutes les phases en fonction de la composition et de la température. On a optimisé les paramètres du modèle en minimisant l'énergie de Gibbs, en considérant les équilibres de phase et les données thermodynamiques disponibles dans la littérature. On a construit une base de données thermodynamiques auto-consistantes avec les paramètres optimisés des trois sous-systèmes. On a calculé les diagrammes de phase binaires, leurs propriétés thermodynamiques, le diagramme de phase ternaire et les points critiques à partir de cette base de données et on les a comparés aux résultats expérimentaux de la littérature.

INTRODUCTION

Mg alloys have drawn attention for their application in automobile and aerospace industries due to their light weight compared to Al and Fe. In spite of this promising property, the application of Mg is still behind that of competing materials such as aluminum and plastics due to its low rigidity, corrosion resistance and yield strength. Therefore, attempts have been made to improve the characteristics of magnesium alloys by employing different alloying elements [1,2]. Aluminum is the most important alloying element for magnesium to enhance mechanical and corrosion properties and for better castability. However, the use of Mg-Al alloys is limited to low temperature applications because of their low creep resistance due to the presence of the γ-phase ($Mg_{17}Al_{12}$) at the grain boundaries in the as-cast condition. The γ-phase is incoherent with the α-Mg matrix and exists at a wide composition range of 48 to 52 wt% Al and has a low melting point of 710 K. The compound is therefore prone to ageing, has poor metallurgical stability as the temperature is increased and may contribute to the poor creep resistance [3].

The addition of rare earth metals (Y, Ce and Nd) to Mg-Al alloys can improve the creep resistance, but they are too expensive to use in the mass automotive industry. Some attempts were made to replace rare earth metals with Ca. It has been found that Mg-Al-Ca based alloys have equal or better creep and corrosion resistance than those of the AE42 series. The increased creep resistance of Mg-Al-Ca alloys is due to the presence of a thermally stable Al_2Ca intermetallic compound along the grain boundary in the as-cast structure. It provides effective pinning to resist grain boundary sliding and improve creep resistance. Moreover, complete elimination of the γ–phase is possible by keeping the ratio of Al and Ca content at less than 2 [3-5]. Mg-Al-Ca based alloys meet the requirements for critical components in the automobile industry where higher creep and corrosion resistance at an elevated temperature are required. Despite the fulfillment of the required properties for use at an elevated temperature, the complete phase diagram of Mg-Al-Ca system with all critical points is scarcely known. Construction of an Mg-Al-Ca phase diagram is necessary for the development of new alloys and a better understanding of their behaviour.

THERMODYNAMIC MODELLING

The calculation of the phase diagram using thermodynamic modelling reduces the effort required to determine the equilibrium conditions of a multicomponent system and focuses the experimental work on a critical region. Equilibrium is best described in terms of Gibbs free energy (G). A system at constant temperature and pressure will approach an equilibrium state that minimizes G. For Mg-Ca and Al-Ca systems, phase diagrams and thermodynamic data were critically assessed for all phases from room temperature to above the liquidus temperatures at atmospheric pressure. All these data were optimized to obtain a set of model parameters for Gibbs energy of the liquid and all solid phases as a function of composition and temperature. Values of the standard Gibbs energies (G°) of each component are stored in the database along with optimized parameters which define the Gibbs energy of mixing according to the Redlich-Kister polynomial model and Gibbs free energy of the formation of stoichiometric compounds. Thermodynamic models for different phases are described in the following sections.

Unary Phases

The Gibbs energy of the pure element, i, with a certain phase, ϕ, is described as a function of temperature by

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

(1)

where H_i^{SER} (the molar enthalpy of the stable element reference (SER)) is at 298.15 K and 1 bar, and T is the absolute temperature. The values of the coefficients a to h are taken from the Scientific Group Thermodata Europe (SGTE) compilation by Dinsdale [6].

Disordered Solution Phases

The Gibbs energy of a disordered solution phase is described by

$$G = x_i \, ^{0}G_i^{\phi} + x_j \, ^{0}G_j^{\phi}$$
$$+ RT[x_i \ln x_i + x_j \ln x_j] + ^{ex}G^{\phi}$$

(2)

where ϕ denotes the phase in question and x_i and x_j denote the mole fraction of component i and j, respectively. The first two terms on the right hand side of Equation 2 represent the Gibbs energy of the mechanical mixture of the components, the third term is the ideal Gibbs energy of mixing and the fourth term is the excess Gibbs energy. The excess Gibbs energy is represented using the Redlich-Kister equation

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

(3)

with $^{n}L_{i,j}^{\phi} = a_n + b_n T \quad (n = 0,...m)$

where a_n and b_n are model parameters to be optimized in terms of experimental and thermodynamic data.

Stoichiometric Phases

The Gibbs energy for stoichiometric compounds is described by

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

(4)

with $\Delta G_f = a + b \times T$

where x_i and x_j are the mole fraction of component i and j, respectively and $^{0}G_i^{\phi_1}$ represents the Gibbs energy of a component in its standard state. However, the Gibbs energy of the compound phase may refer to different crystal structures from those of the pure elements, ϕ_l and ϕ_2. ΔG_f is the Gibbs energy of formation per mole of atoms of the stoichiometric compound; the parameters a and b are obtained by optimization phase equilibria and thermodynamic data. In this work, the computer program WinPhaD [7] was used for optimizing the binary subsystems (Mg-Ca and Al-Ca), whereas the calculation of the Mg-Al-Ca ternary was done using FactSage [8] software.

Mg-Ca SYSTEM

Phase Diagram

First Baar [9] determined the complete liquidus temperatures for the Mg-Ca system. In his work, the purity of the starting elements was low and there was significant loss of Ca during alloying. Paris [10] also determined the complete liquidus temperature but he did not mention the purity of the materials. Haughton [11] determined the liquidus temperature of the Mg-rich side in the composition range of 0 to 17% Ca rigorously avoiding loss of Ca. On the other hand, Vosskühler [12] analyzed Mg-rich alloys up to 47.65% Ca. The measurement of the liquidus temperature by Klemm and Dinkelacker [13] agrees fairly well with both of [11] and [12]. Nayeb-Hashemi and Clark [14] critically evaluated this system. Agarwal *et al*. [15] measured calorimetrically the enthalpies of the mixing of liquid Ca-Mg alloy at 1023 K and the heat contents of Mg_2Ca between 750 and 1150 K. They reoptimized the system with these experimental and literature data to verify the compatibility of the results available from different sources. According to their calculation, the stable phases in the Mg-Ca system are the liquid, the (Mg) solid solution, the Ca-bcc, the Ca-fcc and the congruent intermetallic compound Mg_2Ca which divides the phase diagram into two eutectic systems. Mg_2Ca is reported in the literature as a line compound [14,15]. Several researchers measured the solubility of Ca in

Mg [11,12,16]. Among them, Vosskühler [12] and Burke [16] reported limited solubility and their results agree fairly well, whereas other researchers reported larger solubility. Hence the limited solubility will be considered in this work.

