THERMODYNAMIC MODELING OF THE Mg-Al-Bi AND Mg-Al-Sb SYSTEMS

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RÉSUMÉ

Ces dernières années, l'usage du magnésium dans le secteur de l'automobile a été en croissant. Les études récentes en recherche et développement du magnésium et de ses alliages se sont surtout concentrées sur la réduction de poids, l'économie d'énergie et la limitation des impacts environnementaux. À cet égard, les chercheurs ont identifié certains éléments clés comme Al, Zn, Si, Pb, Ge, Bi, Sr, etc. qui peuvent être incorporés aux alliages de magnésium. Ces éléments sont perçus comme de première importance dans le design de nouveaux alliages de magnésium ayant des propriétés structurales supérieures comparés aux alliages présentement existants dans l'industrie automobile.

Les améliorations continues dans la modélisation des alliages (et autres matériaux) par la technique CALPHAD a conduit au développement de banques de données thermodynamiques. Ces banques de données contiennent la description de l'énergie libre de Gibbs pour toutes les phases présentes dans le système par rapport à la température et la composition. En utilisant des logiciels de minimisation de l'énergie libre de Gibbs tel que FactSage, il est possible d'avoir accès à ces banques de données pour calculer les quantités et les compositions de toutes les phases à l'équilibre à n'importe quelles température et composition dans des alliages à plusieurs composants ou encore pour calculer la quantité des phases à l'équilibre ou non durant le refroidissement.

De telles banques de données thermodynamiques sont conçues grâce à des évaluations critiques, des modélisations et des optimisations. Lors d'une optimisation thermodynamique, les paramètres ajustables du modèle sont calculés en utilisant simultanément toutes les données thermodynamiques et du diagramme de phases afin d'obtenir un ensemble d'équations du modèle en fonction de la température et de la composition. Les données thermodynamiques, telles que les activités, peuvent aider dans l'évaluation du diagramme de phases et les données du diagramme de phases peuvent être utilisées pour déduire les propriétés thermodynamiques. Par conséquent, il est

possible de résoudre des inconsistances dans les données disponibles. À partir des équations du modèle, toutes les propriétés thermodynamiques et les diagrammes de phases peuvent être recalculés et des interpolations et extrapolations peuvent être réalisées de manière thermodynamiquement correcte. Les données sont donc rendues consistantes entre elles et avec les principes de la thermodynamique; de plus, elles peuvent être stockées sous forme de paramètres du modèle dans des banques de données qui peuvent é leur tour être sauvegardées dans des ordinateurs.

Le présent travail fait parti d'un projet à grande échelle de développement de banques de données thermodynamiques pour le système Mg-Sn-Al-Zn-Si-Mn-Pb-Ge-Sb-Bi-Ge-etc. Sous cet aspect, les quatre binaires Mg-Bi, Mg-Sb, Al-Bi et Al-Sb ont été évaluées et optimisées de façon critique en se basant sur les diagrammes de phases et les données thermodynamiques disponibles. Les paramètres du modèle obtenus, suite à l'optimisation simultanée de toutes les données, ont été utilisé pour représenter les énergies libres de Gibbs de toutes les phases en fonction de la température et de la composition. Les paramètres optimisés furent ensuite combinés à ceux obtenus précédemment pour d'autres systèmes binaires pour estimer les propriétés thermodynamiques de solutions ternaires dans les systèmes Mg-Al-Bi et Mg-Al-Sb. Des modèles géométriques appropriés furent alors utilisés pour ces estimations. Les diagrammes ternaires furent calculés et comparés aux données expérimentales disponibles. D'ordinaire, les données ternaires sont très bien reproduites avec les paramètres binaires du modèle. Les prédictions faites à l'aide des nouveaux diagrammes de phases seront utiles pour planifier de futures expériences lors d'une étude détaillée de ces systèmes ternaires.

ABSTRACT

In recent years the magnesium application in automobile sector has been increasing. Recent research and development studies of magnesium and its alloys have focused on weight reduction, energy saving and limiting environmental impact. In this regard researchers have identified incorporating certain key alloying elements like Al, Zn, Si, Pb, Ge, Bi, Sb, Sr, etc. to the magnesium alloys.These alloying elements are seen as potential elements for novel magnesium alloy design with superior structural properties to the existing alloys used for automotive applications.

The continued developments in CALPHAD (Chapter 2) assessment of alloys (and other materials) brought about the development of thermodynamic databases. These databases contain the Gibbs free enegy description of all the phases present in a system with respect to temperature and composition. With the use of Gibbs energy minimization software such as FactSage one can have access to these databases to calculate the amounts and compositions of all phases at equilibrium at any temperature and composition in multicomponent alloys, the amount of phases appearing during equilibrium or non-equilibrium cooling can be calculated too.

Such thermodynamic databases are prepared by critical evaluation, modeling, and optimization. In a thermodynamic "optimization" adjustable model parameters are calculated using, simultaneously, all available thermodynamic and phase-equilibrium data in order to obtain one set of model equations as functions of temperature and composition. Thermodynamic data, such as activities, can aid in the evaluation of the phase diagrams, and information on phase equilibria can be used to deduce thermodynamic properties. Thus, it is frequently possible to resolve discrepancies in the available data. From the model equations, all of the thermodynamic properties and phase diagrams can be back-calculated, and interpolations and extrapolations can be made in a thermodynamically correct manner. The data are thereby rendered self-consistent and

consistent with thermodynamic principles, and the available data can be stored as set of model parameters in databases which can be stored in computers.

The presnt work is the part of wide thermodynamic database development project for Mg-Sn-Al-Zn-Si-Mn-Pb-Ge-Sb-Bi-Ge-etc system. In this regard, for the database development four binaries: Mg-Bi, Mg-Sb, Al-Bi and Al-Sb were critically evaluated and optimized based upon available phase-equilibrium and thermodynamic data. The model parameters obtained as a result of simultaneous optimization have been used to represent the Gibbs energies of all phases as functions of temperature and composition. Optimized binary model parameters were combined with those of previously optimized binary systems to estimate the thermodynamic properties of ternary solutions in the Mg-Al-Bi and Mg-Al-Sb systems. Proper "geometric" models were used for these estimations. Ternary phase diagram were calculated and compared with experimental data where available. Usually, the available ternary data were well reproduced with only the binary model parameters. These phase diagrams predictions will be helpful in future planning of experiments for the detailed study of these ternary systems.

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LIST OF SYMBOLS

C_p	Molar heat capacity (J/mol·K)
G^{0}_{i}	Standard Gibbs energy of <i>i</i>
G^m	Gibbs energy of solution
G^{E}	Excess Gibbs energy in solution
g^{E}	Molar excess Gibbs energy in solution
$g^{0}{}_{i}$	Molar Gibbs energy of <i>i</i>
$\varDelta g_{ij}$	Gibbs energy change for the formation of two moles of <i>i-j</i> pairs
H^{0}_{i}	Standard enthalpy of <i>i</i>
ΔH	Molar enthalpy of mixing
ΔH_T	enthalpy of formation of the compound from elements
n _{ij}	Number of moles of <i>i-j</i> bonds in one mole of solution
q^{ij}_{AB}	Excess interaction parameter between A and B
S^{0}_{i}	Standard entropy of component <i>i</i>
ΔS_T	entropy of formation of the compound from elements
ΔS^{conf}	Molar configurational entropy of solution
S ^{non-conf}	Molar non-configurational entropy of solution
n _i	Number of moles of component <i>i</i>
Т	Absolute temperature (K)
wt. %	Weight percent
${\mathcal Y}_i$	Site fraction of component <i>i</i>
Y_i	Coordination-equivalent fractions
X_i	Mole fraction of component <i>i</i> in solution
X_{ij}	Pair fraction of <i>i-j</i> pairs
Z_i	Coordination number of <i>i</i>
$Z^{i}_{\ ii}$	The values of Z_i when all the nearest neighbors of an <i>i</i> are <i>i</i> 's
Z^{i}_{ij}	The values of Z_i when all the nearest neighbors of an <i>i</i> are <i>j</i> 's
-	

Chapter 1: Introduction

Magnesium is the lightest of all the engineering materials known and has good ductility, better noise and vibration damping characteristics than aluminium and excellent castability Alloying magnesium with aluminium, manganese, rare earths, thorium, zinc or zirconium increases the strength to weight ratio making them important materials for applications where weight reduction is important, and where it is imperative to reduce inertial forces. Because of this property, denser material, not only steels, cast iron and copper base alloys, but even aluminium alloys are replaced by magnesium-based alloys. Auto manufacturing companies have made the most of research and development on magnesium and its alloys. They are being forced by the global trends to manufacture lighter, more environmentlal friendly, safer and cheaper cars and magnesium and its alloys provide them with the alternative to achieve their objectives.

Specific strength and specific stiffness of materials and structures are important for the design of weight saving components. Weight saving is particularly important for automotive bodies, components and other products where energy consumption and power limitations are a major concern. There is a little difference between the specific stiffness of Mg, Al and Fe but specific strength of magnesium alloys is considerably higher than Al and Fe but on the other hand magnesium alloys suffer from their limitations (Tkachenko et al.2006). Magnesium alloys have low high temperature strength and poor creep resistance. Grain boundary sliding has been observed to be the dominant creep mechanism in the stress-temperature ranges required for automotive applications (Pekguleryuz and Kaya, 2003).Magnesium seems to creep at low temperatures where the dominant slip system is basal within the grains and at elevated temperarture the diffusion dependent mechanisms become dominant (Baril et al.2003).Mg-Al based alloys are one major group among magnesium based alloys. The strength of these alloys is improved by forming a solid solution of Al in magnesium matrix. The microstructure of these alloys is characterised by the dispersion of Mg₁₇Al₁₂ eutectic in grain boundary. Being exposed at elevated temperature (>150°C) for longer period of time supersaturated magnesium solution transforms to magnesium matrix with coarsely dispersed Mg₁₇Al₁₂ precipitates in the

matrix which contribute to grain boundary migration and creep deformation.Futhermore $Mg_{17}Al_{12}$ is prone to aging and has poor metallurgical stability which limited its application in high temperatures (Pekguleryuz et al.2003).

A significant research for improving the creep properties of magnesium alloys was underway to improve the creep properties and as result few commercial magnesium alloys are already on the market. These alloys contain mostly aluminum for good castability and strontium, calcium and rare earth elements for high-temperature stability. Several rareearth elements act as grain refiners in magnesium alloys and form the basis of creep-resistant alloys. Moreover Mg-Sn based alloys are also seen as promosing candidates for improving creep resistance without comprising on corrosion and castability. Lot of researchers have focused a lot of attention on Mg-Sn based alloy systems in order to develop alloys with enhanced mechanical properties (Kozlov et al.2008, Bowles et al.2004, Bursikj et al.2006).

Magnesium alloys are perceived as future alloys with widespread applicational in automobile and aeronautical engineering and it is evident that there is urgent need for developing new or improved magnesium alloys to fully exploit the potential of magnesium light weight properties. Conducting experiments for exploring new alloy systems can be expensive and time consuming In view of large number of possible compositions, components and processing parameters a powerfull tool like Computational Thermodynamics is required to proceed in the right direction. Computational thermochemistry based on the Calphad method is a modern tool that supplies quantitative data to guide the development of alloys or the optimization of materials processing. It enables the calculation of multicomponent phase diagrams and the tracking of individual alloys during heat treatment or solidification by calculation of phase distributions and phase compositions. It also allows the simulation of phase transformations during solidification of magnesium-alloys, which are responsible for the development of as-cast microstructures. This can be done either by using the two simple extreme models of equilibrium solidification or Scheil solidification, or by more sophisticated models that require additional kinetic material parameters. In light of all the advantages of application of computational thermodynamics to magnesium alloy desin it was required to develop a database containing model parameters, giving the thermodynamic properties of all the involved phases as functions of temperature and composition. Such a thermodynamic database will provide a clear guideline for selection of these alloys and will help to avoid unproductive long-term experiments with alloys having less potential for commercial purposes. Using these databases with Gibbs energy minimizing software like FactSage (FactSage 2009), one will be able to calculate all the important processing parameters related to magnesium alloy development.

The present work deals with the critical evaluation and optimization of the binary systems Mg-Bi, Mg-Sb, Al-Bi, Al-Sb and Mg-Al-Bi and Mg-Al-Sb systems.

In this work, first the binary systems: Mg-Bi, Mg-Sb, Al-Bi and Al-Sb have been critically evaluated. (All other binary sub-systems have been critically evaluated and optimized previously.) All available thermodynamic and phase diagram data for these systems were collected and critically assessed for their reliability. The Gibbs energies of all phases were represented by appropriate model equations. The parameters of these models were obtained by an optimization procedure using the FactSage (FactSage 2009) software. These binary parameters were then used along with the models to predict the thermodynamic properties and phase diagrams of the ternary systems: Mg-Al-Bi and Mg-Al-Sb .The predictions for the ternary systems were compared with the available ternary data, and the models were refined through the inclusion of ternary parameters, where required, for those systems where sufficient data were available (Chapter 4).

Chapter 2: Literature review

In this chapter a general review of the literature on the topic of evaluation and optimization of phase diagrams is given. In this literature survey, the doctoral thesis by Jung (Jung, 2003) and Master's thesis by Adarsh (Adarsh, 2008) on a similar work on database preparation for oxides and magnesium alloys database was of immense help. The literature on specific systems optimized in the present study are not reviewed in this chapter as they are presented in Chapters 3 and 4 which are in the form of articles submitted to journals.

2.1 CALPHAD

For 30 years now, many international groups of scientists have been working closely on developing methods and to produce data, which provides a mutual consistent description of thermodynamic data and phase diagrams of many material systems. This group is known as CALPHAD (CALculation of PHAse Diagrams) and the methodology that they use has become sufficiently well known and is reffered as "The CALPHAD approach".

Under the CALPHAD technique, all types of thermodynamic information such as phase diagram data and thermodynamic data are critically evaluated and optimized simultaneously. Parametric models that best describe the thermochemistry of phases have been developed and substantial progress has been made in the thermodynamic modeling of solutions especially liquid, intermetallic compounds, oxides, order-disorder transformations etc.

The relation between the thermodynamic properties and the equilibrium phase diagram for a binary system has been described in detail by Van Laar (Van Laar, 1908).Wagner (Wagner, 1952) discussed a number of features of equilibrium phase diagram and their relation to Gibbs energy, enthalpy and entropy values. Meijering (Meijering, 1959) has also summarized earlier work on construction of phase diagram using thermochemical data.

In the early years, the phase diagrams were derived by common tangent construction method for a hand calculated Gibbs energy curve. This approach to the phase diagram calculation has been best summarized by Kubascheweski and Chart (Kubascheweski and Chart, 1965).

A major advance in the capability for wider use of thermodynamic phase diagram calculation techniques was provided by Kaufman (Kaufman and Bernstein, 1970) who illustrated the importance and use of the concept of "lattice stabilities" in calculating phase diagrams. Lattice stability values, the differences in Gibbs energy between different stable and metastable crystallographic forms of an element as a function of temperature, allowed the equilibrium boundaries between the different phases of asystem to be calculated more accurately.

Hillert (Hillert, 1968) assessed that phase equilibrium calculation can be more progressed if experimental phase diagram data and thermodynamic data were combined using computer techniques and resulting assessed values employed more universally. At this time the computer calculations of phase diagram were in nascent stage and apart from Kaufman's group, there were only three groups located at the University of Grenoble, France (led by I. Ansara), the Royal Institute of Technolgy, Stockholm, Sweden (led by M. Hillert) and at the National Physical Laboratory, Teddington, UK (led by O. Kubaschewski) that were engaged in computer calculation of phase diagrams.

The first CALPHAD meet was organised by Larry Kaufmann in 1973 and phase diagram of many binary systems were calculated from the thermodynamic properties of various phases using interaction models. The interpolation techniques (chapeter 2.5) of predicting the higher order systems from the binary sub systems were discussed too. Later in conjuction with the CALPHAD meet the CALPHAD journal, which was first published in 1979 became a primary literature source for articles representing detailed thermodynamic description and optimized parameters of many alloy, slags, oxides and many aqeous systems.

In subsequent years the previous hand calculation procedure in order to establish the consistency between experimentally determined thermodynamic properties and phase boundary values was replaced by the publication of optimization of phase diagram data by least square optimization method by inputting different type of data by Lukas et al.(Lukas

et al. 2007).Currently a number of software packages combined with databases are commercially available for calculating the mulit phase diagrams and phase Equilibria. The most prominent ones include FactSage (FactSage, 2009), MTDATA (MTDATA, 2002), Thermo-Calc (Thermo-Calc, 2002).

2.2 Thermodynamic modeling

Thermodynamic models are required to adequately represent the thermodynamic properties of materials. Complex solutions require sophisticated and refined models for the proper representation of their thermochemical properties. A good model should be able to represent the thermodynamic properties with just a small numbers of adjustable parameters. For this, the model should be based on the structure of the solution to adequately represent the configurational entropy of the solution. Also these models have high predictive capability in higher-order systems. Hence, models should be developed which can describe the configurational entropy of the solutions without the addition of large arbitrary model parameters.

General Equations:

The standard Gibbs energy of a pure component *i* is written as: $G^{0}_{i} = H^{0}_{i} - TS^{0}_{i}$ (2.1) where G^{0}_{i}, H^{0}_{i} and S^{0}_{i} are respectively the standard Gibbs energy, enthalpy and entropy of *i*, and *T* is the absolute temperature.

