Thermodynamic calculations of the Mn–Sn, Mn–Sr and Mg–Mn–{Sn, Sr} systems

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Thermodynamic calculations of the Mn–Sn, Mn–Sr and Mg–Mn–{Sn, Sr} systems

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Abstract: Thermodynamic modelling of Mn–Sn and Mn–Sr binary systems is carried out using the reliable data from the literature. Thermodynamic properties of the binary liquid solutions are described using the modified quasi-chemical model. The calculated phase diagrams and the thermodynamic properties are found to be in good agreement with the experimental data from the literature. A self-consistent thermodynamic database for the Mg–Mn–{Sn, Sr} systems is constructed by combining the thermodynamic descriptions of their constituent binaries. The constructed database is used to calculate and predict liquidus projection and invariant reactions of these ternary systems. The Mg–Mn–Sr system has nine ternary eutectic reactions, two saddle points and eleven crystallisation fields. Mg–Mn–Sn has four saddle points, two quasi-peritectic and six ternary eutectic reactions.

1 Introduction

Automobile manufacturers are continually searching for means to reduce vehicle weight in order to increase fuel economy. With their low density, high stiffness/weight ratio and high damping capacity, magnesium alloys have the potential to make a significant contribution to this weight reduction. Wrought magnesium alloys hold great promise for use in structural applications [1]. However, the possible application of wrought magnesium alloys is strongly reduced by the low formability and mechanical anisotropy of this material [2]. This is mainly caused by its hexagonal crystal structure which offers limited slip systems at room temperature [3]. There are several attempts to improve formability of magnesium alloys in which alloying elements were found to play a key role [4–25]. Among them, rare earth (RE) elements, manganese and strontium additions improve formability of wrought magnesium alloys through grain size refinement, activation of non-basal slip and/or weakening the texture [16–25]. Li and RE additions to Mg are likely to bring numerous advantages including high cost, increased fluidity among processing and decreased corrosion resistance [1, 6, 19]. Mg–Mn–based alloys have some popularity because of their good weldability [26]. They provide medium strength in wrought product form such as extrusion, rolling, sheet and plate [26]. Sr provides good grain refinement in Mg-alloys and thereby enhances mechanical properties [23, 24, 27]. Alloys with Sn is promising for high-temperature applications. Addition of Sn to Mg-based alloys leads to precipitations of thermally stable compound (Mg2Sn) which provides stable microstructure and enhances mechanical properties at 150°C [28, 29].

Thermodynamic descriptions of Mg–Sn, Mn–Sn and Mg–Mn–Sn systems are very important for further improvement in alloy design through providing invaluable information such as solubility of alloying addition in Mg-matrix, heat treatment temperature, amount of secondary phase precipitates and solidus and liquidus temperatures.

In this paper, thermodynamic modelling of Mg–Mn–{Sn, Sr} systems are carried out for the first time according to authors knowledge. Among the constituent binaries, Mn–Sn and Mn–Sr systems were re-optimised using the modified quasi-chemical model (MQM) for the liquid solution. On the basis of calculation of phase diagrams (CALPHAD) method [30], all thermodynamic information such as experimental phase diagram data and thermodynamic properties data are critically evaluated and optimised simultaneously. Thermodynamic optimisation and calculations were performed in this paper using FactSage program [31].

2 Experimental data

2.1 Mn–Sn system

Watchel and Ulrich [32] and Watchel et al. [33] investigated the phase relationships of the Mn–Sn system for a composition range of 0–80 at.% Mn by metallography, magnetic susceptibility and polarisation. Their samples were prepared from 99.999 wt.% Sn and 99.99 wt.% Mn and melted in high-frequency induction furnace under argon. Homogenisation was carried out by annealing the specimen in quartz tube under argon atmosphere. Their alloys were heated from 200°C for 40 days to up to 800°C for 10 h. They [32] reported that Mn2Sn phase melts incongruently at 883°C which is comparable with 897°C, the calculated value of Singh et al. [34] and William [35]. Watchel and Ulrich [33] indicated that MnSn2 melts incongruently at 549°C, compared with Singh et al. [34] and William [35] results as 548°C. Their data [32] indicates that MnSn is a solid solution in the composition range of 76.4–77.6 at.% Mn at 700°C. Singh et al. [34] investigated Mn–Sn phase diagram below 50 at.% Sn using optical microscopy and X-ray diffraction using high purity Mn (99.99 at.%) and Sn (99.99 at.%) starting materials. Their samples were cast in recrystallised alumina crucible using high-frequency induction furnace under protective gas (argon). Moreover, their studied samples were wrapped in molybdenum foil and sealed in evacuated fused silica capsules, then annealed for 15 days at 500°C to 10 h at 1000°C. Singh et al. [34] reported low solubility of Sn in αMn phase which is in agreement with Nail’s [36] observation. Nowotny and Schubert [37] and Zwicker [38] determined the solubility of Sn in βMn phase and reported value of 8.7 at.% Sn at 600°C, whereas Singh et al. [34] indicated this solubility to be about 10 at.% Sn. The experimental phase diagram data from [32–34] are self-consistent and considered as
the most reliable data, therefore these data will be incorporated in the current optimisation of Mn–Sn system.