Thermodynamic Properties

The standard enthalpy of formation of the compound Mg_2Ca measured by King and Kleepaa [17] using tin solution calorimetry is –40.50±1.25 kJ/mol at 298 K. Davison and Smith [18] also measured the enthalpy of formation at room temperature as -39.38 ± 2.63 kJ/mol by acid solution calorimetry and mentioned that the heat of formation determined by King and Kleepaa [17] is "the most precise and probably the most reliable." Sommer *et al.* [19] measured the heat of mixing (ΔH_{mix}) of liquid Mg-Ca by high temperature calorimetry. Although Agarwal *et al.* [15] also measured the enthalpy of mixing calorimetrically at 1023 K, their results were not considered in this study because they contradicted those of Sommer *et al.* [19]. Hultgren *et al.* [20] and Sommer [21] determined the activity of Mg and Ca by vapour pressure measurement at 1010 K and 1200K, respectively. Mishra *et al.* [22] calculated the activity of Mg and Ca at 1200 K. Mashovets [23] also determined the activity of Mg and Ca in liquid at 1073 K by vapour pressure measurement using the gas carrier technique. The activity of Ca reported by Mashovets [23] showed positive deviation from ideal solution, whereas Sommer [21] showed negative deviation. As for the regular solution, with $\Delta H_{mix}<0$, activity is less than that of the ideal solution; the thermodynamic activities calculated from the primary results of the measurements given by Sommer [21] seem to be more reliable. Moreover, they are more recent and consistent with other works; hence, they will be used for the optimization of the Mg-Ca system.

Optimization of Phase Diagram and Thermodynamic Properties

Phase Diagram: The model calculated phase diagram of the Mg-Ca system in relation to calculated and experimental results from the literature is shown in Figure 1.

It can be seen from Figure 1 that there is a good agreement between experimental and calculated results. This indicates that the thermodynamic model is capable of reproducing the measured phase diagram within experimental error limits. The optimized model parameters are given in Table 1. Three Redlich-Kister interaction parameters were required to

Table I – Parameters for the liquid phase, Mg_2Ca stoichiometric phase of the Mg-Ca system

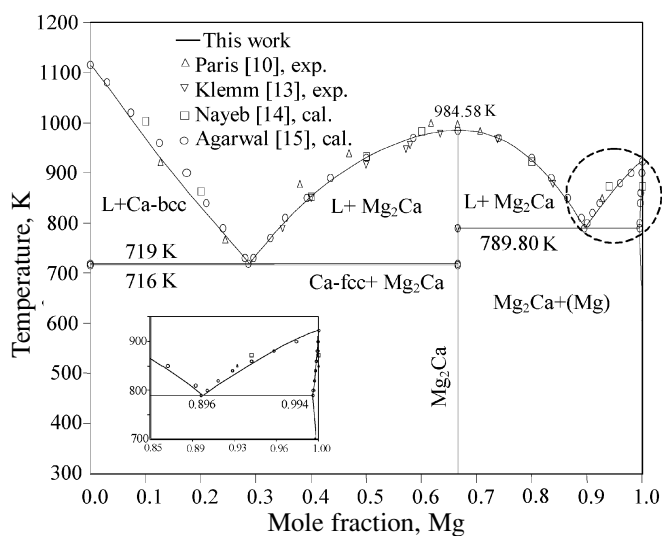| Phase	Terms	a (J/mol-atom)	b (J/mol-atom.K)
	L_0	-24 018.60	1.9432
Liquid	L_1	1 785.73	4.4724
	L_2	14 387.50	-22.9827
Mg-hcp	L_0	7 150.90	-9.4012
Mg_2Ca	ΔG_f	-12 704.40	1.8093

Fig. 1. Optimized Mg-Ca with data from the literature (cal.: calculated, exp.: experimental).

model the liquid phase and two parameters were optimized for the Gibbs energy of formation of the stoichiometric compound. The reference states of the Gibbs energy of formation of Mg_2Ca were considered as Mg- hexagonal close packed (hcp) and Ca- face centred cubic (fcc). No lattice stability values were added to the pure components.

A comparison between calculated and experimental results of the critical regions of Mg-Ca phase diagram is presented in Table II.

There is a small solid solubility range of Ca in Mg. An almost straight line originating from the melting point of Mg and terminating at 99.44 mol% Mg at 789.80 K, shown in Figure 1, represents the (Mg) solidus. This agrees with the results of Nayeb-Hashemi and Clark [14] (99.18 mol% Mg at 789.5 K) and Agarwal *et al.* [15] (99.50 mol% Mg at 790 K.)

Thermodynamic Properties: The data for the enthalpy of mixing measured by Sommer *et al.* [19] at 1150 K was used in the optimization and show very good agreement with the model calculated values shown in Figure 2.

The activities of Mg and Ca in Mg-Ca liquid at 1010 K are shown in Figure 3. It can be seen from this figure that the calculated Mg activity agrees with the experimental results of [14,20,22,23]. The activity of Ca agrees with Sommer [21]. However, the values reported by Hultgren *et al.* [20] and Mishra *et al.* [22] are higher than those of Sommer [21]. This is probably due to the fact that they obtained their results at significantly different temperatures. Sommer [21] measured activities of Ca only for Ca-rich alloys. Later he calculated the activities of Ca for alloys across the phase diagram from those of Mg using the Gibbs-Duhem equation.

Figure 4 shows that calculated partial Gibbs free energies of Mg and Ca in Mg-Ca liquid at 1100 K follow the trend of the experimental data from the literature. Figure 5 shows the calculated partial enthalpy of the mixing of Ca in Mg-Ca

Table II – Comparison between calculated and experimental values of critical regions in the Mg-Ca system