When two components A and B are mixed then the energy of the solution depends upon the interaction between the A and B atoms or molecules. The Gibbs energy of a solution in which there is no interaction between A and B is an ideal solution for which:

$$G^{m} = g^{\theta}_{A} n_{A} + g^{\theta}_{B} n_{B} - T\Delta S^{conf}$$

$$\tag{2.2}$$

where G^m is the molar Gibbs energy of the solution, g^0_i is the molar Gibbs energy of component *i*, and ΔS^{conf} is configurational entropy obtained by randomly mixing n_A moles of A and n_B mole of B on the same sublattice:

$$\Delta S^{cony} = -R \left(n_A \ln X_A + n_B \ln X_B \right) \tag{2.3}$$

Practically however, all solutions do have interactions among the atoms mixing to form a solution. Such interactions can be called g^E , the molar excess Gibbs energy of the solution. In this case the energy of the solution is given by:

$$G^{m} = g^{0}_{\ A}n_{A} + g^{0}_{\ B}n_{B} - T\Delta S^{conf} + (n_{A} + n_{B}) g^{E}$$
(2.4)

 g^E is often expanded as a polynomial in the mole fractions as:

$$\mathbf{g}^E = \Sigma \, q^{ij}{}_{AB} \, X^i{}_A \, X^j{}_B \tag{2.5}$$

where the excess interaction parameters q^{ij}_{AB} (= a +bT +cT² +) may be temperature dependent.

In many cases, the thermodynamic properties of a binary solution can be described by using the expression in Eq. 2.5. Although it is satisfactory in binary systems not showing large deviations from ideality, problems arise when such an expression is used to predict the thermodynamic properties of higher-order systems from the model parameters of the lower-order sub-systems. In this case, large arbitrary parameters are often needed in these higher-order systems to reproduce the available data. Even sometimes in a binary system also a large number of interaction parameters are needed in this simple polynomial based model in order to adequately represent all the thermodynamic properties of the system.

To adequately represent the thermodynamic properties of the liquid phase, Pelton et al. (Pelton et al.2000) and Pelton and Chartrand (Pelton and Chartrand, 2001) developed the Modified Quasichemical Model (MQM). They modified the classical quasichemical model by improving the configurational entropy term of the model. MQM has been applied not only to metallic alloys but to liquid slags, sulphides, and salts. The utility of the MQM over a random- mixing model can be better realized with these solutions which show more ordering than metallic solutions, and where the configurational entropy terms become more important.

2.3 Modified Quasichemical Model (MQM)

In the present work the MQM was used to model the liquid alloys in the binary and ternary systems. Recently, the model has been described in detail by Pelton et al. (Pelton et al. 2000). A brief summary of this model is presented here.

In the MQM in the pair approximation, the following pair exchange reaction between atoms *A* and *B* on neighboring lattice sites is considered:

$$(A - A) + (B - B) = 2(A - B); \quad \Delta g_{AB}$$
 (2.6)

where (i - j) represents a first-nearest-neighbor pair. The non-configurational Gibbs energy change for the formation of two moles of (A - B) pairs is Δg_{AB} .

Let n_A and n_B be the number of moles of A and B, n_{ij} be the number of moles of (i - j) pairs, and Z_A and Z_B be the coordination numbers of A and B. The pair fractions, mole fractions, and "coordination-equivalent" fractions are defined respectively as:

$$X_{ij} = n_{ij} / (n_{AA} + n_{BB} + n_{AB})$$
(2.7)

$$X_{A} = n_{A} / (n_{A} + n_{B}) = 1 - X_{B}$$
(2.8)

$$Y_{A} = Z_{A}n_{A}/(Z_{A}n_{A} + Z_{B}n_{B}) = Z_{A}X_{A}/(Z_{A}X_{A} + Z_{B}X_{B}) = 1 - Y_{B}$$
(2.9)

The following equations may be written:

$$Z_A X_A = 2n_{AA} + n_{AB} \tag{2.10}$$

$$Z_B X_B = 2n_{\rm BB} + n_{AB} \tag{2.11}$$

The Gibbs energy of the solution is given by:

$$G^{m} = \left(n_{A}g_{A}^{\circ} + n_{B}g_{B}^{\circ}\right) - T\Delta S^{\operatorname{config}} + \left(n_{AB}/2\right)\Delta g_{AB}$$

$$(2.12)$$

$$= \left(n_A g_A^\circ + n_B g_B^\circ\right) - T \Delta S^{\text{config}} + g^E \tag{2.13}$$

where g_A° and g_B° are the molar Gibbs energies of the pure components and ΔS^{config} is the configurational entropy of mixing given by randomly distributing the (A - A), (B - B)and (A - B) pairs in the one-dimensional Ising approximation:

$$\Delta S^{\text{config}} = -R(n_A \ln X_A + n_B \ln X_B) - R[n_{AA} \ln(X_{AA}/Y_A^2) + n_{BB} \ln(X_{BB}/Y_B^2) + n_{AB} \ln(X_{AB}/2Y_AY_B)]$$
(2.14)

 Δg_{AB} is expanded in terms of the pair fractions:

$$\Delta g_{AB} = \Delta g_{AB}^{\circ} + \sum_{i \ge 1} g_{AB}^{i0} X_{AA}^{i} + \sum_{j \ge 1} g_{AB}^{0j} X_{BB}^{j}$$
(2.15)

where Δg_{AB}° , g_{AB}^{i0} and g_{AB}^{0j} are the parameters of the model which may be functions of temperature.

The equilibrium pair distribution is calculated by setting
$$\left(\partial G/\partial n_{AB}\right)_{n_A,n_B} = 0 \tag{2.16}$$

This gives the "equilibrium constant" for the "quasichemical reaction" of (Eq. 1):

$$\frac{X_{AB}^2}{X_{AA}X_{BB}} = 4\exp\left(-\frac{\Delta g_{AB}}{RT}\right)$$
(2.17)

As Δg_{AB} becomes progressively more negative, the reaction (Eq. 1) is shifted progressively to the right, and the calculated enthalpy and configurational entropy of mixing assume, respectively, the negative "V" and "m" shapes characteristic of SRO.

The composition of maximum SRO is determined by the ratio of the coordination numbers Z_B/Z_A , as given by the following equations:

$$\frac{1}{Z_A} = \frac{1}{Z_{AA}^A} \left(\frac{2n_{AA}}{2n_{AA} + n_{AB}}\right) + \frac{1}{Z_{AB}^A} \left(\frac{n_{AB}}{2n_{AA} + n_{AB}}\right)$$
(2.18)

$$\frac{1}{Z_B} = \frac{1}{Z_{BB}^B} \left(\frac{2n_{BB}}{2n_{BB} + n_{AB}}\right) + \frac{1}{Z_{BA}^B} \left(\frac{n_{AB}}{2n_{BB} + n_{AB}}\right)$$
(2.19)

where Z_{AA}^{A} and Z_{AB}^{A} are the values of Z_{A} respectively when all the nearest neighbors of an A are A's, and when all nearest neighbors of an A are B's, and where Z_{BB}^{B} and Z_{BA}^{B} are

defined similarly. (Note that Z_{AB}^{A} and Z_{BA}^{B} represent the same quantity and can be used interchangeably.)

Although the model is sensitive to the ratio of the coordination numbers, it is less sensitive to their absolute values. The use of the one-dimensional Ising model in Eq. 2.14 introduces a mathematical approximation into the model which we have found, by experience, can be partially compensated by selecting values of Z_B and Z_A which are smaller than the actual values.

2.3Thermodynamic modeling of solids

Solid phases appear in phase diagrams as stoichiometric compounds, terminal solid solutions or stoichiometric compounds with ranges of homogeneity. Sometimes some compounds have such a large homogeneity range that they are called solutions with specific names.

The Gibbs energy function for any stoichiometric phase A_xB_y per mole of atoms is represented as:

$$g^{A_x B_y}(T) = \frac{x}{x+y} g^0_A + \frac{y}{x+y} g^0_B + \Delta H_T - T\Delta S_T$$
(2.20)

where ΔH_T and ΔS_T are the enthalpy and entropy of formation of the compound from the states *i* and *j* of elements A and B respectively.

The terminal solid solutions appearing in a binary system are usually treated with a random-mixing single-sublattice model. As the name suggests, this model assumes the random mixing of the atoms, one randomly replacing the other by substitution on lattice sites. The Gibbs energy of such a solution in which atoms A and B replace each other on lattice sites is given as:

$$G^{m} = (x \ g_{A}^{0} + x_{B} \ g_{B}^{0}) + RT[x_{A} \ln x_{A} + x_{B} \ln x_{B}] + g^{E}$$
(2.21)

The phases with two or more sublattices exhibiting ranges of homogeneity are modeled using sublattice models. The sublattice model with random-mixing on each sublattice in it's the most general form is called as Compound Energy Formalism (CEF). This formalism was advanced by Hillert who has given a detailed description (Hillert, 2000). In the CEF, the Gibbs energy per mole of solution in the compound (A, B)_P (D,E)_Q is given by;

$$G = y_{A}y_{D}G_{A:D} + y_{A}y_{E}G_{A:E} + y_{B}y_{D}G_{B:D} + y_{B}^{a}y_{E}^{b}G_{B:E} + PRT(y_{A}\ln y_{A} + y_{B}\ln y_{B}) + QRT(y_{D}\ln y_{D} + y_{E}\ln y_{E}) + (\sum_{k=D,E} y_{A}y_{B}y_{k}L_{AB:k} + \sum_{k=A,B} y_{k}y_{D}y_{E}L_{k:DE})$$

In the CEF the atoms are assumed to mix randomly on each sublattice. The interactions between the atoms on different sublattices are taken into account by the Gibbs energy of end members $G_{i;j}$, and interactions among the atoms on the same sublattice is taken into account by excess terms (the last term in the above equation). The Gibbs energy of end members $G_{i;j}$ and excess parameters $L_{ij;k}$ are the model parameters.

2.4 Extension to a ternary system from binary systems

To estimate the excess Gibbs energy of a ternary solution from optimized binary model parameters, several "geometric" models have been proposed. Pelton (Pelton, 2001) presented a detailed description of these models. Some of these models are illustrated in Figure 2.1 (reproduced from (Pelton, 2001)). In all of these models the excess Gibbs energy (g^E in Eq. 2.13) at any composition p can be estimated from the binary interaction parameters or the excess Gibbs energies of the binary sub-systems at points a, b and c. This excess Gibbs energy when the solution is modeled using the MQM is estimated as:

$$g^{E} = X_{12} \Delta g_{12}/2 + X_{13} \Delta g_{13}/2 + X_{31} \Delta g_{23}/2 + (ternary terms)$$
(2.22)
where Δg_{ij} is the Gibbs energy change for the reaction:
 $i - i + j - j = 2(i - j)$ (2.23)

If ternary data are available, they can be used to estimate the ternary interactions. However, these terms should not be large; otherwise doubt is cast upon the predictive ability of the model. These ternary terms are identically zero in the three binary subsystems.

The Kohler and Muggianu models in Figure 2.1 are "symmetric" models, whereas the Kohler/Toop and Muggianu/Toop models in Figure 2.1 are "asymmetric" models inasmuch as one component is singled out. An asymmetric model is more physically reasonable than a symmetric model if component 2 and 3 are chemically similar while component 1 is chemically different. When g^E is large and Δg_{ij} depends strongly upon composition, a symmetric model and an asymmetric model will give very different results.

Pelton and Chartrand (Pelton and Chartrand, 2001) presented a detailed description of the estimation of the excess Gibbs energies in a ternary solution from binary model parameters when the MQM is used to model the liquid phase. If the data for the three binary subsystems of a ternary system have been optimized and the parameters are in the form of Eq. 2.15, when a symmetric Kohler-type approximation is chosen for the 1-2 subsystem, then Δg_{12} can be written:

$$\Delta g_{12} = \Delta g_{12}^0 + \sum_{1 \le (i+j)} g_{12}^{ij} \left(\frac{X_{11}}{X_{11} + X_{12} + X_{22}} \right)^i \left(\frac{X_{22}}{X_{11} + X_{12} + X_{22}} \right)^j$$
(2.21)

If a Toop-type approximation is chosen, then Δg_{12} can be written:

$$\Delta g_{12} = \Delta g_{12}^0 + \sum_{1 \le (i+j)} g_{12}^{ij} X_{11}^i \left(X_{22} + X_{23} + X_{33} \right)^j$$
(2.22)

The form of these expressions was chosen because in the limit of a very small degree of short-range ordering they reduce to the well-known Kohler and Kohler-Toop approximations with the Bragg-Williams random-mixing model.

The FactSage thermodynamic software (FactSage, 2009) allows users to use any of these "geometric models" to increase the flexibility and the ability to estimate the Gibbs energy of ternary or multicomponent solutions from the optimized lower-order parameters.



Figure 2.1 Some geometric models for estimating ternary thermodynamic properties from the optimized binary data (reproduced from Pelton, 2001).

2.5 Predictions using only binary parameters

Pelton and Kang (Pelton and Kang, 2007) showed how the MQM generally predicts better the property of ternary solutions from the optimized model parameters than does the random-mixing model.

In a ternary system A-B-C in which the binary solution A-B exhibits a strong tendency to short-range ordering, while the B-C and C-A binary solutions are closer to ideality, positive deviations from ideal mixing behavior will be observed, centered along the A_xB_y -C join where A_xB_y is the binary composition of maximum short-range ordering. If the ordering in the A-B system is sufficiently large, then a miscibility gap is observed along the join. Such positive deviations are expected because the addition of C atoms breaks the energetically favored A-B pairs, and consequently the solution tends to maximize the number of A-B pairs by separating into A_xB_y -rich and C-rich solutions.

A Bragg-Williams model overestimates the positive deviations observed in such ternary systems. In fact, it may predict a miscibility gap when there is none. An associate model, in which the short-range ordering in the A-B binary solution is modeled as being due to A_xB_y molecules or associates, will not at all predict such deviations. The associate model simply predicts that, along the A_xB_y -C join, the solution is an ideal mixture of A_xB_y associates and C atoms. The MQM, with proper choice of coordination numbers, predicts better such positive deviations along the A_xB_y -C join.

Pelton and Kang (Pelton and Kang, 2007) also showed that usually the MQM better predicts extensions of binary miscibility gaps into a ternary system. A miscibility gap in a binary liquid phase modeled using the MQM is much flatter with a comparatively lower critical temperature than is obtained by a random-mixing model. As a result, the MQM predicts a smaller extension of a binary miscibility gap into a ternary system.

2.6 Approach for Present Work

The objective of the present work was to critically evaluate and develop the thermodynamic database for Mg-Sn based-alloys and in this regard four binary systems: Mg-Bi, Mg-Sb, Al-Bi and Al-Sb and two ternary systems: Mg-Al-Bi and Mg-Al-Sb were critically evaluated and optimized. No optimizations taking short-range ordering in the liquid phase in these systems have been reported before.

All the calculations and optimizations in the present work were performed with the FactSage thermochemical software (FactSage, 2009) The various steps followed in the present work which collectively come under the CALPHAD approach were:

The binary systems to be optimized during the present work were identified.

Collection of data in the literature for the system:

All the data in the literature on the thermodynamic properties of the chosen systems were collected. These data were phase diagram data, thermodynamic properties like enthalpy of mixing in a solution phase or enthalpy of formation for compounds, activity of constituents in a solution, *etc*.

Choosing appropriate thermodynamic model:

As stated in Chapter 2.2, an adequate model representing the Gibbs energy functions for a phase is required. This is very important since a good physical model based on the structure of the phase increases the accuracy of predictions of solution properties in multicomponent systems. In the present work, the Modified Quasichemical Model (MQM) capable of taking into account short range ordering was chosen.

Critical evaluation of collected experimental data:

The experimental data reported in literature sometimes differed from each other beyond the stated experimental error range. The simulatnoeous optimization of various thermodynamic data which includes the phase diagram data and the thermodynamic properties of the phases removed the inconsistency amongst the thermodynamic data.

Optimization of model parameters for the system:

After evaluation of the experimental data, optimization was performed on the basis of selected reliable data to obtain the values of the model parameters. In this stage, optimization software, the OptiSage module in FactSage, was quite useful.

In the present work, the optimized parameters were obtained with the help of OptiSage or sometimes with both OptiSage and the trial and error method.

Back-calculation of all thermodynamic data and phase diagrams: Once satisfactory model parameters were obtained, all the thermodynamic data and experimental data were back-calculated for comparison with the optimized values.

Evaluation of ternary systems:

The presently obtained model parameters for the binary systems were combined with previously optimized binary parameters of the other binary sub-systems to estimate the Gibbs energies of solutions in the ternary systems using the techniques given in Chapter 2.5. With the help of these Gibbs energies, evaluations and predictions were made for the ternary systems.

The various results obtained in the present work following the above steps were prepared as two articles which have been submitted to journals. These articles are presented in Chapters 3 and 4.