Earlier investigations differ on the MnSn phase region. According to Nay [36], the MnSn phase exists between 23 and 24.5 at.% Sn, whereas Guillaud [39] indicated the MnSn phase region between 20 and 22 at.% Sn. On the other hand, Nowotny and Schubert [37] reported the MnSn phase at 21.43 at.% Sn. The structure type of MnSn has been suggested to be Ni3Sn [34, 36, 37]. Elding-Pontén et al. [40] investigated NiAs–Ni3In structure types in the Mn–Sn system using X-ray diffraction and scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDX). Three different phases were detected such as high temperature phase (HTP1) (Mn17Sn7), HTP2 (Mn8Sn5) and MnSn phases. They reported that there were difficulties in preparing the samples since traces of tin were detected on the outside of the ingot. Besides, different phases were not distinguishable because of having very similar compositions. The chemical compositions and crystal structures of HTP1 and HTP2 phases detected in this paper of Elding-Pontén et al. [40] were not reported or verified in the literature. Therefore these phases will not be incorporated in the current paper. Stange et al. [41] studied the crystal structure of binary phases in the Mn–Sn system using X-ray diffraction, neutron diffraction and differential thermal analysis. They revealed the uncertainty on the stability and composition of MnSn. According to their work, MnSn consists of a high-temperature phase Mn23Sn and a low-temperature phase Mn23Sn rather than MnSn or HPT2. Moreover, Mn23Sn is stable between 480 and 884°C and the homogeneity range of this phase at 800°C is 0.18 ≤ x ≤ 0.23 and 0.28 ≤ x ≤ 0.34 at 600°C. Therefore in this paper Mn23Sn will be treated as solid solution and MnSn2 will be modelled as a stoichiometric compound.

The phase diagram of Mn–Sn system was assessed by Massalaski et al. [42] and Stange et al. [41]. According to these works, the composition ranges of (αMn) and (βMn) were 0.0–1.0 and 5.5–10 at.% Sn at 400°C, respectively. Miettinen [43] calculated MnSn phase diagram using the experimental data from [32–34, 44–47]. He [43] also described the liquid phase using the random solution model. According to Miettinen [43], the stable phases in the Mn–Sn system were (αMn), (βMn), (γMn), MnSn, Mn2Sn, Mn3Sn and Mn9Sn (MnSn). In his paper [43], Mn–Sn phase diagram was reported in two figures; MnSn phase was treated as stoichiometric and in the other figure MnSn modelled as a solid solution. Moreover, the calculated activity at 1000°C of Miettinen [43] could not produce good fit with experimental data of Eldemekno et al. [47]. According to Okamoto’s review [48] on the Mn–Sn phase diagram, the stable phases in this system are; (αMn), (βMn), (γMn), MnSn, Mn2Sn, Mn2Sn, Mn3Sn, MnSn and β Sn. In this paper, the stable phases adopted by Okamoto will be considered and re-optimised.

2.2 Mn–Sr system

The work of Ohnaka et al. [49] is the only experimental data that could be found in the literature. According to their work, this system forms a miscibility gap through the interval 0.74–96.5 at.% Sr at 1240°C and no intermetallic compound was observed in their work. Peng et al. [50] modelled all phases in the Mn–Sr binary system as completely disordered solutions. In their work, Gibbs energy is described by Redlich–Kister polynomial and model parameters were evaluated using ThermoCalc, whereas Janz [51] calculated liquidus projection of Mg–Mn–Sr ternary system. However, he did not describe thermodynamic modelling of the Mn–Sr binary system and the optimised parameters were not reported.

In the current paper, the liquid phase of the Mn–Sr system will be modelled using MQM to have consistent thermodynamic description with Mg–Sn, Mg–Mn and Mg–Sr systems.

2.3 Mg–Sn, Mg–Mn and Mg–Sr systems

Optimised Gibbs energy parameters of the constituent binary systems, Mg–Sn, Mg–Mn and Mg–Sr will be adopted from the work of Ghosh et al. [52], Ghosh and Medraj [53] and Aljarrah and Medraj [54], respectively. The calculated phase diagrams of the Mg–Sn, Mg–Mn and Mg–Sr phase diagrams are in reasonable agreement with all reported data in the literature. Liquid phase was optimised using the MQM. Therefore the works of Ghosh et al. [52], Ghosh and Medraj [53] and Aljarrah and Medraj [54] were considered to construct a self-consistent thermodynamic database of the Mg–Mn–(Sn, Sr) ternary systems.