Reaction	Reaction type	Temp, K	Mg mol%	References
L ↔ Mg-hcp	Melting	878.00	100.00	[14]
		923.00	100.00	[15]
		998.00	-	[10]
		923.00	100.00	This work
L ↔ Ca-bcc	Melting	1,115.00	0.00	[14]
		1,115.00	0.00	[15]
		1,115.00	0.00	This work
L ↔ Mg$_2$Ca	Congruent	988.00	66.00	[14]
		984.00	66.00	[15]
		984.58	66.00	This work
Ca-fcc ↔ Ca-bcc	Allotropic	716.00	0.00	[14]
		716.00	0.00	[15]
		716.00	0.00	This work
L ↔ Mg$_2$Ca+ Ca-fcc	Eutectic	718.00	27.00	[14]
		719.00	28.60	[15]
		733.00	26.60	[10]
		718.00	27.0	[13]
		719.00	28.83	This work
L ↔ Mg$_2$Ca+ Mg-hcp	Eutectic	789.50	89.50	[14]
		790.00	89.50	[15]
		798.00	88.60	[10]
		789.80	89.61	This work

liquid at 1032 K compared with experimental results from Agarwal *et al.* [15]. Although these data were predicted, that is why they were not included in the optimization, they agree well with the results calculated from the thermodynamic model. This provides strong evidence of the quality of the model.
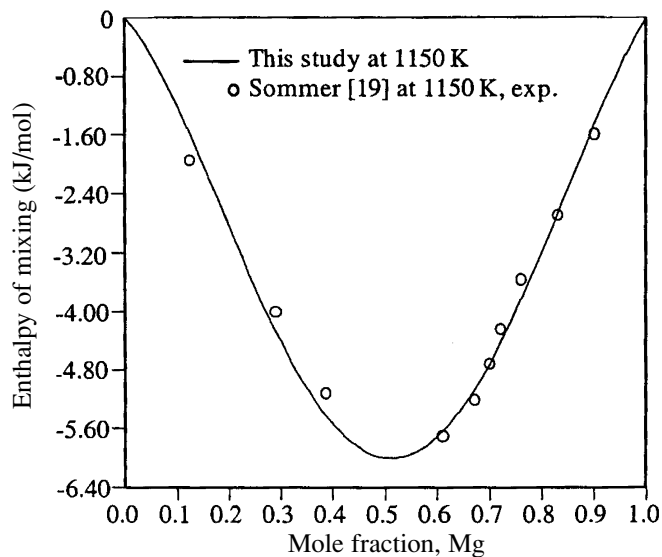
In this study the calculated enthalpy of formation of Mg$_2$Ca intermetallic compound is –12.70 kJ/g-atom at 298 K which is in close agreement with the values proposed by Davison and Smith [18] and King and Kleepaa [17] as –13.17 kJ/g-atom and –13.5 kJ/g-atom, respectively.
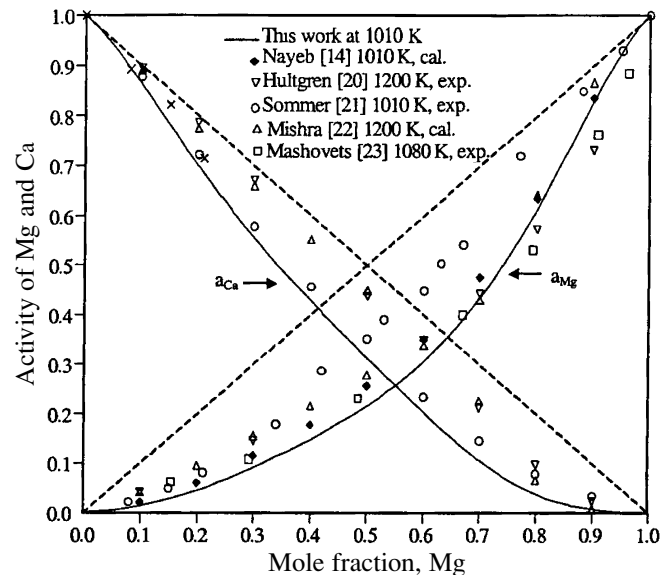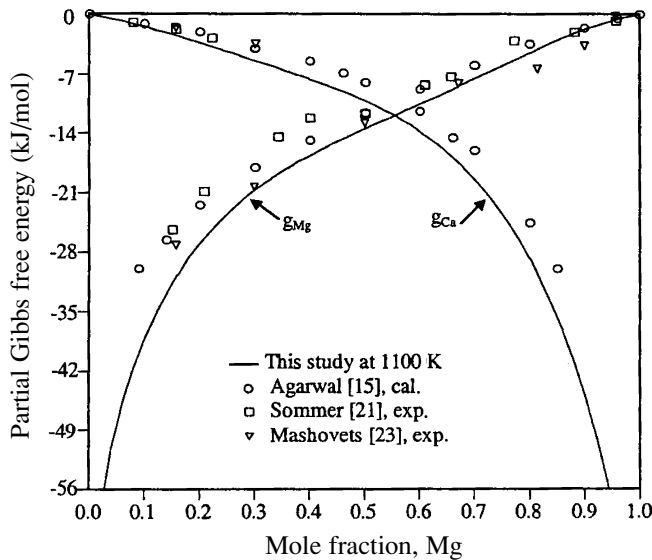

Fig. 2. Enthalpy of mixing Mg-Ca liquid at 1150 K (exp.: experimental).

Fig. 3. Activity of Mg and Ca in Mg-Ca liquid.

Fig. 4. Partial Gibbs energy of Mg and Ca in Mg-Ca liquid.

Fig. 5. Partial enthalpy of Ca in Mg-Ca liquid (cal.: calculated).

Al-Ca SYSTEM

Phase Diagram

Matsuyama *et al.* [24] investigated the Al-Ca system thoroughly by thermal and thermoresistometric analysis and microscopic examination. They reported two intermetallic compounds: Al_2Ca which melts congruently at 1352 K and Al_4Ca which melts incongruently at 973 K [24]. In the Al-Ca system, most experimental investigations deal mainly with the Al-rich corner which is technically interesting for aluminum alloys. Consequently, only limited experimental work for the Ca-rich part was reported. Recently, Kevorkov and Schmid-Fetzer [25] investigated the Al-Ca system experimentally and determined the complete phase diagram. They reported two new intermetallic compounds in the Ca rich region AlCa and Al_3Ca_8. Later, Kevorkov *et al.* [26] optimized this system and determined the thermodynamic properties. They did not report the crystal structure of AlCa because of the slow formation kinetics of this phase during the peritectic reaction from the very stable Al_2Ca phase that prevented the preparation of a single phase sample for the crystallographic investigation. Huang and Corbett [27] reported the occurrence of $Al_{14}Ca_{13}$ compound with monoclinic structure instead of AlCa. From the most recent publications [26-28], it can be concluded that the stable phases in this system are: the liquid, Al-fcc, Ca-bcc, Ca-fcc and the four intermetallic compounds Al_4Ca, Al_2Ca, $Al_{14}Ca_{13}$ and Al_3Ca_8. Later, Ozturk *et al.* [28] used both associate and random solution models to reoptimize the system with $Al_{14}Ca_{13}$ intermetallic compound instead of AlCa. Itkin *et al.* [29] mentioned that the solubility of Ca at 873 K was found to be less than 0.03 at% which contradicts the recent investigation by 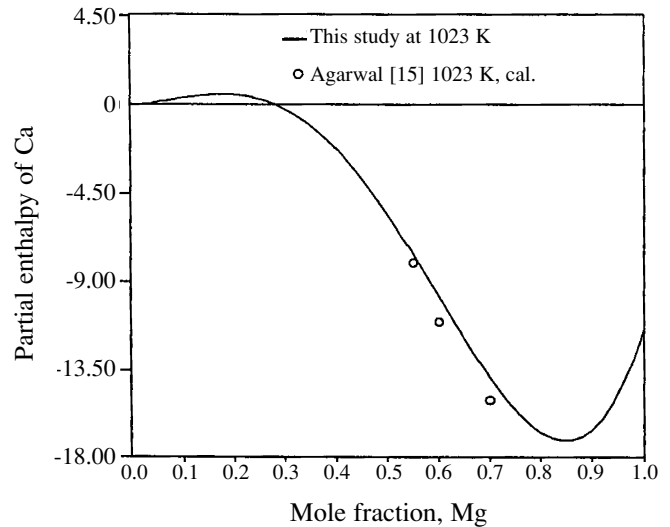Kevorkov and Schmid-Fetzer [25]. During X-ray diffraction (XRD) investigation of the Al and Ca-rich alloys, they found no deviation from the theoretical powder patterns, therefore, the mutual solubility between Ca and Al is considered negligible.