Chapter 3: Article 1 Thermodynamic modeling of the Mg-Bi and Mg-Sb binary systems and short-rangeordering behavior of the liquid solutions

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Abstract

In order to investigate the short range ordering behavior of liquid Mg-Bi and Mg-Sb solutions, thermodynamic modeling of the Mg-Bi and Mg-Sb binary systems was performed. All available thermodynamic and phase diagram data of the Mg-Bi and Mg-Sb binary systems have been critically evaluated and all reliable data have been simultaneously optimized to obtain one set of model parameters for the Gibbs energies of the liquid and all solid phases as functions of composition and temperature. In particular, the Modified Quasichemical Model, which accounts for short-range-ordering of nearest-neighbor atoms in the liquid, was used for liquid solutions. A comparative evaluation of both systems was helpful in resolving inconsistencies in experimental data. Thermodynamic modeling shows strong ordering behavior in the liquid Mg-Bi and Mg-Sb solutions at Mg₃B₂ and Mg₃Sb₂ compositions, respectively, and also suggests the metastable liquid miscibility gaps at sub-solidus temperature. All calculations were performed using the FactSage thermochemical software.

Keywords: thermodynamic modeling, Mg-Bi, Mg-Sb, short-range-ordering of liquid.

3.1. Introduction

A strong tendency for short-range-ordering in the liquid occurs in binary systems in which the electro-negativities of the components are very different. In the liquid solutions of Na-Te [1], Au-Cs [2], K-Bi [3], Rb-Bi [4], Na-Pb [5] and Tl-Te [6], maximum ordering has been observed near the equiatomic composition and/or near the stoichiometric composition (i.e. the composition corresponding to the ratio of chemical valences of the components). Evidence for this ordering has come from thermodynamic studies as well as from measurement of electrical conductivity, magnetic susceptibility, molar volume and thermoelectric power [7].

Liquid Mg-Bi and Mg-Sb solutions exhibit a strong ordering tendency in the liquid solutions at Mg₃Bi₂ and Mg₃Sb₂ compositions, respectively. Liquid Mg₃Bi₂ is one of the classical examples of liquid semiconductor [8-10] with a conductivity as low as 45 Ω^{-1} cm⁻¹. Similarly, liquid Mg₃Sb₂ shows the semiconductor behavior [11, 12]. The resistivities of liquid Mg–Bi and Mg–Sb exhibit extremely sharp peaks at Mg₃Bi₂ and Mg₃Sb₂ compositions.

Binary Mg-Bi and Mg-Sb systems are also interesting for high temperature Mg alloys. Recently magnesium alloy attracted great interests of automotive and aeronautic industries due to its low density compared with aluminum alloy and steel. In order to develop new Mg alloys for high temperature applications, alloying elements such as Sn, Si, Sb and Bi are under consideration [13, 14]. As a high temperature Mg alloy needs to keep its thermal stability and mechanical properties at elevated temperatures, the formation of stable secondary phases is important. The Mg-Sn based alloy shows great potential as high temperature Mg alloys [14] because of the formation of stable Mg₂Sn phase. It also has been found that the addition of Sb can change the morphology of Mg₂Sn precipitates more homogenously within Mg matrix, which results in the improvement of the mechanical properties of Mg alloy. The similar effect can be expected for Bi addition because the chemistry of the Mg-Bi is very similar to that of the Mg-Sb.

The thermodynamic properties of the Mg-Bi and Mg-Sb solutions, which have very negative enthalpy of mixing (about -30 kJ/mol for the Mg-Bi and -60 kJ/mol for the Mg-Sb, which will be discussed in section 3 in details) and strong ordering tendency, are very difficult to describe using the conventional Bragg Williams random mixing solution model. A more sophisticated solution model accounting for the short range ordering tendency is required for the thermodynamic modeling.

The main goal of the present study is to perform a critical evaluation and optimization of the thermodynamic properties and phase diagrams of the Mg-Bi and Mg-Sb binary alloy systems. In the thermodynamic "optimization" of a chemical system, all available thermodynamic and phase equilibrium data are evaluated simultaneously in order to obtain one set of model equations for the Gibbs energies of all phases as functions of temperature and composition. From these equations, all of the thermodynamic properties and the phase diagrams can be back-calculated. In this way, all the data are rendered self-consistent and consistent with thermodynamic principles. Thermodynamic property data, such as activity data, can aid in the evaluation of the phase diagram, and phase diagram measurements can be used to deduce thermodynamic properties. Discrepancies in the available data can often be resolved, and interpolations and extrapolations can be made in a thermodynamically correct manner. Because of the similarity of the Mg-Bi and Mg-Sb systems, a comparative evaluation of two systems can be helpful to resolve the inconsistencies of the experimental data.

In particular, the Modified Quasichemical Model [17-20] taking the short-range-ordering of atom pairs will be used to describe the thermodynamics of liquid Mg-Bi and Mg-Sb solutions. As results, the structure of liquid solutions will be back-calculated from the optimized model parameters in the present study.

3.2. Thermodynamic Models

3.2.1. Liquid phases

Binary Mg-Bi and Mg-Sb liquid solutions show the strong ordering tendencies around Mg₃Bi₂ and Mg₃Sb₂ compositions, respectively. In order to account for the strong ordering tendency in the liquid phase, the Modified Quasichemical Model [19,20], which accounts for a short-range-ordering of nearest-neighbor atoms, was used for the liquid solutions in the present study. That is, the Modified Quasichemical Model can give a more realistic thermodynamic description for liquid Mg-Bi and Mg-Sb solutions, compared with the conventional simple random-mixing Bragg Williams model. The Modified Quasichemical Model has been successfully applied to many liquid metallic solutions [13,15,20] and ionic solutions [16,18] exhibiting the strong short-range-ordering behavior.

The energy of nearest neighbor pair formation in the Modified Quasichemical Model was recently expanded as a polynomial in the pair fractions [19,20] instead of the component fractions [17,18]. In addition, the coordination numbers are now allowed to vary with composition. These modifications provide greater flexibility in reproducing the binary experimental data and in combining optimized binary liquid parameters into a large database for multicomponent solutions [19]. The short description of the model is given below. The details of the model can be found in the previous studies [19,20].

Let's consider the case of binary Mg-Bi liquid solution. The atoms of Mg and Bi are distributed over the sites of a quasi-lattice in liquid solution. The following pair exchange reaction can be considered:

$$(Mg-Mg) + (Bi-Bi) = 2(Mg-Bi)$$
[1]

where (A-B) represents a first-nearest-neighbor pair of A and B. The non-configurational Gibbs energy change for the formation of two moles of (Mg-Bi) pairs according to reaction [1] is Δg_{MgBi} . Then the Gibbs energy of the solution is given by:

$$G = (n_{\rm Mg}G^{\rm o}_{\rm Mg} + n_{\rm Bi}G^{\rm o}_{\rm Bi}) - T\Delta S^{\rm config} + n_{\rm MgBi}(\Delta g_{\rm MgBi}/2)$$
[2]

where G_{Mg}^{o} and G_{Bi}^{o} are the molar Gibbs energies of the pure components Mg and Bi, n_{Mg} and n_{Bi} are the numbers of moles of Mg and Bi atoms, and n_{MgBi} is the number of moles of (Mg-Bi) pairs. ΔS^{config} is the configurational entropy of mixing given by a random distribution of the (Mg-Mg), (Bi-Bi) and (Mg-Bi) pairs in the one-dimensional Ising approximation:

$$\Delta S^{\text{config}} = -R(n_{Mg} \ln X_{Mg} + n_{Bi} \ln X_{Bi}) - R[n_{MgMg} \ln(X_{MgMg} / Y_{Mg}^{2}) + n_{BiBi} \ln(X_{BiBi} / Y_{Bi}^{2}) + n_{MgBi} \ln(X_{MgBi} / Y_{Mg} Y_{Bi})]$$
[3]

where n_{MgMg} , n_{BiBi} and n_{MgBi} are the numbers of moles of each kind of pairs, and the pair fraction (X_{MgMg} , X_{BiBi} and X_{MgBi}) and coordination equivalent fraction (Y_{Mg} and Y_{Bi}) can be calculated as:

$$X_{\rm MgMg} = n_{\rm MgMg} / \left(n_{\rm MgMg} + n_{\rm BiBi} + n_{\rm MgBi} \right)$$
[4]

$$X_{\rm MgMg} = n_{\rm MgMg'} (n_{\rm MgMg} + n_{\rm BiBi} + n_{\rm MgBi})$$

$$X_{\rm BiBi} = n_{\rm BiBi} / \left(n_{\rm MgMg} + n_{\rm BiBi} + n_{\rm MgBi} \right)$$
[5]

$$X_{\rm MgBi} = n_{\rm MgBi} / \left(n_{\rm MgMg} + n_{\rm BiBi} + n_{\rm MgBi} \right)$$
 [6]

$$Y_{Mg} = X_{MgMg} + X_{MgBi} / 2$$
^[7]

$$Y_{Bi} = X_{BiBi} + X_{MgBi} / 2$$
[8]

The Δg_{MgBi} is the model parameter to reproduce the Gibbs energy of liquid phase of the binary Mg-Bi system, which is expanded as a polynomial in terms of the pair fractions, as follows:
$$\Delta g_{\rm MgBi} = \Delta g_{\rm MgBi}^{\rm o} + \sum_{i \ge 1} g_{\rm MgBi}^{i\,0} (X_{\rm MgMg})^i + \sum_{j \ge 1} g_{\rm MgBi}^{0\,j} (X_{\rm BiBi})^j$$
[9]

Where Δg_{MgBi}^{o} , g_{MgBi}^{i0} and g_{MgBi}^{0j} are the adjustable model parameters which can be functions of temperature.

Due to a strong ordering tendency of the Mg-Bi liquid solution around Mg₃Bi₂ composition, (Mg-Mg) and (Mg-Bi) pairs are dominant, and (Bi-Bi) pair is rare in the Mg-rich region. Therefore, $g_{MgBi}^{0,j}$ parameters have little influence on the Gibbs energy of the solution in this composition region. Similarly, the g_{MgBi}^{i0} parameters have little influence at the Bi-rich region. Thus, the model parameters can be more or less independently optimized to reproduce the thermodynamic properties and phase diagram in each side.

The "coordination numbers" of pure Mg and Bi in liquid state should be similar to each other. However, the short-range-ordering of liquid Mg-Bi binary liquid solution occurs at Mg_3Bi_2 composition (not equiatomic MgBi composition), which means the coordination number of a Mg atom surrounded by Bi atoms is no longer the same as that of a Bi atom surrounded by Mg atoms in the binary Mg-Bi solution. In order to reproduce this short-range-ordering, the coordination numbers of Mg and Bi, Z_{Mg} and Z_{Bi} , can now be varied with composition as follows:

$$\frac{1}{Z_{\rm Mg}} = \frac{1}{Z_{\rm MgMg}} \left(\frac{2n_{\rm MgMg}}{2n_{\rm MgMg} + n_{\rm MgBi}} \right) + \frac{1}{Z_{\rm MgBi}} \left(\frac{n_{\rm MgBi}}{2n_{\rm MgMg} + n_{\rm MgBi}} \right)$$
[10]
$$\frac{1}{Z_{\rm Bi}} = \frac{1}{Z_{\rm BiBi}} \left(\frac{2n_{\rm BiBi}}{2n_{\rm BiBi} + n_{\rm MgBi}} \right) + \frac{1}{Z_{\rm BiMg}} \left(\frac{n_{\rm MgBi}}{2n_{\rm BiBi} + n_{\rm MgBi}} \right)$$
[11]

where Z_{MgMg} is the value of Z_{Mg} when all nearest neighbors of an Mg atom are Mg atoms, and Z_{MgBi} is the value of Z_{Mg} when all nearest neighbors are Bi atoms. Z_{BiBi} and Z_{BiMg} are defined in an analogous manner. The composition of maximum short-range ordering is thus determined by the ratio (Z_{MgBi}/Z_{BiMg}) which, in the present case, is set at 2/3 in order to make the maximum short-range-ordering to occur at Mg₃Bi₂ composition. Values of the binary coordination numbers Z_{MgBi} and Z_{BiMg} are unique to the Mg-Bi binary system, while the values of the unary coordination numbers Z_{MgMg} and Z_{BiBi} are common to all systems containing Mg or Bi as a component.

The coordination numbers are set to be: $Z_{MgMg} = Z_{BiBi} = 6$, $Z_{MgBi} = 4$ and $Z_{BiMg} = 6$. These coordination numbers are relatively arbitrary values and non-physical values which result from the use of the one-dimensional Ising approximation for the configurational entropy [19].

An identical model was applied to the binary Mg-Sb liquid solution. In order to make the maximum short-range-ordering occur at Mg₃Sb₂ composition, the binary coordination number of Z_{MgSb} and Z_{SbMg} are set to be 4 and 6, respectively, like the Mg-Bi liquid phase.

3.2.2. Mg₃X₂ solution (Mg₃Bi₂ and Mg₃Sb₂ solid solution)

Both solid Mg₃Bi₂ and Mg₃Sb₂ phases have α (low temperature form, La₂O₃ proto-type, $P\overline{3}m$ l space group) and β (high temperature form, β -Mn₂O₃ proto-type, Ia3 space group). The solid phases are not stoichiometric compounds but dissolve a small amount of excess Mg. Unfortunately, the defect structures of the non-stoichiometric solids have not been well investigated. In the present study, the simple interstitial structures were assumed for both α -Mg₃X₂ and β -Mg₃X₂ solid solutions as follows:

$$Mg_3(Mg,Va)X_2$$
[12]

where Va means vacancy and X means Bi or Sb. The above defect structure assumes that the excess Mg atoms enter to interstitial sites of an original crystal structure. Then, the molar Gibbs energy of the solid solution Mg_3X_2 can be expressed as:

$$G = y_{Va}G^{\circ}_{Mg_{3}X_{2}} + y_{Mg}G^{\circ}_{Mg_{4}X_{2}} + RT(y_{Va}\ln y_{Va} + y_{Mg}\ln y_{Mg}) + L^{0}y_{Va}y_{Mg}$$
[13]

where y_{va} and y_{Mg} are the site fractions of Va and Mg in the interstitial sublattice. The Gibbs energy of an imaginary Mg₄X₂ compound, $G^o_{Mg_4X_2}$, and binary interaction parameters between Va and Mg in the interstitial site, L^o , are adjustable model parameters in the present study. The Gibbs energies of stoichiometric Mg₃Bi₂ and Mg₃Sb₂ ($G^o_{Mg_3X_2}$) are also optimized based on the available thermodynamic data and phase diagrams.

3.2.3. α-Mg solution

 α -Mg hcp solid solution was modeled as a simple random mixture of metallic elements Mg and Bi with the simple polynomial excess Gibbs energy terms, as similar to above Eq. [13]. No noticeable solubility of Sb in α -Mg has been reported.

3.2.4. Stoichiometric compounds

No noticeable solubilities of Mg into solid Bi and Sb phases have been reported in the binary Mg-Bi and Mg-Sb system. Thus, solid Bi and Sb were considered as stoichiometric compounds in the present study.

All thermodynamic calculations and optimizations were carried out using the FactSage thermodynamic software [21], and the optimized model parameters are listed in Table 3.1.

3.3. Results of optimization

3.3.1 The Mg-Bi System

The Mg-Bi system was modeled previously by Oh et al.[24]. The Gibbs energy of the liquid solution was described using a two-sublattice ionic solution model [25], $(Mg^{+2})_P(Bi^{-3},Bi^0,Va^{-v})_Q$, where Va denotes vacancies and v represents the valency of vacancies whose

value is the sum of valancies of species in cation sublattice (in this case v = 2). P and Q represent the number of site of each sublattice. The description of liquid was similar to the associate model considering Mg₃Bi₂ associate formation in liquid phase. The solid non-stoichiometric Mg₃Bi₂ phase was modeled using the Compound Energy Formalism [26] with the consideration of crystal structure of Mg₃Bi₂ as (Mg)₃(Bi,Va)₂.

In the present study, the Mg-Bi system is re-optimized using a Modified Quasichemical Model for the liquid Mg-Bi solution. The experimental phase diagram and thermodynamic data of the Mg-Bi system [28-32,34-40] were previously reviewed by Nayeb-Hashemi and Clark [27]. All thermodynamic and phase diagram data of solid and liquid phases were critically re-evaluated to resolve the inconsistencies of the experimental results, and all reliable data were simultaneously optimized to obtain the best set of thermodynamic model parameters in the present study.

Grube [28] determined the liquidus temperature of the Mg-Bi system using a thermal analysis technique in the entire composition region and proposed the existence of nonstoichiometric Mg₃Bi₂ phase. However, no information was provided for the phase transformation of Mg₃Bi₂, and the purities of the alloys used in his study were unspecified. Grube et al. [29] re-determined the liquidus with high purity Mg (99.93%) and Bi (99.9%) across the whole composition region using the same thermal analysis technique. The polymorphic transformation temperature of Mg₃Bi₂ was also determined. Wobst [30] determined the liquidus temperature in the composition region of $0.30 < X_{Bi} < 0.46$ using a thermal analysis technique. Grube et al and Vosskuhler [31] determined the solubility of Bi into α -Mg by a resistrometry technique, and Foote and Jette [32] determined the same by X-ray analysis. The solubility of Mg into solid Bi phase was found to be negligible [29,31,32]. Grube et al. determined the solubility range of α -Mg₃Bi₂ phase by the thermal analysis and resistrometry techniques. No experimental data have been reported to determine the excess Mg content in β -Mg₃Bi₂ phase.