2.4 Mg–Mn–Sn ternary system

In 1969, Kopetskii and Semenova [55] experimentally identified phases in the Mg-rich region of the Mg–Mn–Sn system and draw isothermal sections at 500 and 400°C. The identified phases in their isothermal section will be compared with the current calculations. They also reported a ternary eutectic at 554°C where L→(Mg) + αMn + MgSn. The work of Kopetskii and Semenova [55] is the only experimental data of Mg–Mn–Sn system that could be found in the literature.

2.5 Mg–Mn–Sr ternary system

Celinkin et al. [27] investigated microstructure and creep behaviour of eight Mg–{0.75–2} wt.% Mn–{3–5} wt.% Sr alloys in the Mg-rich region. In their works, samples were heat treated at 225°C for 150 h and 300°C for 96 h. They measured solid solubility of Mn in Mg-matrix using TEM/EDS. These solubilities will be compared with the current thermodynamic calculation. Three phases were positively identified in the heat treated alloys, namely; Mg17Sr2, (Mg) and α-Mn. XRD analysis in the heat treated alloys show no change in phase constitution compared with the as-cast alloys. In Janz’s doctoral thesis [51], liquids projection and isothermal sections at 500 and 400°C of the Mg–Mn–Sr ternary system were calculated. In the current paper, a comparison between the current liquidus projection and Janz’s work will be discussed.

Mg–Mn–Sn and Mg–Mn–Sr systems are subsystems of multi-components Mg-alloys. The purpose of this paper is to provide a comprehensive thermodynamic description of the Mg–Mn–Sn and Mg–Mn–Sr systems which is the backbone for understanding solidification and phase equilibria in the Mg–Mn-based alloys.

3 Thermodynamic models

3.1 Pure elements

The Gibbs free energy of a pure element with a certain structure φ is described as a function of temperature as

$$G^\phi(T) = a + bT + cT^2 + dT^3 + eT^{-1} + gT^7 + hT^{−9}$$

(1)

The parameters a through h are taken from the SGTE compilation by Dinsdale [56].

3.2 Stoichiometric compounds

Intermetallic compounds in the Mn–Sn phase diagram such as MnSn, MnSn2 and MnSn3 are considered stoichiometric and the Gibbs free energy of these compounds is described by the following equation

$$G_{\text{phase,}\phi} = \sum_i x_i ^\phi G_i ^\phi + \sum_j x_j ^\phi G_j ^\phi + \Delta G_{\text{f}}$$

(2)

where $G_i ^\phi$ and $G_j ^\phi$ denote Gibbs free energy of elements i and j in their standard state and $\Delta G_{\text{f}} = a + bT$ is the Gibbs energy of formation of the stoichiometric compound, where a and b are the
model parameters to be optimised based on experimental data of phase equilibria and thermodynamic properties.

### 3.3 Terminal solid solutions

The Gibbs energy of a disordered solid solution phase is described by the following equation

\[ G = x_i \phi^i + y_j \phi^j + RT \ln (x_i \ln x_i + y_j \ln y_j) + c_i \phi^i \]

where \( \phi \) denotes the phase in question and \( x_i, y_j \) denote the mole fraction of components \( i \) and \( j \), respectively. The excess Gibbs energy is represented using Redlich–Kister equation

\[ c_i \phi^i = x_i \cdot y_j \sum_{n=0}^{m} a_{n} T_{n}^{i,j} (x_i - y_j)^n \]

with \( a_{n} T_{n}^{i,j} = a + b \times T \) \( (n = 0, \ldots, m) \) where \( \sum_{n=0}^{m} a_{n} T_{n}^{i,j} \) is the interaction parameters and \( a \) and \( b \) are model parameters to be optimised using experimental phase diagram and thermodynamic data. In Mn–Sn binary system, \((\alpha\text{Mn}), (\beta\text{Mn}), (\gamma\text{Mn}) \) and \((\delta\text{Mn}) \) phases are treated as disordered solution model.

### 3.4 Liquid phase

In the current paper, the liquid phase is modelled using the MQM where the pair approximation is utilised to describe short-range ordering in the liquid. A detailed description of the MQM for binary and multi-components solutions is available elsewhere [57–59]. Only a brief description will be presented here. The molar Gibbs energy of the liquid phase, derived from the modified quasi-chemical theory [57], is described by the following equation

\[ G^{liq} = n_A \phi^{liq}_A + n_B \phi^{liq}_B - T \Delta S^{config} + \frac{n_{AB}}{2} \Delta G^{liq}_{AB} \]

where \( n_A \) and \( n_B \) are the number of moles of the components \( A \) and \( B \), \( n_{AB} \) is the number of moles of \((A-B)\) pairs, \( \Delta S^{config} \) is the configurational entropy of mixing given for randomly distributing the \((A-B)\), \((B-B)\) and \((A-B)\) pairs.