Thermodynamic Properties

Sommer *et al.* [30] used high temperature calorimetry to determine the enthalpy of the mixing of liquid Al-Ca at temperatures ranging between 1125 and 1190 K. Their experimental results are in good agreement with the results of Notin *et al.* [31]. Ozturk *et al.* [28] compared the calculated enthalpy of mixing data in the liquid phase at 1453 K with Sommer *et al.* [30] and Notin *et al.* [31]. There is a trend that the minimum of the curve is shifted towards the Al side where the most stable intermetallic compound Al_2Ca is formed. This indicates strong interactions between the atoms in the liquid at a composition around that of the Al_2Ca compound. Kevorkov *et al.* [26] mentioned that they considered activities and the integral enthalpy of mixing data from the literature to optimize the thermodynamic parameters of the liquid phase. In order to adjust the liquid phase equilibria to experimental values, their calculated enthalpy of mixing had to deviate from the values reported in the literature [26]. Jacob *et al.* [32] determined the thermodynamic activities at 1373 K for liquid Al-Ca alloys using the Kundsen effusion method for the composition range of 0 to 38 at% Ca and the distribution method for the composition range of 44 to 100 at% Ca. Schürmann *et al.* [33] calculated the activities of Ca in the liquid alloys using the boiling point determination technique. Kevorkov *et al.* [26] calculated the activity coefficient of Ca which agrees fairly well with [33] and shows reasonable agreement with [32]. Ozturk *et al.* [28] calculated the activity of Ca at 1600 K and compared it with both [32] and [33].

Several researchers measured the enthalpy of the formation of Al_2Ca and Al_4Ca compounds. Notin *et al*. [31] determined the enthalpy of the formation of these compounds at 953 and 1038 K experimentally. There is a reasonable agreement with the values of the enthalpy of formation for Al_2Ca between Kevorkov *et al*. [26] and Notin *et al*. [31]. The small difference between them may be due to the difference in heat capacity ΔC_p of the formation reaction between room temperature and 1038 K [26]. For the $Al_{14}Ca_{13}$ intermetallic compound, there is no experimental enthalpy of formation data reported in the current literature up to date due to the sluggish formation kinetics of the phase and thus the difficulty of preparing an $Al_{14}Ca_{13}$-rich sample [28]. The enthalpy of the formation of Al_3Ca_8 stoichiometric phase was determined by Kevorkov *et al*. [26] by drop solution calorimetry. During the optimization of the Al-Ca system, Al-fcc and Ca-fcc are considered as the reference states for the Gibbs energy of formation for the four intermetallic compounds (Al_4Ca, Al_2Ca, $Al_{14}Ca_{13}$ and Al_3Ca_8).

Optimization of Phase Diagram and Thermodynamic Properties

Phase Diagram: The model calculated phase diagram of the Al-Ca system in relation to calculated and experimental results from the literature is shown in Figure 6.

It can be seen from Figure 6 that there is a good agreement between experimental and calculated results. However, the results of Matsuyama *et al*. [24] for the Al-rich side are not consistent with the current analysis. This is due to the fact that they considered Al_4Ca and Al_2Ca as the only intermediate compounds in this system.

The optimized model parameters are given in Table III. Four Redlich-Kister interaction parameters were required to model the liquid phase and two parameters were optimized for the Gibbs energy of formation of each stoichiometric compound. No lattice stability values were added to the pure components.

Comparison between the calculated and experimental results of the critical regions of Al-Ca phase diagram is shown in Table IV.

Thermodynamic Properties: The calculated enthalpy of the mixing of Al-Ca liquid in relation to the experimental results from the literature is presented in Figure 7. Although an
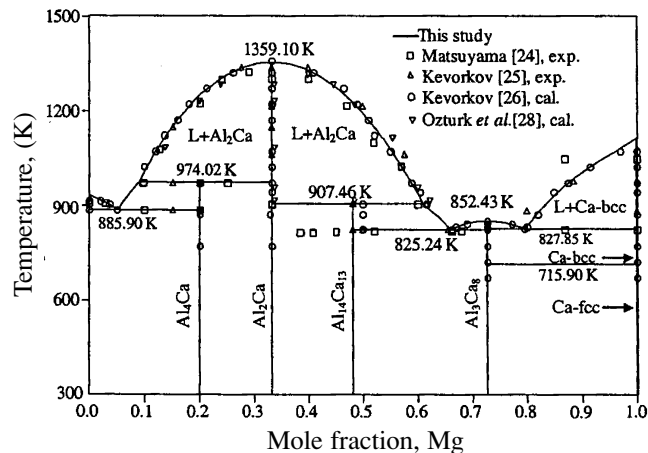
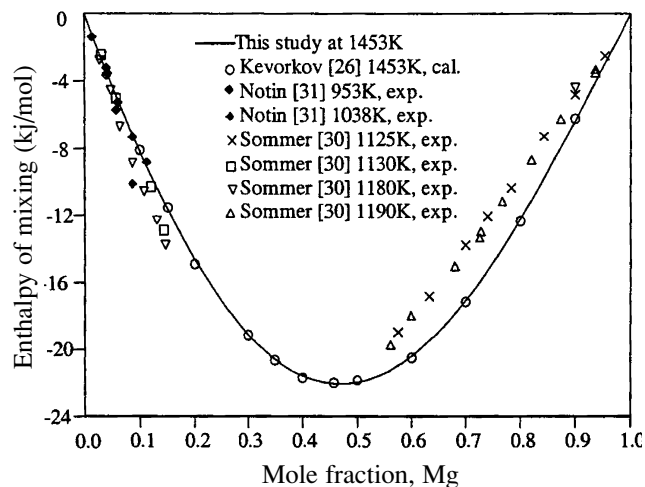Fig. 6. Calculated Al-Ca phase diagram with data from the literature (cal.: calculated, exp.: experimental).