Fig. 3.1 shows the optimized phase diagram calculated in the present study. The calculated phase diagram is compared with the experimental data [28-30]. In the present

thermodynamic modeling, it was found to be difficult to reproduce both sides of β -Mg₃Bi₂ liquidus simultaneously with all available thermodynamic properties of liquid phase. The liquidus temperature of Grube et al. [28,29] is higher than the results of Wobst. The calculated liquidus of of β -Mg₃Bi₂ phase in the Mg rich side is more consistent with the results of Wobst than those of Grube et al. However, it was difficult to reproduce the liquidus of β -Mg₃Bi₂ phase in the Bi rich side. The slopes of liquidus of β -Mg₃Bi₂ phase are related to the enthalpy of melting of β -Mg₃Bi₂ phase, which is known as a limiting slope rule [33]. According to this rule, the slopes of liquidus in both sides of the Mg₃Bi₂ should be reproduced simultaneously. The previous modeling of Oh et al. [24] shows the similar difficulty in reproducing the liquidus. Therefore, there might be certain inconsistencies of the liquidus data and other thermodynamic properties of the liquid phase. Fig. 3.2 shows the enlarged phase diagram of the Mg rich side. The calculated solidus and liquidus of α -Mg and solubility of Bi into α -Mg are consistent with the experimental results.

The optimized invariant reactions of the Mg-Bi are listed in Table 3.2 along with the experimental data.

The thermodynamic properties of low temperature α -Mg₃Bi₂ phase and high temperature β Mg₃Bi₂ phase have not been well investigated. The only experimental data available are the heats of formation of α -Mg₃Bi₂ [34,35,40]. Seith and Kubaschewski [34] measured the heat of formation at room temperature and at 860°C using a high temperature calorimetry, and Kubaschewski and Walter [35] also used the same technique to determine the heats of formation, at temperatures from 600 ° to 650 °C. Moser and Krohan [40] calculated the heat of formation using the partial Gibbs energy of liquid Mg determined from an emf measurement. The optimized heat of formation of α -Mg₃Bi₂ at 298 K in the present study is -170.40 kJ/mol which is close to the experimental values of Seith and Kubaschewski (-150.01 kJ/mol) and Kubaschewski and Walter (-157.03 kJ/mol). The value suggested by Moser and Krohn was -185.9 kJ/mol, which is more negative than present value as well as the other experimental results.

Since the heat capacity (*C*p) of Mg₃Bi₂ has not been investigated previously, it was assumed in this study to be $Cp(Mg_3Bi_2) = 3Cp(Mg) + 2Cp(Bi)$. The entropy of α -Mg₃Bi₂ was set to be that S_{298K} (Mg₃Bi₂) = 3S_{298K} (Mg(s)) + 2S_{298K} (Bi(s)) as a first approximation due to no available experimental data and then slightly modified during the optimization in order to reproduce available phase diagram and thermodynamic data. Neither the heat of transformation of α -Mg₃Bi₂ to β -Mg₃Bi₂ nor the heat of fusion of β -Mg₃Bi₂ has been experimentally determined. From the thermodynamic modeling in the present study, the heat of transformation is calculated to be 13.4 kJ/mol at 976 K and similarly the heat of fusion is calculated to be 55.6 kJ/mol at 1098 K.

Thermodynamic properties of the liquid Mg-Bi solution have been investigated by various methods [36-40]. Prasad et al. [36] derived the thermodynamic properties of the liquid from the Mg vapor pressure over the liquid solution using a transpiration technique. The vapor pressures were measured for the liquid of $0.1 < X_{Bi} < 0.8$ at the temperature of 943 K to 1233 K. Vetter and Kubaschewski [39] used the same technique as Prasad et al. in composition region of $0.1 < X_{Bi} < 0.9$ at 973 K to 1073 K. Egan [37] also determined the activity of Mg at 1108 K in the composition region $0.35 < X_{Bi} < 0.47$ using the emf technique with a CaF₂ solid electrolyte. Later, Egan [38] performed an emf measurement using three different concentration cells and calculated the activity of Mg and thermodynamic properties of the Mg-Bi liquid at 973 K.

Fig. 3.3 shows the calculated activities of Mg of liquid Mg-Bi solution relative to its liquid standard state at various temperatures in comparison to the experimental data [36-39]. The calculated activities of liquid Mg are consistent with the experimental results of Prasad et al. [36] in the entire composition range. The calculated results are consistent with the experimental data of Egan [37,38] in the Bi rich side, but are slightly higher than the experimental data in the Mg rich side. We believe that the vapor pressure measurement is more accurate in the Mg rich side than the emf technique because liquid Mg can be quite reactive with the electrolytes during the emf measurement. As can be seen in Fig. 3, the temperature dependency of the activity is also well reproduced.

The partial molar excess Gibbs energies of Mg in liquid phase ($RT \ln a_{Mg}$) are calculated at various temperatures and compared with experimental data in Fig. 3.4. As can be seen in the figure, the calculated results are in good agreement with experimental data even in the Bi rich side. In particular, the sudden change of the partial Gibbs energy at Mg₃Bi₂ composition, which is related to the strong short range ordering tendency in the liquid Mg-Bi phase, are very well reproduced in the present study.

Thermodynamic properties such as the Gibbs energy, enthalpy and entropy of mixing in liquid Mg-Bi solution are calculated and compared with the experimental data in Figs. 3.5 to 3.7. Prasad et al. [36] and Vetter and Kubaschewski [39] derived the Gibbs energy, enthalpy and entropy of mixing based on their vapor pressure measurement at the temperature range of a couple of hundred °C. Because of the relative small temperature range in the experiments, the error in the enthalpy and entropy can be relatively larger than the Gibbs energy. As can be seen in Fig. 3.5, the calculated Gibbs energies are in good agreement with both experimental data. However, the experimental enthalpy of mixing shows large discrepancies with each other. The calculated enthalpy of mixing is in fair agreement with experimental data within their experimental error limits. The enthalpy of mixing is lower than -30 kJ/mol at $X_{Bi} = 0.4$. In the case of the entropy of mixing, the discrepancies of the experimental data are more significant. According to the short-range-ordering tendency observed in the partial Gibbs energy data in Fig. 3.4, the liquid show the minimum entropy of mixing near $X_{Bi} = 0.4$ (Mg₃Bi₂ composition).

3.3.2 The Mg-Sb System

The Mg-Sb system had been assessed thermodynamically [40,42]. Jonsson and Agren [41] have assessed the system roughly. Liquid phase was modeled using a two-sublattice ionic model [25], $(Mg^{+2})_P(Sb^{-3},Sb^0, Va^{-v})_Q$, like the Mg-Bi liquid by Oh et al.[24] Low temperature α -Mg₃Sb₂ was treated as a stoichiometric compound and β -Mg₃Sb₂ was modeled using the Compound Energy Formalism[26] with the structure of (Mg)₃(Sb⁵⁻, Sb³⁻, Va)₂. However, no details of the thermodynamic modeling results in comparison with

experimental data were provided. Recently, Balakumar and Medraj [42] optimized the system using the conventional Bragg Williams random mixing model for liquid Mg-Sb solution. However, as pointed out later by Malakhov and Balakumar [43], the unreasonable inverted miscibility gaps in liquid solution were calculated above 1900 K from the Gibbs energy function optimized by Balakumar and Medraj. That is, the assessment of Balakumar and Medraj [42] is inaccurate. No complete and reliable thermodynamic modeling study for the Mg-Sb system is available yet.

Like the Mg-Bi system, the experimental data for phase diagram and thermodynamic properties [44-51] of the Mg-Sb system were previously reviewed by Nayeb-Hashemi and Clark [52]. Since there is no new experimental data reported after their review, it is unnecessary to review the entire experimental data in details in the present study again. A short description of critical evaluation of some experimental data is given below.

Grube [44] determined the phase diagram of the Mg-Sb system using a thermal analysis technique in the entire composition region and mentioned the existence of non-stoichiometric Mg₃Sb₂ solid solution. However, no information was provided regarding to the phase transformation of Mg₃Sb₂. Later, Grube and Bornhak [45] re-determined the phase diagram with high purity Mg (99.93 wt%) and Sb (99.9) starting materials using the same technique. The polymorphic transformation temperature of Mg₃Sb₂ was also determined. Rao and Patil [48] determined the liquidus of Mg₃Sb₂ in the Sb rich side from the standard emf measurement. Jones and Powell [46] determined the liquidus of Mg and the eutectic reaction 'L = Mg+Mg₃Sb₂' using a thermal analysis technique.

Fig. 3.8 shows the optimized phase diagram of Mg-Sb system along with experimental data. The calculated diagram in the Bi rich side ($X_{Bi} > 0.4$) is in good agreement with experimental data [44-46,48]. The calculated liquidus in the Mg rich side is also in reasonable agreement with experimental data of Grube [44,45] except for two experimental points at $X_{Sb} = 0.2$ and 0.25. The enlarged phase diagram of the Mg-Sb system in the Mg rich side is shown in Fig. 9. The calculated phase diagram is in good consistency with experimental data of Jones and Powell [46]. As can be seen in the figure,

In fact, the phase diagram presented by Grube [44,45] based on his own experimental data is quite different from the present optimized phase diagram. Nayeb-Hashemi and Clark [52] followed the Grube's diagram. For example, according to the Grube's diagram, the eutectic reaction 'L = Mg+Mg₃Sb₂' occurred at X_{Sb} = 0.115 at 629 °C, while it can occur at $X_{Sb} = 0.03$ at 627 °C based on the present thermodynamic optimization in accord with Jones and Powell [46]. The liquidus of α -Mg by Grube do violate the limiting slope rule [33]. Thus, we believe there might be unknown experimental error in his experiments. The original liquidus data of Grube in the Mg rich region, as shown in Fig. 3.9, are in fact quite scattered too. Because the eutectic composition for 'L = Mg+Mg₃Sb₂' was placed at X_{Sb} = 0.115, the liquidus of α -Mg₃Sb₂ phase by Grube was also quite unusual. He suggested very steep and unusual liquidus of α -Mg₃Sb₂ passing all his experimental data at 0.15 < X_{Sb} < 0.3. Both experimental liquidus of α -Mg and α -Mg₃Sb₂ are also quite unrealistic in comparison with the similar Mg-Bi system. Moreover, the experimental liquidus by Grube et al [44,45] in the Mg rich side is inconsistent with the negative behaviour of Mg activity in the same region, which will be explained below. No other previous thermodynamic assessments [40,42] can reproduce this strange shape of the liquidus.

The optimized invariant reactions of the Mg-Sb are listed in Table 3.2 along with the experimental data.

The only thermodynamic data available for Mg₃Sb₂ phase are the enthalpy of formation of α -Mg₃Sb₂ phase. Kubaschewski and Walter [34] used a high temperature calorimetry to determine the enthalpy of formation at temperatures at 600 ° and 650 °C. Rao and Patil [48] and Eremenko and Lukashenko [50] evaluated the standard enthalpy of formation of α -Mg₃Sb₂ from the temperature dependency of Mg activity data. The calculated thermodynamic properties of α -Mg₃Sb₂ are shown in Table 3.3 along with the experimental values. The calculated values in the present study are in agreement with the experimental values within the reported error limits. No enthalpy of transformation of α -

Mg₃Sb₂ to β -Mg₃Sb₂ has been measured. The enthalpy of transformation is calculated to be 38.02 kJ/mol at 1202K from the present thermodynamic modeling. The calculated enthalpy of fusion of β -Mg₃Sb₂ is 56.89 kJ/mol at 1503 K, which is almost identical to that of β -Mg₃Bi₂ in the present study.

Since the heat capacity (Cp) of Mg_3Sb_2 has not been investigated, Cp (Mg_3Sb_2) = 3Cp(Mg(s)) + 2Cp (Sb(s)) was assumed as a first approximation in the present study. No direct measurement for the entropy of Mg_3Sb_2 at 298 K is available. In the course of the thermodynamic modeling, it was found that the entropy of Mg_3Sb_2 should be lower than the sum of elemental Mg and Sb (3Mg + 2Sb), as estimated by Rao and Patil [48] and Eremenko and Lukashenko [50] based on their emf results.

The thermodynamic properties of liquid Mg-Sb solution have been investigated using various techniques [47-51]. Egan [47] determined the activity of Mg in the liquid Mg-Sb from the same emf technique as he employed for the Mg-Bi solution. Rao and Patil [48] also used the emf technique to determine the activities and other thermodynamic properties of Mg in liquid Mg-Sb alloys in the temperature range of 980 K to 1250 K. Eckert et al. [49] reported the activity of Mg at 1123 K using the emf technique. Using a vapour transpiration technique with H₂ carrier gas, Vetter and Kubaschewski [51] determined the thermodynamic properties of the liquid phase in a wide compositional range at temperatures between 1133 K and 1193 K.

Fig. 3.10 shows the calculated activity of Mg in liquid Mg-Sb solution relative to its liquid standard at various temperatures along with the experimental data [47-49,51]. The calculated activities of Mg are in good agreement with the experimental data in the Sb rich side. They also show fair agreement in the Mg-rich side. We believe the activity of Mg in Sb rich side can be more accurately determined by an emf technique than a vapor pressure measurement. In fact, the values by Vetter and Kubaschewski [51] are several orders of magnitude higher than the results by the emf measurement [47-49] in the Sb rich side. The calculated activities of Mg in the Mg rich side are slightly higher than the experimental data. In order to reproduce the activity more accurately, the liquid should be more

stabilized in this area, which results in the difficulty in the reproduction of the phase diagram data. It was difficult to reproduce both the activity data and phase diagram data simultaneously. However, our calculated activities of Mg are still in reasonable agreement with experimental data.

The partial molar excess Gibbs energy of Mg in liquid phase is presented in Fig. 3.11. As can be seen in the figure, the abrupt change of the partial Gibbs energy near $X_{Sb} = 0.4$, which represents the strong short range ordering behavior of the liquid Mg-Sb solution at this composition, are quite well reproduced in the present study. Certainly, the experimental data of Vetter and Kubaschewski [51] are off from other data. The experimental results of Rao and Patil [48] seem to be slightly inconsistent with the results of Egan [47] and Eckert et al.[49]

The Gibbs energy, enthalpy and entropy of mixing in liquid Mg-Sb solution are calculated and compared with experimental data in Figs. 3.12 to 3.14. The experimental data are well reproduced except for the data from vapor pressure measurement by Vetter and Kubaschewski [51]. It should be noted that the minimum value of the enthalpy of mixing in this system is as low as -60 kJ/mol at $X_{Sb} = 0.4$. Liquid Mg-Sb solution shows one of the most negative enthalpies of mixing among binary metallic system. In fact, the negativity is similar to the ionic oxide liquids such as CaO-SiO₂ [18] and MgO-SiO₂ [16]. The entropy of mixing does show a strong short-range-ordering tendency at Mg₃Sb₂ composition.

3.3.3. Short-range-orderings in liquid Mg-Bi and Mg-Sb solutions

As can be seen in the above optimization results, the Mg-Bi and Mg-Sb systems show similar thermodynamic properties and phase equilibria. Intermetallic Mg_3X_2 which has both low temperature α and high temperature β structures exist and melt congruently. The liquid solutions show a strong ordering tendency.

As discussed in the section 3.2, the modified Quasichemical Model can calculate the bonding structure of liquid solution from the optimized model parameters. It has been

demonstrated that the calculated liquid structures of oxide systems like the CaO-SiO₂, MgO-SiO₂ and Na₂O-SiO₂ from the Quasichemical Model parameters are in good agreement with experimental data [54]. Fig. 3.15 presents the liquid structures of the Mg-Bi and Mg-Sb predicted from the model parameters in the present study. Both systems shows the maximum ordering of Mg-X pairs (X = Bi or Sb) at X_{Mg} = 0.6. The Mg-Sb liquid shows ordering tendency stronger than Mg-Bi, as expected from the Gibbs energy and enthalpy of mixing of liquid solutions.

One of the best indicators of a tendency toward ordering is the excess stability function (ES) defined by Darken [53].

$$\mathbf{ES} = \left(\frac{\partial^2 G^E}{\partial X_i^2}\right)_{T,P}$$
[14]

The excess stability functions of the liquid phases are calculated in Fig. 16. Strong peaks in the excess stability functions can be observed at Mg₃Bi₂ and Mg₃Sb₂ compositions. The calculated excess stability function of the Mg-Sb is almost three times higher than that of the Mg-Bi at the same temperature. The short-range-ordering tendency of the liquid solutions decreases with the increase of temperature, as reasonably expected. Another indication of short range ordering in liquid solution is the variation of Δ Cp function with temperature and composition. From the thermodynamic relationship,

$$\Delta C_p = T \frac{\partial}{\partial T} (\Delta S_m)$$
[15]

Fig. 17 shows the calculated Δ Cp function for the liquid solution of Mg-Bi and Mg-Sb. The Δ Cp function shows the similar behavior like ES in Fig. 16.