Pelton et al. [57] made modification to (5) by expanding \( \Delta G^{liq}_{AB} \) as a polynomial in terms of the pair fractions \( X_{AA} \) and \( X_{BB} \) as shown in (6)

\[ \Delta G^{liq}_{AB} = \sum_{i=1}^{2} g_{AB}^{i} X_{i} + \sum_{j=1}^{2} g_{BB}^{j} X_{j} T \]

where \( g_{AB}^{i} \) and \( g_{BB}^{j} \) are the model parameters to be optimised and can be expressed as \( \Delta G^{liq}_{AB} = a + bT \).

The configurational entropy of mixing is described by the following equation

\[ \Delta S^{config} = -R [\ln (x_A) + \ln (x_B)] - R \left[ \frac{n_{AB}}{n_A} \ln \left( \frac{n_{AB}}{n_A} \right) + \frac{n_{AB}}{n_B} \ln \left( \frac{n_{AB}}{n_B} \right) + \frac{n_{AB}}{2} \ln \left( \frac{x_{AB}}{2y_{AB}} \right) \right] \]

where \( x_A \) and \( x_B \) are the overall mole fractions of the components \( A \) and \( B \), respectively.

Mole fraction of component \( A \) can be described as follows

\[ X_A = \frac{n_A}{n_A + n_B} \]

Pair fraction

\[ X_{AA} = \frac{n_{AA}}{n_A + n_{AB} + n_{BB}} \]

And the coordination-equivalent fractions

\[ y_A = \frac{Z_A n_A}{Z_A n_A + Z_B n_B} \]

In addition, further modification has been made to permit coordination number to vary with composition as follows

\[ \frac{1}{Z_A} = \frac{2 n_{AA} + n_{AB}}{Z_{AA} n_A} + \frac{n_{AB}}{Z_{AB} n_A + n_{AB}} \]

\[ \frac{1}{Z_A} = \frac{2 n_{BB} + n_{AB}}{Z_{BB} n_B} + \frac{n_{AB}}{Z_{BB} n_B + n_{AB}} \]

where \( Z_{AA} \) and \( Z_{BB} \) are the values of the coordination number of the \( A \)th atom when all nearest neighbours are \( A \)'s and \( B \)'s, respectively. The coordination number of pure elements in the metallic solution, 

### Table 1

<table>
<thead>
<tr>
<th>Crystal data</th>
<th>Atoms</th>
<th>WP1</th>
<th>CN2</th>
<th>PS3</th>
<th>Atomic position</th>
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WP1 Wyckoff position, CN2 coordination number and PS3 point symmetry

### Table 2

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<th>Crystal data</th>
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<th>CN2</th>
<th>PS3</th>
<th>Atomic position</th>
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</thead>
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</table>

WP1 Wyckoff position, CN2 coordination number and PS3 point symmetry
centred along the Mg$_2$Sn ideality. Positive deviations from ideal mixing will be observed, 

\[ \Delta G_{MnSn} = -418.4 - 1.72T; \Delta G_{MnSn} = -20292.4 + 10.9T \]

\[ Z_{Mn} = 4; Z_{MnSn} = 5 \]

Liquid Mn–Sn

\[ \Delta G_{MnSn} = -1522; \Delta G_{MnSn} = 5326.2 \]

\[ Z_{Mn} = 6; Z_{MnSn} = 6 \]

\[ \Delta G_{MnSn} = -1252; \Delta G_{MnSn} = 53262 \]

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\[ \Delta G_{MnSn} = -1252; \Delta G_{MnSn} = 53262 \]

<table>
<thead>
<tr>
<th>Phase</th>
<th>Optimised parameters of Mn–Sn and Mn–Sr binary systems</th>
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<td>αMn</td>
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<tr>
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<td>Sn in βMn</td>
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<td>δMn</td>
<td>Sn in δMn</td>
</tr>
<tr>
<td>Mn–Sn</td>
<td>Mn$_2$Sn</td>
</tr>
<tr>
<td></td>
<td>Mn$_{12-\gamma}$Sn</td>
</tr>
<tr>
<td></td>
<td>MnSn$_2$</td>
</tr>
<tr>
<td></td>
<td>Mn$_2$Sn$_2$</td>
</tr>
</tbody>
</table>

Fig. 1  Re-optimised Mn–Sn phase diagram with the experimental data from the literature

\[ Z_{MgMg} = Z_{SnSn} = Z_{MgSn} = Z_{MgMg} \] was set to be 6. Since this value gave the best possible fit for many binary systems and was also recommended by Pelton et al. [57], Pelton and Chartrand [58] and Pelton and Blander [59]. The values of $Z_{MgMg} = 4$, $Z_{SnSn} = 5$ and $Z_{MgSn} = Z_{MgMg} = 6$ are chosen to permit the composition of maximum short-range ordering in the binary system to be consistent with the composition that corresponds to the minimum enthalpy of mixing.