Fig. 7. Enthalpy of mixing of Al-Ca liquid at 1453 K.

excellent agreement between this study and Kevorkov *et al*. [26] and Notin *et al*. [31] was obtained, Figure 7 shows that there is a reasonable agreement with Sommer *et al*. [30].

The calculated activity of Ca at 1373 K agrees very well with the results obtained by Ozturk *et al*. [28]. There is also a

Table III – The model parameters for the liquid phase and stoichiometric compounds of the Al-Ca system

Phase	Terms	a(J/mol-atom)	b(J/mol-atom.K)
Liquid	L_0	-87 894.60	29.8567
	L_1	-12 077.60	4.80628
	L_2	11 427.80	-2.45047
	L_3	-1 058.76	-0.95372
Al_4Ca	ΔG_f	-17 304.40	2.28098
Al_2Ca	ΔG_f	-29 281.70	5.41175
$Al_{14}Ca_{13}$	ΔG_f	-26 058.50	5.63473
Al_3Ca_8	ΔG_f	-15 627.30	2.30139

Table IV – Comparison between calculated and experimental values of critical regions in the Al-Ca system

Reaction	Reaction type	Temp, K	Mole %, Ca in liquid	References
L ↔ Al-bcc	Melting	933.00	0.00	[26]
		933.33	0.00	[28]
		933.45	0.00	This work
L ↔ Ca-bcc	Melting	1,114.90	100.00	[26]
		1,116.66	100.00	[28]
		1,115.00	100.00	This work
Ca-fcc ↔ Ca-bcc	Allotropic	715.9	100.00	[26]
		714.28	100.00	[28]
		715.90	100.00	This work
L ↔ Al_4Ca+ Al-fcc	Eutectic	889.00	5.20	[24]
		886.00	-	[25]
		886.00	5.10	[26]
		885.90	5.45	[28]
		885.90	5.20	This work
L ↔ $Al_{14}Ca_{13}$+ Al_3Ca_8	Eutectic	829.00	-	[25]
		825.10	66.20	[26]
		830.50	66.40	[28]
		825.24	65.97	This work
L ↔ $Al_{14}Ca_{13}$+ Ca-bcc	Eutectic	833.00	-	[25]
		827.50	79.50	[26]
		822.50	80.53	[28]
		827.85	79.69	This work
L + Al_2Ca ↔ Al_4Ca	Peritectic	973.00	10.00	[24]
		973.00	-	[25]
		974.30	9.80	[26]
		974.00	9.89	[28]
		974.02	9.06	This work
L+ Al_2Ca ↔ $Al_{14}Ca_{13}$	Peritectic	906.00	-	[25]
		906.20	61.60	[26]
		905.50	61.97	[28]
		907.46	60.95	This work
L ↔ Al_2Ca	Congruent	1,352.00	33.30	[24]
		1,359.00	-	[25]
		1,359.60	33.30	[26]
		1,354.00	33.33	[28]
		1,359.10	33.33	This work
L ↔ Al_3Ca_8	Congruent	852.00	-	[24]
		853.40	72.70	[26]
		852.00	72.72	[28]
		852.43	72.72	This work

good agreement between the calculated values and the results of Schürmann *et al*. [33] and Jacob *et al*. [32] as shown in Figure 8. The calculated activity of Al agrees fairly well with Sommer *et al*. [30].

The calculated thermodynamic properties for the four intermetallic compounds are compared with other data from the literature in Table V. The thermodynamic properties of

enthalpy, entropy and Gibbs energy of formation of Al_2Ca and Al_4Ca obtained in this study agree very well with the most recent experimental results from the literature [26,34,35]. The existence of the two intermetallic compounds Al_3Ca_8 and $Al_{14}Ca_{13}$ is indicated only in recent studies [25,27] and few experimental values for their thermodynamic properties are reported in the literature. The enthalpy and Gibbs energy of

Table V – Thermodynamic properties of different stoichiometric compounds in the Al-Ca system with experimental data from the literature

Compound	Method [Ref]	T(K)	$\Delta_f H$ kJ/g-atom	$\Delta_f S$ J/g-atom.K	$\Delta_f G$ kJ/g-atom
Al$_2$Ca	HT [34]	673-903	-31.28±0.46	-5.67±0.93	
	PC [31]	1038	-33.40±0.60		
	Emf [35]	800	-34.30±3.50	-6.10±1.10	-28.30±0.30
	DC [26]	298	-29.40±0.90		
	A [26]	800	-29.70	-5.02	-25.70
	Cal*	298	-29.28	-5.38	-27.70
Al$_4$Ca	HT [34]	673-903	-20.18±0.38	-4.29±0.78	
	PC [31]	1038	-18.70 ±0.30		
	Emf [35]	800	-19.40 ±3.30	-1.10±0.50	-17.80±0.14
	A [26]	800	-21.00	-5.49	-16.60
	Cal*	298	-17.27	-2.24	-16.60
Al$_3$Ca$_8$	DC[26]	298	-13.70±1.30		
	A [26]	800	-14.00	-0.47	-13.60
	Cal*	298	-15.63	-2.30	-14.94
Al$_{14}$Ca$_{13}$	A [26] AlCa	800	-22.80	-2.15	-21.10
	Cal*Al$_{14}$Ca$_{13}$	298	-26.06	-5.63	-24.38

HT : Hydrogen Titration, PC: Precipitation Calorimetry, DC: Dissolution Calorimetry A: Assessed, Cal*: Calculated in this work. As temperature does not have any effect on the enthalpy and entropy of the formation of stoichiometric compounds, the calculated values are compared with the values reported at different temperatures.

formation of Al$_3$Ca$_8$ compound agree fairly well with the results from the literature [26], whereas, the thermodynamic properties for Al$_{14}$Ca$_{13}$ are not available in the literature yet. Hence, the calculated thermodynamic properties for this compound were compared with the properties of AlCa in Table V. Nevertheless, it was noticed that the thermodynamic properties of these two compounds are very close.