Very interesting thermodynamic aspect of the liquid Mg-Bi and Mg-Sb solutions revealed in the present study is that the model parameters of the Modified Quasichemical Model for liquid solutions are almost symmetrical against Mg₃X₂ composition for both solutions. As mentioned in Eq. [9], the model parameters are mainly composed of three terms, Δg_{MgX}^{o} , g_{MgX}^{i0} and g_{MgX}^{0j} . In the present study for the Mg-Sb and Mg-Bi liquid solutions, the Δg_{MgX}^{o} parameter, which is very negative, gives a major influence on the strong short-range-ordering behavior of the liquid solutions. Then, the other two sets of parameters, g_{MgX}^{i0} and g_{MgX}^{0j} , can slightly modify the Gibbs energy of liquid phase in the Mg rich side and X rich side, respectively. From the present optimization, we found that g_{MgX}^{i0} is very similar to g_{MgX}^{0j} . In particular, the identical parameters of $g_{MgBi}^{10} = g_{MgBi}^{01}$ and $g_{MgSb}^{10} = g_{MgSi}^{01}$ can reproduce the phase diagram and thermodynamic properties of the Mg-Bi and Mg-Sb system. This means the liquid Mg-Sb and Mg-Bi can have quite symmetric Gibbs energy function and ordering behaviors against Mg_X2 composition.

Fig. 18 shows the metastable miscibility gaps in the Mg-Bi and Mg-Sb systems. The miscibility gaps can be readily expected from the liquidus shape of the Bi or Sb rich side in both systems. However, it is not obvious to expect the miscibility gaps in Mg rich side especially only from experimental phase diagram. As explained above, as the thermodynamic properties of the liquid solutions are almost symmetrical against Mg_3X_2 composition, two metastable miscibility gaps are calculated in each system. The miscibility gap in Mg rich side has slight higher critical temperature than that in Bi or Sb rich side. No strange inverse miscibility gap exists in the liquid solutions above liquidus temperature.

3.4. Summary

All available thermodynamic and phase diagram data of the binary Mg-Bi and Mg-Sb systems have been critically evaluated and all reliable data have been simultaneously optimized. A comparative study of two similar systems was helpful to resolve inconsistencies of available experimental data. As results of the optimization, one set of model parameters for the Gibbs energies of all phases as functions of composition and temperature was obtained. In order to describe the strong short-range-ordering behavior of liquid Mg-Bi and Mg-Sb solutions, the Modified Quasichemical Model, which properly takes into account the ordering tendency of solution, was employed. The present thermodynamic modeling shows very strong short-range-ordering of the liquid solutions at Mg₃Bi₂ and Mg₃Sb₂ compositions. Moreover, the existence of

symmetric metastable liquid miscibility gaps is predicted for both systems. The optimized model parameters can be readily used with general thermodynamic software and databases, such as FactSage [21], to calculate phase equilibria and thermodynamic properties for the Mg-Bi and Mg-Sb system at any given set of conditions.

Table 3.1. Optimized thermodynamic model parameters in the Mg-Bi and Mg-Sb systems (J/mol, J/mol-K).

Liquid phase			
Mg-Bi system: $\Delta g^0_{MgBi} = -31426.46 + 4.119T$			
$\Delta g_{MgBi}^{10} = 19263.13 - 8.368T$, $\Delta g_{MgBi}^{20} = -7949.60$			
$\Delta g^{01}_{MgBi} = 19263.13 - 8.368 \text{T}$, $\Delta g^{02}_{MgBi} = -5355.52$			
Mg-Sb system: $\Delta g_{MgSb}^0 = -52258.16 + 8.611$ T			
$\Delta g_{MgSb}^{10} = 28242.00 - 4.184 \text{T} - 0.4 \text{T}^2 \Delta g_{MgSb}^{20} = -4184.40$			
$\Delta g_{MgSb}^{01} = 28242.00 - 4.184\text{T} - 0.4\text{T}^2$, $\Delta g_{MgSb}^{02} = -7112.80$			
$\mathbf{M}_{\mathbf{r}} \mathbf{V}_{\mathbf{r}} = 1^{\prime} 1_{\mathbf{r}} 1_$			
Mg_3X_2 solid solution (Mg_3Bl_2 - Mg_3Sb_2 solid solution)			
α -Mg ₃ B1 ₂ solution :			
α -Mg ₃ Bi ₂ : H_{29815K}^{o} = -170401.00, $S_{298.15K}^{o}$ = 198.636, C_{p} (Mg ₃ Bi ₂) = 3 C_{p} (Mg)+ 2 C_{p} (Bi)			
$\alpha - \mathrm{Mg}_{4}\mathrm{Bi}_{2}: \mathrm{G} = 4 G_{Mg}^{o} + 2 G_{Bi}^{o} + 7740.40 - 11.213\mathrm{T}$			
$L^{0}_{\alpha - Mg_{3}Bi_{2}} = -6819.92 + 7.573 \mathrm{T}$			
β -Mg ₃ Bi ₂ solution :			
β-Mg ₃ Bi ₂ : H_{29815K}^o = -157000.00, $S_{298.15K}^o$ = 212.370, C_p (Mg ₃ Bi ₂) = 3 C_p (Mg) + 2 C_p (Bi)			
$(\Delta H_{\alpha - Mg_3 Bi_2 \to \beta - Mg_3 Bi_2}^{Tr} = 13401.10 \text{ at } 976 \text{ K})$			
$\beta - Mg_4 Bi_2: G = 4 G_{Mg}^o + 2 G_{Bi}^o + 6987.28 - 11.213T$			
$L^{0}_{\beta - Mg_{3}Bi_{2}} = L^{0}_{\alpha - Mg_{3}Bi_{2}}$			
α -Mg ₃ Sb ₂ solution:			
α -Mg ₃ Sb ₂ : $H_{298.15K}^{o}$ = -291910.00, $S_{298.15K}^{o}$ = 151.547, C_{p} (Mg ₃ Sb ₂) = $3C_{p}$ (Mg) + $2C_{p}$ (Sb)			
α -Mg ₄ Sb ₂ : G = 4 G_{Mg}^{o} + 2 G_{Sb}^{o} + 12426.48 - 5.439T			
$L^0_{lpha - Mg_3Sb_2} = 0.0$			
β -Mg ₃ Sb ₂ solution:			
β-Mg ₃ Sb ₂ : $H_{298.15K}^o$ = -253894, $S_{298.15K}^o$ =183.165, C_p (Mg ₃ Sb ₂) = $3C_p$ (Mg) + $2C_p$ (Sb)			
$(\Delta H_{\alpha - Mg_3Sb_2 \rightarrow \beta - Mg_3Sb_2}^{Tr} = 38016.00 \text{ at } 1202 \text{ K})$			
β -Mg ₄ Sb ₂ : G = 4 G_{Mg}^o + 2 G_{Sb}^o + 6694.20 - 5.439T			
$L^{0}_{eta - Mg_{3}Sb_{2}} = L^{0}_{lpha - Mg_{3}Sb_{2}}$			
α -Mg hcp solid solution			
Mg-Bi binary $L^0 = -28827.76 - 27.614T$			

Mg-Bi binary : $L^{\circ} = -28827.76 - 27.614T$ The Gibbs energies of solid and liquid phases of Mg, Bi and Sb are taken from SGTE database [55].

Invariant Reaction	T °(C)	Composition (mole fractions)				
Mg- Bi system						
$I \rightarrow Ma \pm a Ma Pi (autactia)$	553	L: 0.143Bi -0.857Mg				
$L \rightarrow \log + u - \log_3 D_2$ (cutcette)	554	L:0.133Bi-0.867 Mg				
$L \rightarrow \beta - Mg_3Bi_2$ (congruent)	821					
	825					
β -Mg ₃ Bi ₂ $\rightarrow \alpha$ -Mg ₃ Bi ₂ (allotropic)	702					
	701					
$L \rightarrow Bi + \alpha - Mg_3Bi_2$ (eutectic)	260±2	L:0.957Bi-0.043Mg				
	261	L:0.954Bi-0.046 Mg				
Mg-Sb system						
$L \rightarrow Mg + \alpha - Mg_3Sb_2$ (eutectic)	629	L: 0.115Sb -0.885Mg				
	627	L: 0.030Sb -0.070Mg				
$L \rightarrow \beta$ -Mg ₃ Sb ₂ (congruent)	1245±5					
	1227					
β -Mg ₃ Sb ₂ \rightarrow α-Mg ₃ Sb ₂ (allotropic)	925 <i>±</i> 5					
	929					
$L+\beta-Mg_3Sb_2 \rightarrow \alpha-$	930 <i>±</i> 2	L:0.456Sb -0.544 Mg				
Mg ₃ Sb ₂ (peritectic)	928	L:0.489Sb -0.511 Mg				
$L \rightarrow Sb + \alpha - Mg_3Sb_2$ (eutectic)	579	L:0.860Sb- 0.140Mg				
	580	L:0.863Sb- 0.137Mg				

Table 3.2. Optimized invariant reactions in the Mg-Bi and Mg-Sb systems in the present study compared with the assessment of Nayeb-Hashemi and Clark [27 and 52] (in *italic*).

Temperature(K)	Δ H $_{\rm f}$	Δ S _f	Method	Reference
900	-299±3	-59±5	EMF	48
	-291.89	-37.449		
923	-285		Calorimetry	35
	-291.88	-37.442		
773	-235±6	-15±10	EMF	50
	-291.89	-37.451		
298				
	-291.89	-37.447		

Table 3.3. The comparison of calculated thermodynamic quantity of α -Mg₃Sb₂ with the experimental data (kJ/mol, J/mol-K). Values in *italics* are experimental results.

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Figure Captions

Fig. 3.1. Optimized phase diagram of Mg-Bi system.

Fig. 3.2. Optimized phase diagram of Mg-Bi system in the Mg rich side.

Fig. 3.3. Calculated activities of Mg in liquid Mg-Bi solution against its liquid standard state. (a) linear scale and (b) logarithm scale.

Fig. 3.4. Calculated excess partial Gibbs energy of Mg in liquid Mg-Bi solution.

Fig. 3.5. Optimized Gibbs energy of liquid Mg-Bi solution at 975 K and 1123 K.

Fig. 3.6. Optimized enthalpy of mixing of liquid Mg-Bi solution at 975 K and 1123 K.

Fig. 3.7. Optimized entropy of mixing of liquid Mg-Bi solution at 975 K and 1123 K.

Fig. 3.8. Optimized phase diagram of Mg-Sb system.

Fig. 3.9. Optimized phase diagram of Mg-Sb system in the Mg rich side.

Fig. 3.10. Calculated activities of Mg in liquid Mg-Sb solution against its liquid standard state. (a) linear scale and (b) logarithm scale.

Fig. 3.11. Calculated excess partial Gibbs energy of Mg in the liquid Mg-Sb solution.

Fig. 3.12. Optimized Gibbs energy of liquid Mg-Sb system at 1073 K.

Fig. 3.13. Optimized enthalpy of mixing of liquid Mg-Sb solution at 1073 K.

Fig. 3.14. Optimized entropy of mixing of liquid Mg-Sb solution at 1073 K.

Fig. 3.15. Calculated bond fractions in liquid Mg solutions at 1123 K. (a) Mg-Bi and (b) Mg-Sb.

Fig. 3.16. Calculated excess stability function of liquid Mg-Bi and Mg-Sb at 975 K and 1123 K.

Fig. 3.17. Calculated Δ Cp functions for liquid Mg solutions. (a) Mg-Bi and (b) Mg-Sb.

Fig. 3.18. Phase diagrams of (a) Mg-Bi and (b) Mg-Sb systems with meta-stable miscibility gaps at 1 bar.



Fig. 3.1. Optimized phase diagram of Mg-Bi system.



Fig. 3.2. Optimized phase diagram of Mg-Bi system in the Mg rich side.



Fig. 3.3 Calculated activities of Mg in liquid Mg-Bi solution against its liquid standard state. (a) linear scale and (b) logarithm scale.



Fig.3.4. Calculated excess partial Gibbs energy of Mg in liquid Mg-Bi solution.



Fig. 3.5. Optimized Gibbs energy of liquid Mg-Bi solution at 975 K and 1123 K.



Fig. 3.6. Optimized enthalpy of mixing of liquid Mg-Bi solution at 975 K and 1123 K.



Fig. 3.7. Optimized entropy of mixing of liquid Mg-Bi solution at 975 K and 1123 K.



Fig. 3.8. Optimized phase diagram of Mg-Sb system.



Fig. 3.9. Optimized phase diagram of Mg-Sb system in the Mg rich side.



Fig. 3.10. Calculated activities of Mg in liquid Mg-Sb solution against its liquid standard state. (a) linear scale and (b) logarithm scale.



Fig. 3.11. Calculated excess partial Gibbs energy of Mg in the liquid Mg-Sb solution.



Fig. 3.12. Optimized Gibbs energy of liquid Mg-Sb system at 1073 K.



Fig. 3.13. Optimized Enthalpy of Mixing of liquid Mg-Sb system at 1073 K.



Fig. 3.14. Optimized entropy of mixing of liquid Mg-Sb system at 1073 K.



Fig. 3.15. Calculated bond fractions in liquid Mg solutions at 1123 K. (a) Mg-Bi and (b) Mg-Sb.



Fig. 3.16. Calculated Excess Stability function of liquid Mg-Bi and Mg-Sb at 975 K and 1123 K.



Fig. 3.17. Calculated Δ Cp functions for liquid Mg solutions. (a) Mg-Bi and (b) Mg-Sb.



Fig.3.18. Phase diagrams of (a) Mg-Bi and (b) Mg-Sb systems with meta-stable miscibility gaps at 1 bar.

Chapter 4: Article 2

Thermodynamic modeling of the Al-Bi, Al-Sb, Mg-Al-Bi and Mg-Al-Sb systems

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All available thermodynamic and phase diagram data of the binary Al-Bi and Al-Sb systems and ternary Mg-Al-Bi and Mg-Al-Sb systems have been critically evaluated and all reliable data have been simultaneously optimized to obtain the best set of the model parameters for each ternary system. The Modified Quasichemical Model used for the liquid solution shows the high predictive capacity for the ternary systems. The ternary liquid miscibility gap in the Mg-Al-Sb system due to the ordering behaviour of the liquid solution can be predicted reasonably without any ternary parameters. Using the optimized model parameters, the unexplored phase diagrams of the Mg-Al-Bi and Mg-Al-Sb systems were properly predicted for the first time. All calculations were performed using the FactSage thermochemical software.

Keywords: Al-Bi, Al-Sb, Mg-Al-Bi, Mg-Al-Sb, liquid miscibility gap, Modified Quasichemical Model.
4.1. Introduction

As following of the previous study [1] on the Mg-Bi and Mg-Sb systems, the critical evaluation and optimization of all thermodynamic and phase diagrams of the Mg-Al-Bi and Mg-Al-Sb systems have been performed in the present study. Since the results on the previous thermodynamic assessments for binary Al-Sb [2, 3] and Al-Bi [4] are less satisfactory, the two binary systems were also optimized in the course of the present study. The thermodynamic properties of the ternary liquid phase were described with the Modified Quasichemical Model [5, 6], which showed the high predictive capacity in the ternary systems were reasonably predicted from the binary model parameters without any ternary additional parameter.

This is part of the wide thermodynamic database development project for the Mg-Sn-Al-Zn-Si-Mn-Bi-Sb-Pb-Ge-etc system.

4.2. Thermodynamic Models

4.2.1. Liquid phase

The Modified Quasichemical Model [5, 6], which takes into account a short-rangeordering of the nearest-neighbour atoms, was used for liquid phase. The binary liquid Mg-Al, Mg-Bi and Mg-Sb solutions were already modeled [1, 7] using the Quasichemical Model. In the present study, two binary liquid solutions, Al-Bi and Al-Sb, are optimized using the Modified Quasichemical Model. Then, the thermodynamic properties of the ternary Mg-Al-Bi and Mg-Al-Sb solutions were calculated from the binary optimized model parameters with one small adjustable ternary model parameter. The short description of the model is given below. For binary A-B solution, the following quasichemical pair exchange reaction can be considered:

$$(A-A) + (B-B) = 2(A-B)$$
 [1]

where (i-j) represents a first-nearest-neighbour pair of *i* and *j*. The non-configurational Gibbs energy change for the formation of two moles of (A-B) pairs according to reaction [1] is Δg_{AB} . Then the Gibbs energy of the solution is given by:

$$G = (n_A G_A^o + n_B G_B^o) - T\Delta S^{\text{config}} + n_{AB} (\Delta g_{AB}/2)$$
^[2]

where G_A^o and G_B^o are the molar Gibbs energies of the pure components A and B, n_A and n_B are the numbers of moles of A and B atoms, and n_{AE} is the number of moles of (A-B) pairs. ΔS^{config} is the configurational entropy of mixing given by a random distribution of the (A-A), (B-B) and (A-B) pairs in the one-dimensional Ising approximation. The Δg_{AB} is the model parameter to reproduce the Gibbs energy of liquid phase of the binary A-B system, which is expanded as a polynomial in terms of the pair fractions, as follows:

$$\Delta g_{AB} = \Delta g_{AB}^{o} + \sum_{i \ge 1} g_{AB}^{i0} (X_{AA})^{i} + \sum_{j \ge 1} g_{AB}^{0j} (X_{BB})^{j}$$
[3]

Where Δg_{AB}^{o} , g_{AB}^{i0} and g_{AB}^{0j} are the adjustable model parameters which can be functions of temperature, and X_{AA} and X_{BB} are the pair fractions of (A-A) and (B-B).