For binary systems with approximately the same number of model parameters, random solution model and MQM can provide very similar and good fits for many binary systems and was also recommended by Pelton et al. [57], Pelton and Chartrand [58] and Pelton and Blander [59]. The values of $Z_{MgMg} = 4$, $Z_{SnSn} = 5$ and $Z_{MgSn} = Z_{MgMg} = 6$ are chosen to permit the composition of maximum short-range ordering in the binary system to be consistent with the composition that corresponds to the minimum enthalpy of mixing.

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mathematically very similar. However, Kang and Pelton [60] proved that the associate model does not correctly predict the thermodynamic properties of ternary and high-ordered system. Therefore the MQM with pair approximation is used in this paper to model the liquid phase.

3.5 Intermediate solid solutions

Gibbs energy of intermediate solid solution phase is described by the compound energy formalism [61] which can be expressed as

$$G = G^{\text{eff}} + G^{\text{ideal}} + G^{\text{excess}}$$  \hspace{1cm} (13)

$$G^{\text{eff}} = \sum y_i y_j^m, \ldots, y_k G (i, j, \ldots, k)$$  \hspace{1cm} (14)

<table>
<thead>
<tr>
<th>Reaction type</th>
<th>Reaction</th>
<th>Composition, at.%Sn</th>
<th>T, °C</th>
<th>Reference</th>
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<td>40</td>
<td>540</td>
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</tbody>
</table>

Table 4 Calculated invariant points of the Mn–Sn system in comparison with the literature

Fig. 2 Calculated activities of Mn and Sn in the Mn–Sn liquid at

a 1244°C
b 1000°C
\[ G_{\text{ideal}} = RT \sum_l f_l \sum_i y_i^l \ln y_i^l \]  
\[ G_{\text{excess}} = \sum_{i,j} y_i^l y_j^m \gamma_{i,j,k} \times (y_i^l - y_j^m) \]  

where \( i, j, \ldots, k \) represent components or vacancy, \( l, m \) and \( q \) represent sublattices. \( y_i^l \) is the site fraction of component \( i \) on sublattice \( l \), \( f_i \) is the site fraction of sublattice \( l \) relative to the total lattice site. \( \gamma_{i,j,k} \) represents the energy of a real or hypothetical compound (end member). \( \gamma_{i,j,k} \) represents the interaction parameters between components \( i \) and \( j \) on one sublattice when the other sublattice is occupied only by \( k \).

3.5.1 Mn3Sn phase: According to Hari Kumar et al. [62] and Hari Kumar and Wollants [63], attention should be given to the crystallographic data and the solubility range of the phase during the optimisation of the sublattice model parameters. The crystal structure data of the Mn3Sn intermediate solid solutions is obtained by Weitzer and Rogl [64] and listed in the Pearson handbook [65] as shown in Table 1.

On the basis of crystallographic data of Mn3Sn phase, there are two atoms at different sites in the unit cell with the same coordination number and different points of symmetry as shown in Table 1. To obtain an intermediate phase which has an ideal stoichiometry, two sublattices are needed and each sublattice is occupied only by one constituent species. In other words, the direct sublattice model which is composed based on the crystallographic data of Mn3Sn phase only is the following model

\[(\text{Mn})_3: (\text{Sn})_1\]
This model does not represent the homogeneity range of Mn$_3$Sn phase which was obtained by Stange et al. [41]. To achieve the deviation from stoichiometry, it is necessary to allow mixing of atoms in one or more sublattices. For the phases which have relatively a narrow range of homogeneity such as Mn$_3$Sn the mixing is performed by ‘defects’, which may be vacancies or anti-structure atoms (i.e. atoms at lattice sites belonging to the other kinds of atoms in the ideal structure) [62, 63]. Since the structure of Mn$_3$Sn phase is not closed packed, vacancy is more appropriate than anti-structure atom. Therefore vacancies (Va) in Sn sublattice is the defect considered in this model. Therefore the model takes the form

\[
(Mn_{\text{\%}})_i : (Sn_{\text{\%}}, \text{Va})_1
\]

The range which is covered by this model is Mn$_3$Sn to pure Mn. Therefore this satisfies the homogeneity range requirement for Mn$_3$Sn phase which was obtained by Stange et al. [41]. Hence, the Gibbs energy per mole of formula unit of Mn$_3$Sn is described by the compound energy formalism as shown in the following equation (see (17) at the bottom of the next page)

\[
G_{\text{Mn$_3$Sn}} = G^0_{\text{Mn$_3$Sn}} + G_{\text{Mn$_3$Sn}} + G_{\text{Va}}
\]

where \(i\) is the species inside the sublattice, \(y_{\text{Mn,Sn, Va}}\) is the site fraction of sublattice \(L_i\), \(y^\text{II}_{\text{Mn,Sn, Va}}\) is the site fractions of lattice II, \(G_{L_i}^{\text{Mn,Sn, Va}}\) represents real or hypothetical compound (end member) energy, \(G_{\text{Mn$_3$Sn}}\) and \(G_{\text{Va}}\) represent the interaction parameters which describe the interaction within the sublattice.