The enthalpy of formation of the four stoichiometric compounds from the previous experimental results and present calculated values are shown in Figure 9. It can be seen that the results obtained in this study agree with those from the literature. The difference obtained for Al$_{14}$Ca$_{13}$ is due to the fact that Kevorkov *et al.* [26] considered this compound as AlCa as discussed earlier.
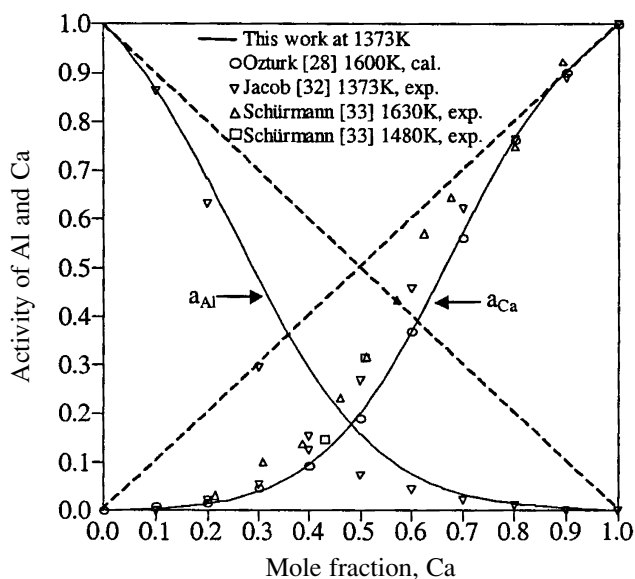

Fig. 8. Activity of Al and Ca in Al-Ca liquid (cal.: calculated, exp.: experimental).
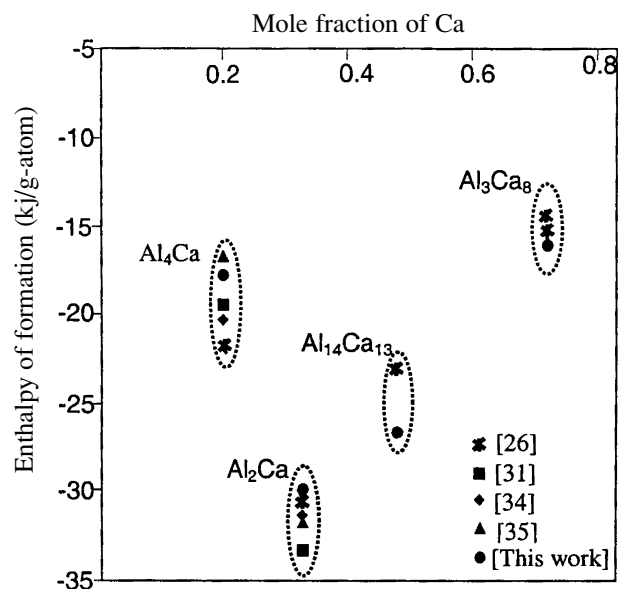

Fig. 9. Enthalpy of formation of different stoichiometric compounds in the Al-Ca system.

Mg-Al SYSTEM

The Mg-Al system has already been optimized. The optimized parameters for this system were taken from COST 507 database [36] because this is the most recent and reliable database. More importantly, this is consistent with the thermodynamic description of the other two binary systems.

Mg-Al-Ca SYSTEM

Phase Diagram

Prince [37] mentioned that Portnoi and Spektorova first published preliminary work on the Mg-Al-Ca system in 1948. They reported a pseudobinary section Mg-Al$_2$Ca with a eutectic liquid composition of about 79 at% Mg. They also report-

Table VI – Calculated invariant points of the Mg-Al-Ca system based on mole fraction

Reaction / reaction type	Temp (K)	Mole fraction			Reference
		Ca	Mg	Al	
L ↔ Mg$_2$Ca + Ca-fcc + Al$_3$Ca$_8$ / eutectic E$_1$	710.54 683.00 703.10	0.716 0.680 0.719	0.252 0.190 0.232	0.032 0.130 0.049	This work [5] [40]
L ↔ Mg$_2$Ca + Al$_3$Ca$_8$ + Al$_{14}$Ca$_{13}$ / eutectic E$_2$	764.19 761.00 769.40	0.612 0.640 0.612	0.133 0.080 0.153	0.255 0.280 0.235	This work [5] [40]
L ↔ Mg$_2$Ca + Al$_2$Ca + (Mg) / eutectic E$_3$	754.72 783.00 770.20	0.109 0.120 0.110	0.799 0.790 0.840	0.092 0.090 0.050	This work [37] [40]
L ↔ γ + Al$_2$Ca + (Mg) / eutectic E$_4$	701.50 697.00 706.40	0.012 0.020 0.005	0.672 0.650 0.682	0.316 0.330 0.313	This work [5] [40]
L ↔ Al$_2$Ca + γ + β / eutectic E$_5$	715.92	0.011	0.412	0.577	This work
L ↔ Al$_4$Ca+ (Al)+ β / eutectic E$_6$	717.00 715.00 720.40	0.011 0.020 0.006	0.347 0.340 0.351	0.642 0.640 0.643	This work [5] [40]
L ↔ Mg$_2$Ca + Al$_3$Ca$_8$ / saddle S$_1$	768.11 765.00 771.80	0.632 0.640 0.627	0.153 0.100 0.173	0.215 0.260 0.200	This work [5] [40]
L ↔ Mg$_2$Ca+Al$_2$Ca / saddle S$_2$	902.96 1,008.00 912.10	0.337 0.360 0.334	0.456 0.230 0.496	0.207 0.410 0.170	This work [5] [40]
L ↔ Al$_2$Ca+ (Mg) / saddle S$_3$	773.88 808.00 - 808.00 815.00	0.075 - 0.790 - 0.740- 0.830 - 0.054	0.778 0.780- 0.790 - 0.832	0.147 - - [37] - 0.114	This work [5] [37] [38] [40]
L ↔ Al$_2$Ca + γ / saddle S$_4$	723.80 717.00 732.50	0.013 0.030 0.006	0.565 0.490 0.541	0.423 0.480 0.453	This work [5] [40]
L ↔ Al$_2$Ca + β / Saddle S$_5$	718.37	0.015	0.372	0.613	This work
L + Al$_2$Ca ↔ Al$_{14}$Ca$_{13}$+ Mg$_2$Ca / ternary quasiperitectic P$_1$	823.89 757.00 829.20	0.539 0.580 0.542	0.184 0.130 0.195	0.277 0.290 0.263	This work [5] [40]
L+ Al$_2$Ca ↔ Al$_4$Ca+ β / ternary quasiperitectic P$_2$	717.39	0.011	0.356	0.633	This work

ed a ternary eutectic point at about 9 at% Al and 79 at% Mg. In 1959 the Dow Chemical Company confirmed the eutectic nature of the Mg-Al$_2$Ca section and placed the eutectic composition between 74 and 83 at% Mg. According to Prince [37], a partial isothermal section of the Mg-rich corner at 563, 643 and 723 K was reported by Catterall and Pleasance in 1957 and in 1958, Stacey recognized the possibility of a solid solution of Mg in Al$_2$Ca instead of a separate ternary phase.