The Gibbs energy of the ternary A-B-C liquid phase is estimated by the extended Modified Quasichemical Model from the binary parameters as described in a recent publication [4].

$$G = (n_{\rm A}G_{\rm A}^{\circ} + n_{\rm B}G_{\rm B}^{\circ} + n_{\rm C}G_{\rm C}^{\circ}) - T\Delta S^{\rm config} + 1/2(n_{\rm AB}\Delta g_{\rm AB} + n_{\rm BC}\Delta g_{\rm BC} + n_{\rm AC}\Delta g_{\rm AC})$$
[4]

The thermodynamic properties of the ternary liquid solution was calculated from the binary and ternary parameters using an asymmetric "Kohler-like" [8] approximation. Then, the Gibbs energy, Δg_{AB} , forming (A-B) pairs according to reaction (Eq. [1]) is given in the ternary system by:

$$\Delta g_{AB} = \Delta g_{AB}^{\circ} + \sum_{i \ge 1} g_{AB}^{i \ 0} Y_{A}^{i} + \sum_{j \ge 1} g_{AB}^{0 \ j} (1 - Y_{A})^{j} + \sum_{j \ge 1} q_{AB(C)}^{ijk} Y_{A}^{i} (1 - Y_{A})^{j} (\frac{Y_{C}}{Y_{A} + Y_{B}})^{k}$$
[5]

Where $Y_m = X_{mm} + \sum_{n \neq m} X_{mn}/2$. $q_{AB(C)}^{ijk}$ are ternary additional model parameters for the adjustment of the Gibbs energy of ternary A-B-C liquid phase. The details of the present model can be found in the previous studies [5, 6]. In the present study, we found out that only one small $q_{MgX(Al)}^{00k}$ parameter is enough to explain the thermodynamic properties of the Mg-Al-Bi and Mg-Al-Sb systems. The optimized model parameters of the Modified Quasichemical Model for liquid phase are listed in Table 4.1.

4.2.2. Solid solutions

The thermodynamic properties of γ -Mg₁₇Al₁₂, \hat{a} -AlMg, \hat{a} - and \hat{a} -Mg₃Xi₂(X=Bi and Sb) solid solutions were previously optimized by Kang et al.[7] and the present authors [1] using the two sublattice Compound Energy Formalism [9]. \hat{a} -Mg hcp solution and FCC-Al rich solution were also described [1, 7] using the one sublattice Compound Energy Formalism. All the previous model parameters are adopted in the present study without any further modification. All the solutions were assumed as binary solutions except for \hat{a} -Mg hcp phase.

4.2.3. Stoichometric Compounds and Elements

All the Gibbs energies of pure solid and liquid element Mg, Al and Bi and Sb are taken from SGTE database [10]. The Gibbs energy of å-AlMg(Al₃₀Mg₂₃) was optimized previously [7]. The thermodynamic properties of AlSb stoichometric compound are optimized in the present study.

4.3 Critical Evaluation and Optimization

4.3.1. Al-Sb system

Although the Al-Sb system has been reviewed and thermodynamically assessed several times [2, 3, 15, 21], the results of assessments are found to be less satisfactory. Moreover, new key experimental data [15] which can constrain the Gibbs energies of solid and liquid phases of the Al-Sb system were reported recently. Thus, the Al-Sb system was critically evaluated and reoptimized in the present study.

The phase diagram of the Al-Sb system has been investigated by many researchers. Urazova [11], Guetler and Bergmann [12] and Loofs-Rassow [13] performed the thermal analysis and metallographic phase examination to determine the liquidus of AISb phase. Linnebach and Benz [14] obtained liquidus temperatures on the Sb rich side by liquid phase epitaxy technique. Later, Yamaguchi et al.[15] reported the liquidus of the AlSb from the indirect heat content measurement, where phase transformation temperatures were determined from the non-linearity of heat content curves with temperatures. Two eutectic reactions, $L \rightarrow Al + AlSb$ and $L \rightarrow Sb + AlSb$ were determined relatively well. Loofs-Rassow determined the first eutectic reaction at 650 °C and 0.002 X_{Sb}. Guetler and Bergmann determined the first and second eutectic reaction at 656 °C and 0.001 X_{Sb} and at 624 K and 0.956 X_{Sb}, respectively. Yamaguchi et al. determined the eutectic temperatures as 659 °C and 628 °C, respectively. The melting temperature of AlSb compound is also relatively well determined. Lichter and Sommelet [16] and Yamaguchi et al. reported the melting temperature of AlSb to be 1330 K and 1335 K respectively from their calorimetric data. Guetler and Bergmann and Urazova obtained the melting temperature as 1322 K and 1335 K respectively using thermal analysis technique. Gerdes and Predel [17] reported 1330 K from the DTA measurement. No mutual solubilities between solid Al and Sb have been reported, and no non-stoichiometry of AlSb has been reported. In general, the phase diagram data are consistent with each other.

The thermodynamic properties of liquid Al-Sb phase have been well investigated. Girard et al.[18] used the drop calvet calorimeter to determine the mixing enthalpy of liquid Al-Sb solution in the temperature range of 1119 to 1225 K and the composition ranges of $0 < X_{Al} < 0.24$ and $0.83 < X_{Al} < 0.98$. Lee and Sommer [19] determined the partial enthalpy of mixing of the Al rich liquid solution at 1200 K using a high temperature solution calorimeter. Yamaguchi et al.[15] measured the heat contents of the entire Al-Sb system between 800 and 1450 K. They calculated the enthalpy and entropy of mixing of liquid Al-Sb solution form the experimental data, which can constrain the thermodynamic properties of the liquid solution. Predel and Schallner [20] determined the activities of Al in the liquid Al-Sb solution using the molten AlCl₃-NaCl galvanic cell in the temperature range of 933 to 1423 K. Zajaczkowski and Botor [21] reported the activities of Sb from the Knudsen cell vapour pressure measurement between 940 and 1461 K.

The thermodynamic data of AlSb compound are rather limited. Yamaguchi et al.[15] measured the low temperature heat capacity of solid AlSb compound from 4 to 300 K using an adiabatic calorimeter and suggested the S_{29815K}^o of AlSb phase to be 63.9 J/mol-K. They also determined the enthalpy of formation of AlSb at 773 K using a twin solution calorimeter. Piesbergen [22] also performed the low temperature heat capacity measurements of AlSb compound over the temperature range of 4 to 300 K using adiabatic calorimetry and reported S_{29815K}^o of AlSb = 64.2 J/mol-K. Lichter and Sommelet [17] measured the heat content of solid AlSb phase over the temperature range of 573 to 1723 K using a drop calorimeter. From the measured heat content data, they derived the Cp of AlSb. Similarly, Itagaki and Yamaguchi [23] measured the heat content of AlSb in the temperature range from 800 to 1450 K using a drop calorimeter. Martosudirdjo and Pratt [24] also determined the enthalpy of formation of AlSb at 298 K using a solution calorimeter with Sn solvent.

Coughanowr et al.[3] carried out the thermodynamic modeling of the Al-Sb system. They attempted to describe the Gibbs energy of liquid phase using both Bragg Williams Redlich-Kister (BWRK) model and Associate Solution Model and compared the optimization results. They claimed that the BWRK model reproduced the thermodynamic

data and phase diagram data of the Al-Sb system more accurately than the Associate solution model. In their assessment, using the BWRK model 7 model parameters including four temperature dependent parameters was required for liquid phase. One of the temperature dependent parameter was TlnT term. Later, Zajaczkowski and Botor [21] presented the thermodynamic assessment of the system using the Associate solution model with AlSb as associates. But the result of their assessment was rather unsatisfactory. Yamaguchi et al.[15] performed the thermodynamic assessment of the system based on their own experimental data. Liquid Al-Sb solution was described using the BWRK model with 12 model parameters including 8 temperature dependent parameters. Four parameters among the 8 parameters were TlnT terms. Very recently, Balakumar and Medraj [2] performed the thermodynamic optimization of the Al-Sb system again. They used the BWRK model to describe the liquid phase. Although they could reproduce the phase diagram reasonably well, a large discrepancy for the thermodynamic data of solid AlSb phase was found. This will be discussed below.

In the present study, the Al-Sb system was re-optimized using the Modified Quasichemical Model for liquid Al-Sb solution. All the solid phases were treated as stoichometric phases. All phase diagram data and thermodynamic data for solid and liquid phases discussed above were simultaneously optimized to obtain the best set of model parameters reproducing all reliable experimental data within experimental error limits.

Fig. 4.1 shows the phase diagram of the Al-Sb system calculated in the present study along with all experimental data [11-15]. Excellent agreement between the calculated phase diagram and experimental liquidus data was achieved. The optimized eutectic reactions are calculated to be 658 °C at 0.004 X_{Sb} and 625 °C at 0.980 X_{Sb} . The melting temperature of AlSb compound is calculated to be 1335 K. The invariant reactions are compared with the experimental data in Table 4.2.

Fig. 4.2 shows the optimized heat capacity and heat content of solid AlSb phase along with experimental data. As can be seen in Fig. 2 (a), the low temperature heat capacity (Cp) data by Yamaguchi et al.[15] are consistent with Cp data derived by Lichter and Sommelet

[17]. In the present study, the entropy of AlSb compound at 298 K ($S_{298,15K}^{o}$) was set to be 64.0 J/mol-K based on the experimental low temperature Cp data [16, 22], and the Cp function of solid AlSb from 298 K to melting temperature was derived from the Cp data of Lichter and Sommelet. The heat contents of AlSb are compared in Fig. 2(b). The present optimization can reproduce the heat content of solid AlSb as well as the enthalpy of fusion accurately. The results of the previous assessments [2, 3] are also plotted in Fig. 2 for comparison. As can be seen in the figure, the results of Balakumar and Medraj [2] are quite different from the experimental data. The optimized $S_{298,15K}^{o}$ of the previous assessments are 64.9 J/mol-K by Coughanowr et al.[3] and 42.2 J/mol-K by Balakumar and Medraj [2].

The enthalpy and Gibbs energy of formation of AlSb phase from pure elements are plotted in Fig. 4.3. The optimized enthalpy curve of the present study is in agreement with the experimental data of Yamaguchi et al.[15] at 773 K. However, it was impossible to reproduce the experimental data of Martosudirdjo and Pratt [24] simultaneously. The previous assessment by Coughanowr et al.[3] are more consistent with the results of Martosudirdjo and Pratt [24]. The optimized Gibbs energy of the AlSb phase in the present study is about 4 kJ/mol lower than the assessed value by Coughanowr et al.[3], which results from the difference in ΔH_{29815K}^o . The results of Balakumar and Medraj [2] are completely different from the experimental data. As mentioned above, the thermodynamic data of the AlSb phase assessed by Balakumar and Medraj is erroneous.

The thermodynamic properties of liquid Al-Sb solution are plotted in Fig. 4.4. Yamaguchi et al.[15] reported a noticeable positive deviation of the mixing enthalpy in the Al rich side using a drop calorimetry technique, while Girard et al.[18] found a negative deviation in the same composition range. The calculated enthalpy of mixing in the present study is more consistent with Girard et al. in the Al rich side. The calculated enthalpy is also in good agreement with Yamaguchi et al. at $X_{Al} > 0.2$. The calculated entropy and Gibbs energy of mixing show good agreement with the results derived by Yamaguchi et al. The results of previous assessment by Balakumar and Medraj [2] for the liquid Al-Sb are quite

similar to the present optimization results. While, the results of Coughanowr et al.[3] are unsatisfactory for liquid Al-Sb solution.

Fig. 4.5 shows the activities of Al and Sb in liquid Al-Sb solution at 1350 K along with experimental data. Predel and Schallner [20] determined the activities of Al using an emf technique and Zajaczkowski and Botor [21] determined the activities of Sb from the Knudsen effusion cell results. They also calculated the activities of Al and Sb using the Gibbs-Duhem equation. Both experimental data are consistent with each other in the Sb rich side. However, the experimental results are quite different in the Al rich side. The activity of Al calculated in the present study shows positive deviations from ideality in the Al rich side, which is more consistent with the results of Zajaczkowski and Botor. It was difficult to reproduce the activities of Al by Predel and Schallner in the Al rich side, which shows slight negative deviation from ideality, together with the other thermodynamic properties of liquid solution in Fig. 4.

In order to reproduce all the thermodynamic properties of liquid phase and phase diagram, four model parameters including a very small temperature dependent parameter were used for the Modified Quasichemical Model [5,6] in the present study. Compared with the previous assessment, the number of model parameters is significantly reduced even with much better reproduction of the experimental results. The thermodynamic properties of solid AlSb phase are also well reproduced in the present study.

4.3.2. Al-Bi system

The phase diagram and mixing enthalpy of liquid solution for the Al-Bi system are relative well investigated. No comprehensive thermodynamic optimization on the system has been performed.

Hansen [25] summarized the earlier research on the Al-Bi system. Wittig and Keil [26] investigated the phase diagram and mixing enthalpy of liquid phase using the thermal analysis and high temperature calorimetry techniques. The wide liquid immiscibility of the Al-Bi system was determined up to 900 °C. The mixing enthalpies of the entire Al-Bi

liquid were determined at 940, 973 and 1177 K. Later, Martin-Garin et al.[27] investigated the phase diagram using a thermal analysis technique up to 1000 °C. They also investigate the thermodynamic properties of the Bi rich liquid ($X_{Bi} > 0.675$) using the AlCl₃-KCl-LiCl molten electrolyte cell. Auxiliary information on the liquidus of Al and immiscibility boundary was derived from the emf measurement. Predel and Sandig [28] investigated the phase diagram of the entire Al-Bi system using the DTA technique. The monotectic temperature was determined to be 657 °C, and the critical temperature of liquid miscibility gap was determined to be 1050 °C at 0.175 X_{Bi}. In addition, they determined the enthalpy of mixing of liquid phase at 1373 K using a calorimeter and found positive deviation of the Al-Bi liquid from ideal behaviour.

McAlister [29] performed thermodynamic assessment of the Al-Bi system. Liquid solution was described with the BWRK model using 8 model parameters including 4 temperature dependent parameters. Recently the system was reinvestigated by Kim and Saunders [4] using the BWRK model. However, neither critical review of the literature data nor thermodynamic optimization was given in details.

Fig. 4.6 shows the optimized phase diagram of the Al-Bi system. The liquidus of Al determined by Predel and Sandig [28] and Martin-Garin et al.[27] are consistent with each other. However, the liquidus measured by Witting and Keil [26] is rather inconsistent with the other data, in particular, in high Bi region. The optimized liquidus in the present study is in good agreement with Predel and Sandig and Martin-Garin et al. The optimized critical temperature of liquid miscibility gap is 1068 °C at X_{Bi} =0.20 and the optimized monotectic temperature is 654 °C. The invariant reactions are compared with experimental data in Table 4.2. Although the critical temperature of liquid immiscibility, 1068 °C, optimized in the present study is slightly higher than the reported value, 1050 °C, by Predel and Sandig [28], this seems to be acceptable in the consideration of the difficulty in accurate determination of the critical temperature.

The mixing enthalpy of liquid Al-Bi solution is calculated in Fig. 4.7 along with experimental data [26, 28]. The linear changes of the mixing enthalpy in liquid

immiscibility region at 940, 973, 1077 K by Wittig and Keil [26] are well reproduced in the present study. The experimental data of Predel and Sandig [28] at 1373 K are also reasonably reproduced.

Fig. 4.8 shows the activities of Al and Bi in liquid Al-Bi solution. The experimental activities of Al derived from the emf curves of Martin-Garin et al.[27] show a positive deviation from ideal behaviour, which is well reproduced in the present study.

In the present optimization, four model parameters including a temperature dependent parameter were used for the Modified Quasichemical Model [5, 6] to simultaneously reproduce the phase diagram and thermodynamic properties of Al-Bi system.

4.3.3. Mg-Al-Bi System

No thermodynamic assessment has been performed for the Mg-Al-Bi system previously. Although the phase diagram of the ternary system has been relatively well studied, no thermodynamic properties of the ternary system have been investigated.

The phase diagram experiment for the Mg-Al-Bi system requires the special care to prevent the oxidation of Mg which can change the alloy compositions during the experiment. The ternary system has been studied by Masing and Reinbach [30] and Scheil and Glauner [31] using a thermal analysis technique associated with metallographic phase examination. Masing and Reinbach used the graphite crucibles under the protective fluxes of 40% KCl-60% MgCl₂, and Scheil and Glauner used the silica crucibles under the LiCl containing protective fluxes. The phase diagram of the pseudo-binary Mg₃Al₂ (Mg₁₇Al₁₂)-Mg₃Bi₂ section was investigated in both studies. In addition, the extension of binary liquid miscibility gap of Al-Bi system to the ternary system was investigated relative well. In particular, Scheil and Glauner provided the phase diagrams of the Mg-Al-20wt%Bi and Mg-Bi-10wt%Al isopleths. No new ternary solid phase was reported.

Fig. 4.9 shows the calculated optimized ternary liquidus projection of the Mg-Al-Bi system in the present study. The pseudo-binary phase diagrams of the Mg₃Al₂-Mg₃Bi₂, Mg-AlBi and Al-Mg3Bi2 sections and two isopleths of 10 wt% Al and 20 wt% Bi are calculated in Fig. 4.10 along with experimental data [30, 31]. The phase diagram experiments for the Mg₃Al₂-Mg₃Bi₂ section are consistent with each other except for the temperature corresponding to the liquid miscibility gap formation. Fig. 4.11 shows the experimental primary phase areas of all solid phases and liquid miscibility gap determined by Masing and Reinbach [30] and the liquidus projection of Scheil and Glauner [31]. In general, the experimental data are consistent with each other.