### 3.5.2 Thermodynamic modelling of the Mn$_{12-x}$Sr phase:

The crystallographic data of the Mn$_{12-x}$Sr phase were listed in Table 2. On the basis of the crystallographic data of Mn$_{12-x}$Sr phase, there are three atoms at different sites in the unit cell with different points of symmetry as shown in Table 2. To obtain an
intermediate phase which has an ideal stoichiometry, three sublattices are required and each sublattice is occupied by only one constituent species. In other words, the direct sublattice model which is derived from the crystallographic data of Mn\(_{2-x}\)Sn phase is as follows

\[(\text{Mn1}) : (\text{Sn}) : (\text{Mn2})\]

To obtain a deviation from this stoichiometry, mixing of constituents is applied. Grouping was not allowed in this model because the atomic position and point symmetry for each atom is different from the other atoms as shown in Table 2. To obtain the homogeneity range, mixing of Mn anti-structure atom in the second lattice and vacancy (Va) in the first lattice are considered.

To obtain a deviation from this stoichiometry, mixing of constituents is applied. Grouping was not allowed in this model because the atomic position and point symmetry for each atom is different from the other atoms as shown in Table 2. To obtain the homogeneity range, mixing of Mn anti-structure atom in the second lattice and vacancy (Va) in the first lattice are considered.

\[G_{\text{Mn3Sn}} = y_{\text{Mn1}} y_{\text{Sn}}^0 G_{\text{Mn3Sn}}^{\text{Mn,Sn}} + y_{\text{Mn1}} y_{\text{Va}}^0 G_{\text{Mn3Sn}}^{\text{Mn,Sn}} + RT \left( 0.75 \sum_{i=Mn}^{\text{Mn}} y_i^I \ln y_i^I + 0.25 \sum_{i=\text{Sn}} y_i^I \ln y_i^I \right) + y_{\text{Mn1}} y_{\text{Sn}}^0 G_{\text{Mn3Sn}}^{\text{Mn,Sn}} + y_{\text{Mn1}} y_{\text{Va}}^0 G_{\text{Mn3Sn}}^{\text{Mn,Sn}} \]

\[+ y_{\text{Sn1}} y_{\text{Va}}^0 G_{\text{Mn3Sn}}^{\text{Mn,Sn}} + y_{\text{Mn1}} y_{\text{Va}}^0 G_{\text{Mn3Sn}}^{\text{Mn,Sn}} \]

(17)
in this model. Therefore the model takes the form

$$(\text{Mn} \%, \text{Va}) : (\text{Sn} \%, \text{Mn}) : (\text{Mn} \%)$$

(see (18))

The optimised model parameters of different phases in the Mn–Sn and Mn–Sr binary systems are summarised in Table 3.

4 Results and discussion

4.1 Mn–Sn binary system

The re-optimised Mn–Sn binary phase diagram in relation to the experimental data from the literature is shown in Fig. 1. Table 4 summarises the calculated and experimental invariant points of this system. As can be seen in the table, all the deviations between the calculated temperature for the invariant reactions and the literature values are within ±4°C. Fig. 2 shows the calculated activities of Mn and Sn in the Mn–Sn liquid at 1000 and 1244°C in comparison with literature values and both show good agreement. The calculated enthalpy of mixing for liquid at 139°C compared with the experimental data [66] is shown in Fig. 3. The reference states are liquid Mn and liquid Sn. As can be seen in Fig. 3, the presently calculated enthalpy of mixing agrees with the experimental data [66].

In the current optimisation, Mn$_2$Sn$_2$ phase is modelled as a stoichiometric phase. Mn$_2$Sn$_2$ phase was only reported by Stange et al. [41] and adopted by Okamoto [48], whereas Miettinen [43] excluded this phase from his calculations. According to the work of Stange et al. [41], Mn$_2$Sn$_2$ appears as low-temperature stoichiometric phase in the Mn–Sn system. The latter precisely determined the crystal structure of Mn$_3$Sn$_2$ using XRD and neutron diffraction. It is worth mentioning that the synthesis of pure Mn$_3$Sn$_2$ phase was difficult [41] and its crystal structure was determined from two-phase region containing MnSn$_2$ and Mn$_3$Sn$_2$. (Mn$_2$Sn) melts incongruently at 883°C which is in accord with the

![Diagram of Mg–Mn–Sn system](image)