Gröbner et al. [5] investigated the phase equilibria of the Mg-Al-Ca system experimentally. They reported several invariant reactions in the ternary Mg-Al-Ca system. Two peritectic reactions, one eutectic reaction and two saddle points were confirmed by experimental data. Large ternary solubilities for three binary phases Mg$_2$Ca, Al$_2$Ca and Al$_3$Ca$_8$ were reported in their work.

At the same time, Tkachenko et al. [38] published their experimental work on this system. They studied the phase equilibira in the composition range of 50 to 100 wt% Mg and reported an isothermal section at 150 °C, the liquidus projection on Mg-rich corner and vertical section at 4.5, 8.5 and 16 wt% Al. They determined the peritectic transformation Lp + Al$_2$Ca (Mg) + Mg$_{17}$Al$_{12}$ that occurs at 470 °C.

On the other hand, Ozturk et al. [39] performed experimental work to verify the thermodynamic database developed for the Mg-Al-Ca system. During their study, the experimental work was still underway. Due to a lack of experimental data, they did not consider the solubility of the binary compounds and no ternary interactions were introduced either. Hence, the thermodynamic description of the Mg-Al-Ca ternary system was obtained by combining the data of the three binary systems. They also calculated five isothermal sections at 298, 563, 643, 673 and 723 K. There was a good agreement between the experimental and calculated values except for the extent of the Mg phase field at 643 K where the calculation predicted less Ca% than the measured values.

They mentioned that this inconsistency might be due to the calcium loss during alloy preparation.

A detailed XRD and transmission electron microscopy (TEM) investigation by Luo [4] suggested the presence of a ternary solid solution phase. It was represented by the chemical formula of (Mg,Al)$_2$Ca. This is in agreement with the result of Ozturk et al. [39]. In fact, the metallurgical stability of the ternary (Mg,Al)$_2$Ca phases and their interfacial coherency with the magnesium matrix were reported to be responsible for the improved creep resistance of Mg-Al-Ca alloys at temperatures up to 473 K.

Calculated Mg-Al-Ca Phase Diagram

The ternary phase diagram was calculated by not considering any ternary interaction parameters. Ternary compounds were not included because of the uncertainty related with their existence, stability, homogeneity range and melting temperature. In this work the solid solubility between the binary compounds was not considered due to a lack of experimental data. Taking into consideration all the thermodynamic and phase equilibria data stated for the binary phases and SGTE data [6] for pure elements, the Mg-Ca-Al system was calculated.

Liquidus Projection of Mg-Al-Ca System

Isothermal sections are directly calculated from the database developed for this system. Prior to solidification at high temperatures (above 1360 K), the whole concentration triangle is composed of a homogeneous liquid phase and obviously no phase boundaries exist. At 1300 K, the primary crystallization of Al$_2$Ca sets in but is still above the melting point of the three components. At 700 K, no residual liquid phase was present. A two-dimensional representation of the ternary liquidus surface

Table VII – Thermodynamic analysis of three alloys in the Mg-Al-Ca system with DSC measurements from [41] and [42]

Sample #	Composition (wt%)			DSC thermal signals (ºC)	Thermodynamic prediction from this work	
	Ca	Mg	Al		Temp. (ºC)	Reactions
1	4.5	78	17.5	555h/550c 443h/431c	539 485 427	L/(Mg)+L (Mg)+L/Al$_2$Ca+(Mg)+L Al$_2$Ca+(Mg)+L/ (Mg)+ Al$_2$Ca+ γ
2	23.4	44	32.6	760c 535h/523c 472/443c	742 504 170	L/L+ Al$_2$Ca L+ Al$_2$Ca/Al$_2$Ca+(Mg) Al$_2$Ca+(Mg)/ Al$_2$Ca+(Mg) + γ
3	24.19	73.08	2.73	445.37c 521.32c 570c	480 503 600	L/L+Mg$_2$Ca L+Mg$_2$Ca/ L+Mg$_2$Ca+(Mg) L+Mg$_2$Ca+(Mg)/ Mg$_2$Ca+(Mg)+Al$_2$Ca

may be obtained as an orthogonal projection of a liquidus line from isothermal sections at different temperatures upon the base composition triangle. Such polythermal projection of the liquidus of the Mg-Al-Ca system is shown in Figures 10 and 11 which are based on mole and weight fraction, respectively. The univariant valleys are shown as heavier lines. By convention, the large arrows indicate the directions of decreasing temperature along these lines. As solidification proceeds by the precipitation of primary phases, the composition of the liquid changes and this change is represented by a path on the liquidus projection, occurring in a direction representing a lowering of the temperature on the liquidus surface. Figures 10 and 11 show the six ternary eutectic (E_1 to E_6) points, two ternary quasi peritectic points (P_1 to P_2) and five saddle points (S_1 to S_5). In the ternary phase diagram, e_1 to e_8 and p_1 to p_2 indicate the binary eutectic and peritectic points, respectively. Calculated ternary invariant points are listed in Table VI.

    Recently, Parvez *et al.* [41] and Wang *et al.* [42] investigated the Mg-Al-Ca system experimentally using DSC and XRD techniques. For different samples, the DSC measurements and the calculated thermal arrests along with the phase field boundary are listed in Table VII. These experimental results are compared with thermodynamic calculations to confirm the phase transformation temperature and associated reactions. The vertical sections calculated using the database from this study are shown in Figure 12.

    Figure 12 and Table VII show that the calculated liquidus temperature match well with the experimental results of [41] and [42]. However, there is some discrepancy between the calculated phase transformation temperatures and those reported in [41] and [42]. For instance, the transformation temperature predicted by thermodynamic modelling at 485 and 170°C for samples 1 and 2, respectively were not observed in the DSC signals.
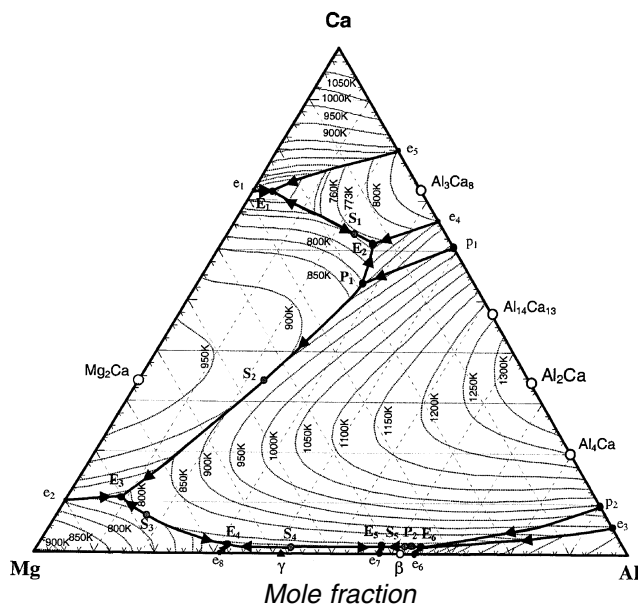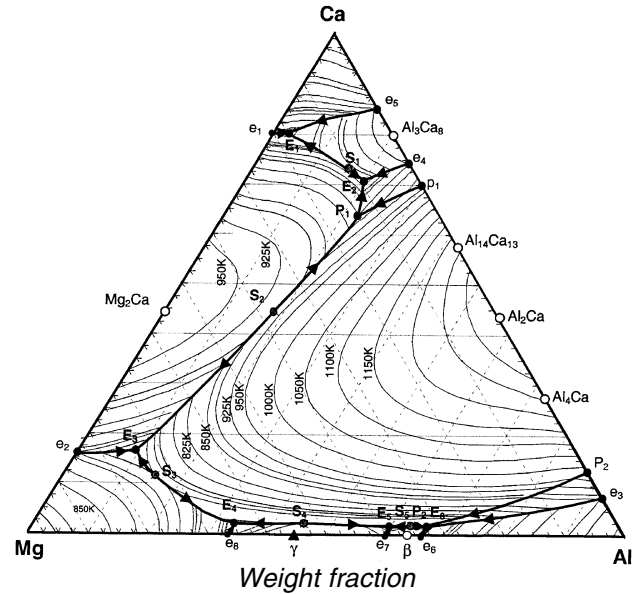