The calculated phase diagrams and liquidus projection of the present study are in good agreement with experimental data within experimental error limits. In the present study, the Gibbs energy of the ternary liquid phase was calculated from the previously optimized binary model parameters of Mg-Al [7] and Mg-Bi [1] and the present model parameters of Al-Bi using the symmetric "Kohler" interpolation technique [8]. One small ternary parameter was introduced to reproduce the experimental data more accurately. The optimized invariant reactions for the ternary system are listed in Table 4.3.

Fig. 4.12 shows the liquidus projection of the Mg-Al-Bi system just predicted from the Modified Quasichemical Model [5, 6] with the Kohler interpolation technique [8] without any ternary model parameters. The predicted liquidus projection is very similar to the optimized diagram in Fig. 9. The predicted two liquids area (liquid miscibility gap) is slightly smaller than the final optimized diagram with one ternary parameter. This can stress that the model parameters of the binary sub-liquid systems are well applicable to the high order system. The predictive ability of the Modified Quasichemical Model can be emphasised too.

4.3.4. Mg-Al-Sb System

The phase diagram of the Mg-Al-Sb system was firstly investigated by Loofs-Rassow [13] using the thermal analysis associated with metallographic phase determination. They

performed the thermal analyses for 46 different alloys in the Al-Mg₂Al₃-Mg₃Sb₂-Sb region, and provided the primary crystalline phases and eutectic phase assemblages from metallographic observation. Unfortunately, the details of the experimental description are lacking and the thermal arrest temperatures in the experiment are not given in their paper except for the Al-Mg₃Sb₂ pseudo-binary section. The development of a large ternary liquid miscibility gap along the Al-Mg₃Sb₂ diagonal was reported. He also mentioned the possibility of small Al solubility (maximum 3 wt% of Al) into Mg₃Sb₂ with no chemical analysis result. Although the alloy compositions can largely change during the experiment due to the oxidation of Mg, the final alloy compositions were not analyzed after the experiment. No ternary solid phase was found in the Mg-Al-Sb system.

Later, Guetler and Bergmann [12] investigated the Mg-Al-Sb system using the classical quenching and thermal analysis techniques associated with metallographic phase examination. In order to minimize the oxidation of Mg alloys like the Mg-Al-Bi system, they performed the experiments in porcelain crucible under a CO₂ gas atmosphere or a molten salt protection layer. The main purpose of the experimental study by Guetler and Bergmann was to determine the ternary liquid miscibility gap. In the most of cases, two separate layers of immiscible liquids were analyzed by a wet chemical analysis after equilibration at around 1000 °C. The actual equilibration temperatures were not mentioned in their paper except for one sample. Since the temperatures of liquid Mg alloys covered by molten salts were measured using a pyrometer, the actual experimental temperature of the miscibility gap experiments could be about 1000 ± 100 °C. Guetler and Bergmann also mentioned that the experimental results from the alloys belonging to the Al-Mg-Mg₃Sb₂ triangle composition are less reliable due to the strong oxidation of Mg, high impurity of Si (maximum 1.7 wt%), and incomplete settling of two immiscible layers of liquids. Whereas, the experiments for the Al-AlSb-Mg₃Sb₂ region were considered to be more reliable. The partial phase diagram for the Mg₃Sb₂-Al pseudo binary section was also determined using the thermal analysis technique. No ternary solid phase was found in the experiment.

Recently, Balakumar and Medraj [2] performed the thermodynamic optimization of the Mg-Al-Sb system. In their paper, the liquid projection of the Mg-Al-Sb system and two pseudo-binary sections for the Al-Mg₃Sb₂ and AlSb-Mg₃Sb₂ were predicted from their binary model parameters using the Bragg Williams Redlich-Kister liquid model with Muggiano [8] interpolation technique. Although they claimed that their predicted diagrams are consistent with the experimental data of Loofs-Rassow [13] and Guetler and Bergmann [12], the shape of miscibility gap and size are quite different from the experimental data. In addition, as pointed out by the present authors [1] and Malakhov and Balakumar [32], the thermodynamic modeling results of the Mg-Sb system were erroneous. As mentioned in section 3.1 in the present study, the modeling results of Al-Sb system by Balakumar and Medraj are unsatisfactory too. Thus, it can be said that no accurate thermodynamic optimization on the Mg-Al-Sb system is presently available.

Fig. 4.13 shows the calculated optimized liquidus projection of the Mg-Al-Sb system. Like the Mg-Al-Bi system, the Gibbs energy of the ternary liquid phase was calculated from the previously optimized binary model parameters of Mg-Al [7] and Mg-Sb [1] and the present model parameters of the Al-Sb using the symmetric "Kohler" interpolation technique. A small ternary parameter was introduced to reproduce the experimental data more accurately.

The comparisons of the present calculations with the available experimental data are presented in Figs. 4.14 to 4.16. The optimized primary crystalline regions are compared with experimental data of Guetler and Bergmann [12] and Loofs-Rassow [13] in Fig. 4.14. The experimental data for liquid immiscibility region are rather inconsistent with each other. If we consider the difficulty in the detection of small amount of secondary liquid phase in liquid immiscibility using a thermal analysis and as-cast microstructure examination, the real liquid miscibility gap could be wider than the experimental results. Considering the discrepancy between the experimental data and possible experimental error, the present optimized primary regions seem to be reasonable.

The ternary liquid miscibility gap is compared with experimental data of Guetler and Bergmann [12] in Fig. 4.15. Since the specific experimental temperatures were not provided by Guetler and Bergmann, it is hard to compare the experimental results accurately. In the present study, we assumed the experimental temperatures were between 900 °C and 1100 °C. The experimental tie-lines of the liquid miscibility gap for the alloys in the Mg rich region are quite unlikely. As seen in the Fig. 4.15, tie-lines for the Mg rich alloys are directed to Mg₃Sb₂ composition, which might be induced by the formation of Mg₃Sb₂ phase during quenching process. In addition, the overall liquid compositions after equilibration were off from the initial alloy composition too, possibly due to the oxidation of Mg. Guetler and Bergmann mentioned that the results in the high Mg region are less reliable. So, the experimental data in this region were weighed less in the present optimization. The liquid miscibility gap determined by Guetler and Bergmann is larger than the result of Loofs-Rassow [13]. The optimized liquid miscibility gap is consistent with experimental data of Guetler and Bergmann within experimental error limits.

The calculated pseudo-binary diagrams of the Al-Mg₃Sb₂ and AlSb-Mg₃Sb₂ sections are presented in Fig. 4.16. There is inconsistency in liquidus of Mg₃Sb₂ in the Al-Mg₃Sb₂ section. The optimized liquidus are in agreement with the result of Guetler and Bergmann [12] and slightly higher than the results of Loofs-Rassow [13]. The thermal arrests detected by Guetler and Bergmann [12] in the Al-Mg₃Sb₂ section are well reproduced in the present study. The thermal arrest at about 1170 °C postulated as monotectic temperature by Loofs-Rassow was hard to reproduce. In fact, this seems to be closer to the liquidus temperature. According to Guetler and Bergmann, the monotectic temperature should be about 1000 °C, which is well reproduced in the present study. Loofs-Rassow determined the primary crystalline phase regions of AlSb and Mg₃Sb₂ in the AlSb-Mg₃Sb₂ section without providing the liquidus temperatures. The calculated phase diagram in Fig. 16 (b) can reproduce the primary phase regions of Loofs-Rassow.

Fig. 4.17 shows the liquidus projection of the Mg-Al-Sb system just predicted from the Modified Quasichemical Model [5, 6] with the Kohler interpolation technique [8] without any ternary model parameters. The ternary liquid miscibility gap is predicted directly from

the binary model parameters. This results from the strong ordering behaviour of Mg-Sb pair in the Al-Mg₃Sb₂ diagonal:

$$2 (Mg-Al) + (Sb-Sb) = 2(Mg-Sb) + (Al-Al)$$
 [6]

where the Gibbs energy of the reaction, $\Delta G_{[6]} \ll 0$. The predicted liquidus projection is similar to the optimized diagram in Fig. 4.13 except that the predicted liquid miscibility gap is rather smaller than the optimized miscibility gap. One small ternary liquid parameter was introduced to enlarge the liquid miscibility gap, which is similar to the above Mg-Al-Bi system. This can stress that the model parameters of the binary sub-liquid systems are well applicable to the high order system and the predictive capacity of the Modified Quasichemical Model is justified too. The ternary parameter for the Mg-Al-Sb system is about half of the parameter for the Mg-Al-Bi system.

4.4 Summary

All available thermodynamic and phase diagram data of the binary Al-Sb and Al-Bi systems and ternary Mg-Al-Bi and Mg-Al-Sb systems have been critically evaluated and all reliable data have been simultaneously optimized. As results of the optimization, one set of model parameters for the Gibbs energies of all phases as functions of composition and temperature was obtained for each ternary system. The strong ordering behaviour of Mg-Al-Bi and Mg-Al-Sb liquid solution was well described by the Modified Quasichemical Model. In particular, the ternary liquid miscibility gap was predicted reasonably without any ternary additional model parameters. The unexplored phase diagrams of the Mg-Al-Bi and Mg-Al-Sb systems were properly predicted for the first time. The optimized model parameters can be readily used with general thermodynamic software and databases, such as FactSage [33], to calculate phase equilibria and thermodynamic properties for the Mg-Al-Bi and Mg-Al-Sb systems at any given set of conditions.

4.5. References

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Figure Captions

Table 4.1 Optimized thermodynamic model parameters for the Al-Bi, Al-Sb, Mg-Al-Bi and Mg-Al-Sb systems in the present study (J/mol and J/mol-K).

Table 4.2 Invariant reactions for the Al-Bi and Al-Sb systems optimized in the present study compared with the experimental results.

Table 4.3 Invariant reactions for the Mg-Al-Bi and Mg-Al-Sb systems optimized in the present study.

Fig. 4.1. The calculated optimized phase diagram of the Al-Sb system in the present study along with experimental data [11-15].

Fig. 4.2. Thermodynamic properties of the AlSb phase optimized in various assessments [2, 3] along with experimental data [15, 23]. (a) heat capacity and (b) heat content.

Fig. 4.3. Thermodynamic properties of the AlSb phase optimized in various assessments [2, 3] along with experimental data [15, 24]. (a) enthalpy of formation and (b) Gibbs energy of formation from solid Al and Sb.

Fig. 4.4. Thermodynamic properties of liquid Al-Sb solution at 1350 K optimized in the present study in comparison with experimental data [15, 18] and the previous assessment results [2, 3]. (a) enthalpy of mixing, (b) entropy of mixing and (c) Gibbs energy of mixing.

Fig. 4.5. Activities of Al and Sb in liquid Al-Sb solution optimized in the present study along with experimental data [20, 21] and previous assessment results [2, 3, 15].

Fig. 4.6. The calculated optimized phase diagram of the Al-Bi system in the present study along with experimental data [26-28].

Fig. 4.7. Optimized enthalpies of mixing of the Al-Bi system at various temperatures in the present study along with experimental data [26, 28].

Fig. 4.8. Activities of Al and Bi in liquid Al-Bi solution against its liquid standard state optimized in the present study along with experimental data [27].

Fig. 4.9. The calculated optimized liquidus projection of the Mg-Al-Bi system in the present study. Temperatures in °C.

Fig. 4.10. Phase diagrams of various sections in the Mg-Al-Bi system calculated in the present study along with experimental data [30, 31]. (a) Mg₃Bi₂-Mg₃Al₂, (b) Mg-AlBi, (c) Al-Mg₃Bi₂, (d) 10 wt% Al isopleth and (e) 20 wt% Bi isopleths.

Fig. 4.11. Calculated primary crystalline phase regions and liquidus projection of the Mg-Al-Bi system in comparison to experimental data [30, 31].

Fig. 4.12. Liquidus projection of the Mg-Al-Bi system just predicted from binary model parameters without any ternary parameters.

Fig. 4.13. Calculated liquidus miscibility gaps of the Mg-Al-Sb ternary system at 900 °C and 1000 °C in comparison with experimental data [12]. (Open circle: overall initial composition, closed circle: liquid composition after phase separation.)

Fig. 4.14. Optimized primary crystalline regions in the Mg-Al-Sb system in the present study in comparison with experimental data [12, 13].

Fig. 4.15. Calculated liquidus miscibility gaps of the Mg-Al-Sb ternary system at (a) 900 °C and (b) 1000 °C in comparison with experimental data [12].

Fig. 4.16. Calculated phase diagrams of (a) $Al-Mg_3Sb_2$ section and (b) $AlSb-Mg_3Sb_2$ section in the Mg-Al-Sb system along with experimental data [12, 13].

Fig. 4.17. Liquidus projection of the Mg-Al-Sb system just predicted from binary model parameters without any ternary parameters.

Table 4.1. Optimized thermodynamic model parameters for the Al-Bi, Al-Sb, Mg-Al-Bi and Mg-Al-Sb systems in the present study (J/mol and J/mol-K).

Liquid solution				
Al-Sb system:	$\Delta g^0_{AlSb} = -5768.40 + 1.674 \mathrm{T}$			
	$\Delta g_{AlSb}^{10} = 5836.68$			
	$\Delta g_{AlSb}^{01} = 1334.70$			
	$Z_{A1A1} = Z_{SbSb} = Z_{A1Sb} = Z_{SbA1} = 6.$			
Al-Bi system:	$\Delta g^0_{AlBi} = 6745.67$			
	$\Delta g_{AlBi}^{10} = 16669.77 - 9.246T$			
	$\Delta g_{AlBi}^{01} = 6174.28$			
	$Z_{A A } = Z_{B B } = Z_{A B } = Z_{B A } = 6.$			
Ternary addition	onal parameters			
Mg-Al-Bi system: $q_{MgBi(Al)}^{003} = 14225.60$				
Mg-Al-Sb system: $q_{MgSb(Al)}^{003} = 7531.20$				
Solid phase				
AlSb stoichom	etric phase			
H_{29815K}^{o} = -57207.30, $S_{298.15K}^{o}$ = 63.976.,				
$C_{\rm p} = 46.13 + 0.00771 \text{T} + 4.0 \times 10^{-8} \text{T}^2 (300 \text{ K} - 1335 \text{ K})$				
= 56.494 (T > 1335)			

The thermodynamic model parameters for the Mg-Al, Mg-Bi and Mg-Sb systems were taken from the previous studies [1,7] without any modifications.

The Gibbs energies of pure solid and liquid Al, Bi and Sb were taken from the SGTE database [10]

Invariant reaction	T (°C)	Composition (mole fractions)	Reference			
Al-Sb system						
	650	L: 0.002 Sb -0.098 Al	[13]			
$L \rightarrow Al + AlSb$	656	L: 0.001 Sb-0.099 Al	[12]			
(eutectic)	659	-	[15]			
×	658	L: 0.004 Sb-0.096 Al	This work			
	624	L: 0.956 Sb-0.044 Al	[12]			
$L \rightarrow Sb + AlSb$	628	-	[15]			
(eutectic)	625	L: 0.980Sb-0.020Al	This work			
	1057		[16]			
	1062		[15]			
$AlSb \rightarrow L$	1049		[12]			
(congruent melting)	1057		[17]			
	1062		[11]			
	1062		This work			
Al-Bi system						
	1050	L: 0.175Bi -0.825Al	[28]			
consulate temperature	1068	L: 0.200Bi -0.800Al	This work			
	657	L ₁ : 0.045Bi-0.955Al				
$L1 \rightarrow L2 + Al$		L ₂ : 0.840Bi-0.160Al	[28]			
(monotectic)	654	L ₁ : 0.055Bi-0.945Al	This work			
	0.54	L ₂ : 0.850Bi-0.150Al	THIS WOLK			
$L \rightarrow Al + Bi$	270	L: 0.995Bi-0.005Al	[28]			
(eutectic)	270	L: 0.993Bi-0.007Al	This work			

Table 4.2. Invariant reactions for the Al-Bi and Al-Sb systems optimized in the present study compared with the experimental results.