**Fig. 7** Liquidus projection of Mg–Mn–Sn system

<table>
<thead>
<tr>
<th>Table 7</th>
<th>Invariant reaction in Mg–Mn–Sn ternary system</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction</td>
<td>Type</td>
</tr>
<tr>
<td>----------</td>
<td>------</td>
</tr>
<tr>
<td>L1 #2 $\leftrightarrow$ L1 + $\beta$Mn</td>
<td>S1</td>
</tr>
<tr>
<td>L1 #2 $\leftrightarrow$ L1 + L1 #2 + $\beta$Mn</td>
<td>U1</td>
</tr>
<tr>
<td>L1 #2 $\leftrightarrow$ L1 + L1 #2 + Mn$_3$Sn</td>
<td>U2</td>
</tr>
<tr>
<td>L1 #2 $\leftrightarrow$ L1 #1 + Mn$_3$Sn + Mg$_3$Sn</td>
<td>E1</td>
</tr>
<tr>
<td>L1 #2 $\leftrightarrow$ L1 #1 + Mn$_3$Sn + Mg$_3$Sn</td>
<td>E2</td>
</tr>
<tr>
<td>Mg$_3$Sn</td>
<td>E3</td>
</tr>
<tr>
<td>L $\leftrightarrow$ hcp + Mg$_2$Sn</td>
<td>S3</td>
</tr>
<tr>
<td>L1 #2 $\leftrightarrow$ L1 + Sn + Mg$_2$Sn</td>
<td>S4</td>
</tr>
<tr>
<td>Mn$_2$Sn</td>
<td>S4</td>
</tr>
<tr>
<td>Mg$_3$Sn + Mn$_2$Sn$_2$</td>
<td>E4</td>
</tr>
<tr>
<td>L1 #2 $\leftrightarrow$ L1 +</td>
<td>E5</td>
</tr>
<tr>
<td>Mg$_2$Sn + MnSn$_2$</td>
<td>E6</td>
</tr>
<tr>
<td>Mg$_2$Sn + MnSn$_2$</td>
<td></td>
</tr>
</tbody>
</table>

\[ G_{\text{Mn}_2\text{Sn}} = y_{\text{Mn}}^2 y_{\text{Sn}}^2 G_{\text{Mn}_2\text{Sn}}^{\text{Mn} \cdot \text{Sn} \cdot \text{Sn} \cdot \text{Mn}} + y_{\text{Mn}}^2 y_{\text{Mn}}^2 G_{\text{Mn}_2\text{Sn}}^{\text{Mn} \cdot \text{Mn} \cdot \text{Mn} \cdot \text{Mn}} + y_{\text{Va}}^2 y_{\text{Mn}}^2 G_{\text{Va}_2\text{Sn} \cdot \text{Mn}} + y_{\text{Va}}^2 y_{\text{Mn}} y_{\text{Va}} y_{\text{Mn}} G_{\text{Va}_2\text{Sn} \cdot \text{Va} \cdot \text{Mn} \cdot \text{Mn}} + RT \left( 0.667 \sum_{j=x} y_j^1 \ln y_j^1 + 0.333 \sum_{j=x} y_j^1 \ln y_j^1 \right) \]
work of [41, 48], whereas Miettinen [43] reported that Mn$_3$Sn as Mn$_{19}$Sn$_6$ that melts congruently.

### 4.2 Mn–Sr binary system

The calculated Mn–Sr phase diagram in relation to the few available experimental data of [49] is shown in Fig. 4. Table 5 summarises the calculated and experimental invariant points of this system. In Sr-rich region, the monotectic reaction \( L_1 \leftrightarrow L_2 + \alpha \text{Mn} \) was observed experimentally [49] and well produced in the current calculations. The calculated monotectic reaction is 96.5 at.% Sr at 1236°C, whereas the measured one is 96.5 at.% Sr at 1240°C.

### 4.3 Mg–Mn–Sr ternary system

Thermodynamic properties of the Mg–Mn–Sr liquid were estimated from the optimised binary parameters using Kohler extrapolation [67]. The projection of the liquidus surface of the Mg–Mn–Sr system is shown in Fig. 5. As can be seen in Fig. 5, the miscibility gap covers most of the composition triangle and the primary crystallisation field of (Mg) is very small. Since there is no experimental data available for the entire Mg–Mn–Sr system, it is possible that the size of the miscibility gap is over or underestimated by the extrapolation. One important clue for understanding Mg-alloy development is its narrow crystallisation field of (Mg). Since changing the alloy’s composition slightly can
lead to precipitate secondary phase(s) that enhance mechanical properties of Mg-alloys.

Invariant reactions of Mg–Mn–Sr are listed in Table 7. The calculated liquidus projection of Mg–Mn–Sr is divided into 11 narrow crystallisation fields: (Mg), αMn, βMn, γMn, δMn, Mg3Sr2, Mg5Sr3, Mg23Sr5, Mg2Sr, α Sr and β Sr. The model predicted nine ternary eutectic reactions and two saddle points. All of these reactions are in the Mg–Sr side.