Fig. 11. Liquidus projection for the Mg-Al-Ca system based on weight fraction.

SUMMARY

In this research, Mg-Al-Ca system was thermodynamically modeled and from the results, the following conclusions are drawn.

1.   A minimum number of optimized thermodynamic coefficients was used to calculate the phase diagram and other integral and partial thermodynamic properties which were in good agreement with data reported in the literature.

2.   A self-consistent thermodynamic description for the Mg-Al-Ca system was obtained.

3.   The optimized model parameters can also be used to predict thermodynamic properties which are not available in the literature.

4.   By combining model equations for the Gibbs energy of the phases of the three binary systems, the ternary Mg-Ca-Al phase diagram was obtained. In this system, six ternary eutectic points in the temperature range of 701 to 764 K, two peritectic points in the temperature range of 717 to 825 K and five saddle points in the temperature range of 724 to 904 K were found.

5.   Vertical sections for different alloys were calculated and compared with the experimental data reported in the literature which confirmed the melting and the phase transformation temperatures satisfactorily.

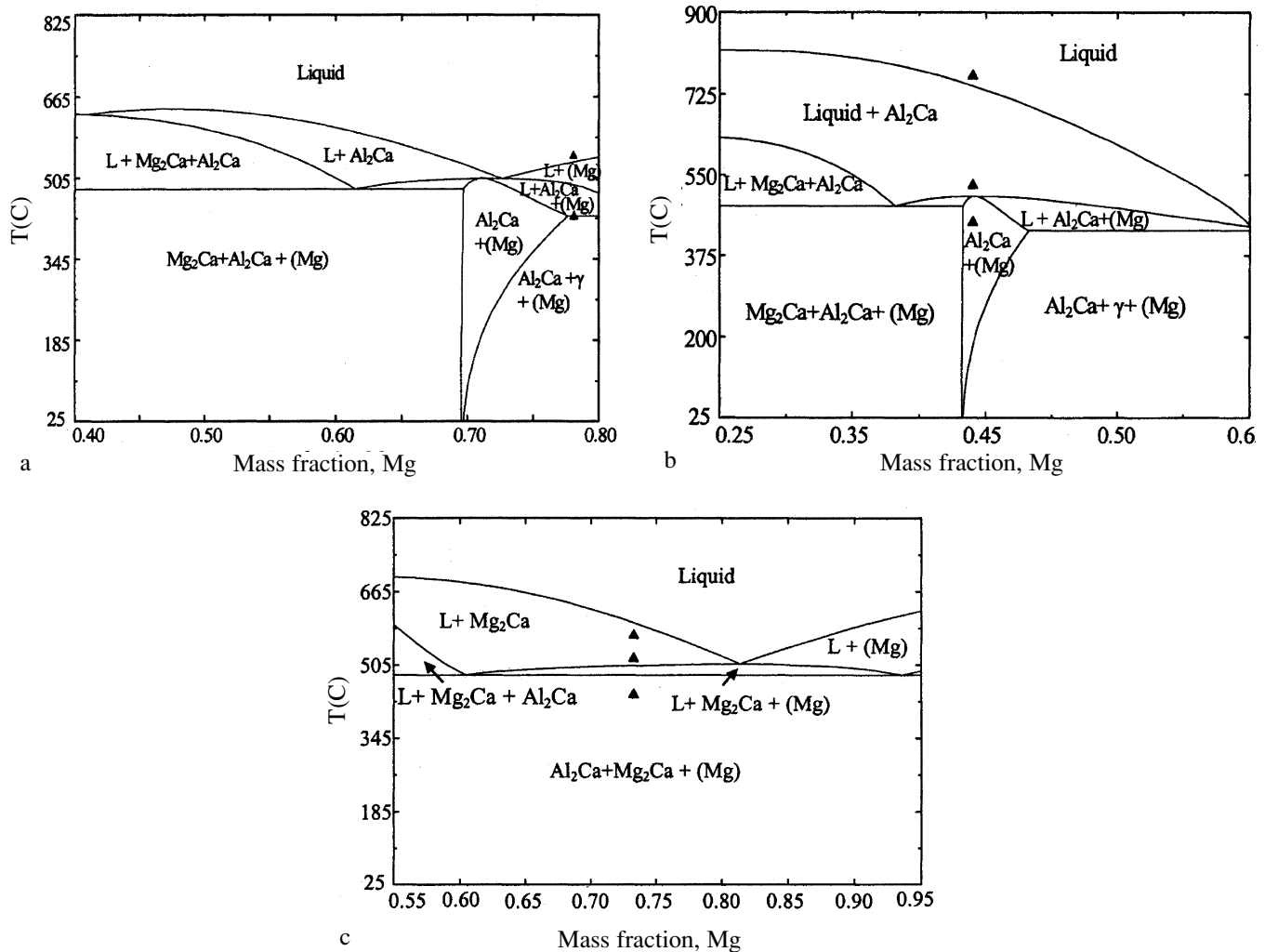Fig. 10. Liquidus projection for the Mg-Al-Ca system based on mole fraction.

Fig. 12. Calculated vertical sections with experimental results from [41, 42] a) at constant 17.5 wt% Al with DSC signals of sample 1 (4.5/78/17.5 wt% Ca/Mg/Al), b) at constant 32.6 wt% Al with DSC signals of sample 2 (23.4/44/32.6 wt% Ca/Mg/Al) and c) at constant 2.73 wt% Al with DSC signals of sample 3 (24.19/73.08/2.73 wt% Ca/Mg/Al).

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