Invariant reaction	T (°C)	Composition (mole fraction)				
Mg-Al-Bi system						
		L ₁ :0.509Mg-6.174×10 ⁻² Al-0.429Bi				
$L_1+\beta-Mg_3Bi_2\rightarrow L_2+\alpha-$	702.46	L ₂ :2.252×10 ⁻² Mg-0.977Al-6.458×10 ⁻² Bi				
Mg ₃ Bi ₂	(I_1)	β-Mg ₃ Bi ₂ :0.600Mg-0.400Bi				
		α-Mg ₃ Bi ₂ :0.600Mg-0.400Bi				
		L ₁ :0.708Mg-3.973×10 ⁻² Al-0.253Bi				
$L_1+\beta-Mg_3Bi_2 \rightarrow L_2+\alpha-$	689.45	L ₂ :0.715Mg-0.164Al-0.121Bi				
Mg ₃ Bi ₂	(I_2)	β-Mg ₃ Bi ₂ :0.620Mg-0.380Bi				
		α-Mg ₃ Sb ₂ :0.618Mg-0.382Bi				
		$L_1:0.479Mg-6.802 \times 10^{-2}Al-0.4Bi$				
$I \rightarrow I + \alpha M \alpha B + f \alpha \alpha$	654.95 (m ₁)	$L_2: 1.036 \times 10^{-2}$ Mg-0.989-Al-6.235×10 ⁻⁴ Bi				
$L_2 \rightarrow L_1 + \alpha - 1 M g_3 D I_2 + 1 e c$		α-Mg ₃ Bi ₂ :0.600Mg-0.400Bi				
		fcc:2.971×10 ⁻³ Mg-0.997Al				
		L:0.375Mg-0.625Al-1.755×10 ⁻⁴ Bi				
$L \rightarrow \beta$ -AlMg+ α -	451.26	β-AlMg:0.382Mg-0.618Al				
Mg ₃ Bi ₂ +fcc	(e ₁)	α-Mg ₃ Bi ₂ :0.606Mg-0.394Bi				
		fcc:0.174Mg-0.826Al				
		L:0.402Mg-0.598Al-2.682×10 ⁻⁴ Bi				
$L \rightarrow \beta$ -AlMg+ γ -Mg ₁₇ Al ₁₂	450.94	β-AlMg:0.384Mg-0.616Al				
$+ \alpha - Mg_3Bi_2$	(e_2)	α -Mg ₂ Bi ₂ ·0.612Mg-0.388Bi				
	(-/	v-Mg ₁₇ Al ₁₂ :0.454Mg-0.546Al				
		L:0.709Mg-0.284Al-6.653×10 ⁻³ Bi				
$L \rightarrow hcp + \gamma - Mg_{17}Al_{12} + \alpha$	435 44	$v - Mg_{17}A_{112} \cdot 0.621Mg - 0.379A1$				
Mg ₃ Bi ₂	(e ₂)	$\alpha - M \alpha_2 B \alpha_2 B \alpha_2 B \alpha_3 M \alpha_2 O 367 B \alpha_2 $				
	(-5)	hcp: $0.898Mg-0.102Al-2.632 \times 10^{-4}Bi$				
		L:4 284×10 ⁻⁴ Mg-4 569×10 ⁻³ A1-0 953Bi				
$L \rightarrow \alpha - M g_2 B i_2 + B i_1 + f c c$	260.47 (e ₄)	a-Mg2Bi2 0 600Mg-0 400A1				
		fcc:1.000Al				

Table 4.3. Invariant reactions for the Mg-Al-Bi and Mg-Al-Sb systems optimized in the present study.

Invariant Reaction	T (°C)	Composition			
Mg-Al-Sb system					
		L ₁ :0.314Mg-0.343Al-0.344Sb			
$L_1 + \beta Mg_3Sb_2 \rightarrow L_2 + \alpha$ -	928.37	$L_2:2.882 \times 10^{-2}$ Mg-0.908Al-6.271 ×10 ⁻² Sb			
Mg_3Sb_2	(I_1)	β-Mg ₃ Bi ₂ :0.399Mg-0.600Sb			
		α-Mg ₃ Sb ₂ :0.399Mg-0.600Sb			
		L ₁ :0.566Mg-0.191Al-0.243Sb			
$L_1 + \beta - Mg_3Sb_2 \rightarrow L_2 + \alpha -$	910.19 (I ₂)	L ₂ :0.235Mg-0.719Al-1.408 ×10 ⁻² Sb			
Mg_3Sb_2		β-Mg3Bi ₂ :0.611Mg-0.389Sb			
		α-Mg ₃ Sb ₂ :0.606Mg,0.394Sb			
		$L_1:2.765 \times 10^{-2}$ Mg-0.866Al-0.107Sb			
$L_1 \rightarrow L_2 + \alpha - M \alpha_2 S b_2 + A lS b_3$	877.10	L ₂ :0.280Mg-0.378Al-0.0.342Sb			
$E_1 \rightarrow E_2 + \alpha + M_{23} + \delta C_2 + M_{13} + \delta C_2$	(m ₁)	α -Mg ₃ Sb ₂ :0.600Mg,0.4Sb			
		AlSb			
		L:1.694×10 ⁻³ Mg-0.993Al-5.03×10 ⁻³ Sb			
$I \rightarrow fcc + \alpha - M \sigma_2 S h_2 + A 1S h_3$	656.32	fcc:3.917×10 ⁻⁴ Mg-0.999Al			
$L \rightarrow 100 + 0.000 + A100$	(e ₁)	α-Mg ₃ Sb ₂ :0.600Mg-0.400Sb			
		AlSb			
		L:0.131Mg-7.406×10 ⁻³ Al-0.969 Sb			
	579.49	Sb			
$L \rightarrow Sb + \alpha - Mg_3Sb_2 + AISb$) (e ₂)	α-Mg ₃ Sb ₂ :0.600Mg-0.400Sb			
		AlSh			
		L:0 400Mg-0 599A1-1 846×10 ⁻⁵ Sb			
$I \rightarrow \beta_{-} A M \alpha + \alpha_{-}$	451 33	$\beta_{-}A1M\sigma_{-}0$ 382M $\sigma_{-}0$ 618A1			
$M_{\sigma_2}S_{b_2}+f_{c_2}$	(e ₃)	$\alpha M\alpha Sh : 0.606M\alpha 0.204Sh$			
11123502 1100		$a - 101g_3 S U_2 = 0.0000101g - 0.394 S U$			
		$1 \div 0.374 \text{Mg} = 0.626 \text{A}1 + 280 \times 10^{-5} \text{Sb}$			
	451.05	1.0.374 Mig-0.020AI-1.280×10 SU			
$L \rightarrow p$ -AlMg+ γ -Mg ₁₇ Al ₁₂	451.05	p-AIMg:0.384Mg-0.616AI			
$+ \alpha$ -1VIg ₃ SO ₂	(e_4)	α-Mg ₃ Sb ₂ :0.607Mg-0.393Sb			
		γ-Mg ₁₇ Al ₁₂ :0.454Mg-0.546Al			
		L:0.703Mg-0.297AI-1.932×10 ⁻ Sb			
$L \rightarrow hcp + \gamma - Mg_{17}AI_{12} + \alpha$ -	438.73	γ-Mg ₁₇ Al ₁₂ : 0.621Mg-0.379Al			
Mg_3Sb_2	(e ₅)	α-Mg ₃ Sb ₂ :0.614Mg-0.386Sb			
		hcp:0.886Mg-0.114Al.			



Fig.4.1. The calculated optimized phase diagram of the Al-Sb system in the present study along with experimental data [11-15].



Fig.4.2. Thermodynamic properties of the AlSb phase optimized in various assessments [2, 3] along with experimental data [15, 23]. (a) heat capacity and (b) heat content.



Fig.4.3. Thermodynamic properties of the AlSb phase optimized in various assessments [2, 3] along with experimental data [15, 24]. (a) enthalpy of formation and (b) Gibbs energy of formation from solid Al and Sb.



Fig.4.4 Thermodynamic properties of liquid Al-Sb solution at 1350 K optimized in the present study in comparison with experimental data [15, 18] and the previous assessment results [2, 3]. (a) enthalpy of mixing, (b) entropy of mixing and (c) Gibbs energy of mixing.



Fig.4.5 Activities of Al and Sb in liquid Al-Sb solution optimized in the present study along with experimental data [20, 21] and previous assessment results [2, 3, 15].



Fig.4.6. The calculated optimized phase diagram of the Al-Bi system in the present study along with experimental data [26-28].



Fig.4.7. Optimized enthalpies of mixing of the Al-Bi system at various temperatures in the present study along with experimental data [26, 28].



Fig 4.8. Activities of Al and Bi in liquid Al-Bi solution against its liquid standard state optimized in the present study along with experimental data [27].



Fig.4.9. The calculated optimized liquidus projection of the Mg-Al-Bi system in the present study. Temperatures in °C.



Fig.4.10. Phase diagrams of various sections in the Mg-Al-Bi system calculated in the present study along with experimental data [30, 31]. (a) $Mg_3Bi_2-Mg_3Al_2$, (b) Mg-AlBi, (c) Al-Mg_3Bi_2, (d) 10 wt% Al isopleth and (e) 20 wt% Bi isopleths.



Fig.4.11. Calculated primary crystalline phase regions and liquidus projection of the Mg-Al-Bi system in comparison to experimental data [30, 31].



Fig.4.12. Liquidus projection of the Mg-Al-Bi system just predicted from binary model parameters without any ternary parameters.



Fig.4.13. The calculated optimized liquidus projection of the Mg-Al-Sb system in the present study. Temperatures in °C.



Fig.4.14. Optimized primary crystalline regions in the Mg-Al-Sb system in the present study in comparison with experimental data [12, 13].



Fig.4.15. Calculated liquidus miscibility gaps of the Mg-Al-Sb ternary system at (a) 900 °C and (b) 1000 °C in comparison with experimental data [12]. (Open circle: overall initial composition, closed circle: liquid composition after phase separation.)



Fig.4.16. Calculated phase diagrams of (a) $Al-Mg_3Sb_2$ section and (b) $AlSb-Mg_3Sb_2$ section in the Mg-Al-Sb system along with experimental data [12, 13].


Fig.4.17. Liquidus projection of the Mg-Al-Sb system just predicted from binary model parameters without any ternary parameters.

Chapter 5: Applications of Thermodynamic calculations to Mg alloy design

The optimized parameters of the systems in the present study (Chapter 3 and 4) are stored in the databases and these optimized and evaluated computer databases can be used with FactSage (FactSage,2009) to permit the calculation of phase diagrams, phase equilibria and thermodynamic properties of magnesium alloys.

Jung et al.(Jung et al. 2007) investigated the phase relationship of Mg-Sn-Al-Zn alloys with additions of Si and Sb and compared them with their experimental microstructures. They validated the applicability of thermodynamic calculation to Mg alloy design as they found good agreement between the calculated experimental results and experimental microstructure.

Jung et al. (Jung et al. 2006, Jung et al. 2007)The thermodynamic optimization of Mg-Al-Mn-Si-Sn-Zn was carried previously and the optimized parameters for the binary Mg-Sb were taken from the present study.

Alloy	Mg	Sn	Al	Si	Sb	Zn	Mn
TA	Bal.	7.28	2.68			0.43	0.20
TAS	Bal.	7.79	2.73	0.70		0.69	0.19
TAS-Sb	Bal.	7.06	2.70	0.62	4.44	0.49	0.21

Table1. Chemical Composition of alloys (in wt %) (Jung et al. 2007)



5.1 Microstructural Observation of as cast Microstructures (Jung et al. 2007).

Fig. 5.1(a), (b) SEM image of TA alloys, (c), (d) TAS alloys, (e), (f) TAS-Sb alloys.





Fig. 5.2 (a) Scheil Cooling Calculations for TA alloys (b) TAS alloys (c) TAS-Sb alloys Scheil cooling calculations assume no diffusion of solute elements in solid phases once it is solidified and complete homogenization of liquid phases during solidification.

5.3 Comparison of Experimental Microstructure with Thermodynamic Calculations

The microstructure of Mg-Sn-Al-Zn (TA) changes drastically with the addition of Si (TAS) and Sb (TASb) alloys Coarse Mg2Sn appears in the as cast microstructure of TA alloys (Fig. 5.1(a),(b)). In addition a small amount of $Mg_{17}Al_{12}$ was also observed. Coring effect is also noted in the microstructure as the contrast of the SEM imgae varies continuously from center to the edge of the grain. The contrast of the grain is grey in the center and it changes to black at the edges. Moreover most Mg_2Sn and $Mg_{17}Al_{12}$ precipitates are located in the grain boundary area. This means the precipitates are formed at the end of the solidification process. Scheil cooling calculations (Fig 5.2(a)) are consistent with the observed as cast microstructure. According to the calculations Mg_2Sn is calculated to form at 514°C where the liquid fraction is less than 15% and $Mg_{17}Al_{12}$ forms at the end of eutectic reaction at 423°C. On addition of Si to to Mg-Sn based alloys TAS

alloys (Fig. 5.1(a), (b)), precipitates of a Chinese scipt shaped Mg-Si rich phase connected to a granular Mg-Sn rich phase are observed. Moreover Mg₂Sn rich precipitates are observed in the grain boundaries. Scheil cooling calculations (Fig.5.2(b)) show that Mg₂Si can form at 564°C where liquid fraction is about 40% followed by precipitation of Mg₂Sn at 540°C. Because of the same crystal structure of Mg₂Si and Mg₂Sn phases, the Mg₂Si phase can act as nucleation site for Mg₂Sn.Since Mg₂Si phase start to precipitate at the middle of solidification process, the distribution of Mg₂Si precipitates inside α -Mg grains can be understood.

The microstructure changes completely on the addition of Si and Sb to the Mg-Sn-Al-Zn alloy (TAS-Sb). As cast microstructure (Fig.5.1 (e), (f)) shows typical precipiates which arrandomly distributed. They are composed of inner core which is Mg-Sb rich, radial branch which is Mg-Si rich and outer grain which is Mg-Sn rich. The size of precipitate is also smaller than that observed in TAS alloys. According to Scheil cooling calculations (Fig 5.2(c)) Mg₃Sb₂ could be precipitated at the same temperature at which α -Mg dendrites start to form. This means Mg₃Sb₂ can start to precipitate directly from the liquid. Mg₂Si rich phase start to precipitate next followed by Mg₂Sn rich phase.Due to the similarity of the crystal structure of all the three phases Mg₃Sb₂ can act as a nucleation site for Mg₂Sn rich phase.

5.4 Phase Diagrams of Mg-Al-Mn-Sb-Si-Zn alloy system

FactSage 2009 (2009) also permits us to calculate the phase diagram of multicomponent systems and in the case of Mg-Al-Mn-Sb-Si-Sn-Zn alloy system the multiple phase Equilibria and phase diagram can be calculated based on the set of input conditions.



Fig. 5.3 Calculated Phase Diagram of Mg-Sn-0 wt%Sb-1 wt% Si-3 wt%Al-1 wt%Zn system



Fig. 5.4 Calculated Phase Diagram of Mg-Sn-5wt%Sb-1wt% Si-3 wt%Al-1wt%Zn system

Assuming the solidification to be complete at 400°C, from Fig. 5.3 and Fig. 5.4 it is evident that Mg₂Sn phase can be precipitated at Sn>4 wt% and at Sn>9 wt%, Mg₂Si phase cannot form. Thus in order to simulataneously ustilize the thermal stability of Mg₂Si and Mg₂Sn phases the appropriate range of Sn content in this alloy system should be about $4 \le 10^{\circ}$ Sn<9. Thus, multicomponent phase diagrams as shown in Fig. 5.3 and Fig. 5.4 can provide valuable information regarding the alloying range for any alloying element for any multicomponent alloy system.

6. Summary

The aim of the present work was to critically optimize and evaluate the binary systems Mg-Bi, Mg-Sb, Al-Sb and Al-Bi and ternary systems Mg-Al-Bi and Mg-Al-Sb as a part of research initiative to develop the Mg-Sn based alloy databases. Chapter 1 deals with the general introduction on magnesium alloys and discusses the superiority of the magnesium alloys over the steel and Al alloys; moreover the chapter also discusses the high temperature instability of Mg-Al alloys which limits its applications in the automotive industry. It emphasizes on improving the high temperature stability of magnesium alloys as an important aspect of magnesium alloy design and the importance of significant research to identify key alloying elements that would extend the commercial usability of magnesium alloys at high temperatures.

Chapter 2 deals with the history of CALPHAD and discusses the research approach followed in CALPHAD community in order to thermodynamically assess a system. It also discusses the modified quasichemical model that can take in to account the short range ordering in liquid for modeling the liquid phases. Thermodynamic modeling of solids under the framework of Compound Energy Formulism has been discussed too. Prediction of thermodynamic properties of a ternary system from the optimized binary parameters using "proper geometric models" has been described in detail too.

Chapter 3 discusses the thermodynamic assessment of the Mg-Bi and Mg-Sb system. The liquid phases of both the systems were modeled using the modified quasichemical model capable of predicting the short range ordering. Thermodynamic evidences supporting the short range ordering in liquid phase's lile Δ Cp function and excess stability function were investigated for both the systems and the degree short range ordering present in the liquid phases around Mg₃Sb₂ or Mg₃Bi₂ was found comparable to certain ionic solutions like Na-Te, K-Bi, and Cs-Rh etc.All the experimental phase diagram data and thermodynamic data was critically assessed and reviewed to obtain one set of model parameters to describe the Gibbs energy of all the phases present in the two systems. Due to similarity of both the systems inconsistencies in experimental data for the systems could be easily resolved.

Chapter 4 deals with the thermodynamic assessment of the Al-Bi, Al-Sb and Mg-Al-Bi and Mg-Al-Sb systems. Like Chapter 3 modified Quasichemical model was used to model the liquid phases for the above said systems. It also discusses the predictive ability of modified quasichemical model for the ternary systems by the use of optimized binary parameters. The ternary miscibility gap occurring in the ternary systems was reasonably predicted and small ternary term was introduced for both the ternary systems to render the calculated miscibility gap consistent with the experimental data.

Chapter 5 deals with the application of thermodynamic calculations to the Mg alloy design. The optimized parameters of Mg-Sb were incorporated in the database which already contains the optimized parameters for great number of binary systems like Mg-Al, Mg-Sn, Mg-Si, Mg-Ge, Mg-Pb etc. The optimized data base permits the calculation of complex phase Equilibria, phase diagrams and Scheil cooling calculations. Phase relationships of Mg-Sn-Al-Zn alloys with addition of Si and Sb were calculated and compared with their as cast microstructures. The thermodynamic calculations were in good agreement with the experimental microstructures and it suggests the fact that thermodynamic calculations can act as an effective tool in magnesium alloy design.

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