In the current calculations of the Mg–3 wt.%Sr–(0–5) wt.% Mn and Mg–5 wt.%Sr–(0–5) wt.% Mn alloys indicate that up to 0-12 wt.% Mn, αMn precipitates from Mg-matrix, whereas above 0-12 wt.% Mn, α-Mn phase formation occurs from liquid and Mg-matrix. To estimate the amount of Mn in Mg solid solution under casting conditions, equilibrium simulations are carried out and compared with the TEM/EDS data of Celinkin et al. [27] as shown in Fig. 6. Fig. 6 shows that the amount of Mn in Mg-matrix increases with Mn alloying addition up to 1.75 wt.% Mn. According to Celinkin et al. [27] works, TEM and XRD analyses for heat treated alloys at 225°C (Mg–(3–5 wt.%) Sr–(0.75–2 wt.% Mn) show that the stable phases are Mg17Sr2, Mg and eMn. These phases are in good agreement with the current FactSage calculations. In the composition range experimentally studied, Celinkin et al. [27] observed in TEM/EDS scan that Mn dissolves in interdendritic phase Mg17Sr2. No experimental data could be found in the literature to prove the amount of Mn solubility in Mg17Sr2. This demands experimental investigation in order to verify the solid solubility of Mn in the intermetallic phases of the Mg–Mn–Sr system.

Janz [51] calculated liquidus projection of Mg–Mn–Sr system as extrapolation of the binary subsystems. In his work, miscibility gap cover most of the ternary system that is in accord with the current calculations. In Mg–Sr-rich region, Janz [51] projection showed very narrow crystallisation field for all phases in the ternary system compared with the current paper. In the current calculations, liquidus projection displays smooth and gradual curving, whereas Janz [51] calculations showed curvature of γ and δMn phase boundaries in the ternary system. This particular change in the curvature might be because of not modelling liquid phase by the MQM since the MQM predicts flatter liquidus projection compared with random solution model which is in accord with Kang and Pelton [60] observations. It is worth mentioning that Janz [51] and current isothermal sections of the Mg–Mn–Sr system at 400 and 500°C are identical.

4.4 Mg–Mn–Sn ternary system

In the present paper, the constituent binaries are extrapolated according to the Kohler extrapolation model [67] to construct Mg–Mn–Sn ternary system without addition of any ternary parameters. Liquidus projection of Mg–Mn–Sn is shown in Fig. 7 and invariant reactions of this system are listed in Table 7. Ten primary crystallisation fields are predicted in Mg–Mn–Sn system: hcp, αMn, βMn, γMn, δMn, Mn2Sn, Mn4Sn, Mn3Sn, Mn23Sn3 and Mn5Sn.

Isothermal sections of the Mg–Mn–Sn system in the Mg-rich region were calculated at 500 and 400°C and compared with the work of Kopekstii and Semenova [55] as shown in Figs. 8a and b. Experimental data covered wider region of (Mg) + MgSn and (Mg) compared with calculated isothermal section at 500°C, whereas the predicted (Mg) + MgSn + eMn region is in accord with the work of Kopekstii and Semenova [55]. Wide experimental regions of (Mg) + MgSn and (Mg) might belong to supersaturated solid solution of (Mg). The calculated phase regions of (Mg) + MgSn + eMn, (Mg) + MnSn and (Mg) are in accord with the experimental data of [55]. It is worth mentioning that the work of Kopekstii and Semenova [55] is the only ternary experimental data that could be found in the literature.

The differences between Mg–Mn–Sr and Mg–Mn–Sn liquidus projections drawn in Figs. 5 and 7, respectively, are: miscibility gap in Mg–Mn–Sr system is wider than that of Mg–Mn–Sn, intermetallic compounds of Mn–Sn show wide crystallisation field in the ternary system and the Mg–Mn–Sr system has nine ternary eutectic reactions, and two saddle points and 11 crystallisation fields. Mg–Mn–Sn has four saddle points, two quasi-peritectic and six ternary eutectic reactions.

5 Summary

A self-consistent thermodynamic database has been constructed for the Mn–Sn, Mn–Sr, Mg–Mn–Sn and Mg–Mn–Sr systems using CALPHAD method. The liquid phase is modelled using the MQM to account for the short-range ordering in Mn–Sn liquid. The model parameters of the Mn–Sn and Mn–Sr systems are evaluated by incorporating all experimental data available in the literature. The phase diagrams and thermodynamic properties of the two binaries show good agreement with the experimental data. The established database for Mg–Mn–Sr system predicted two saddle points and nine ternary eutectics, whereas four saddle points, six ternary eutectic and two quasi-peritectic reactions were predicted in Mg–Mn–Sn system. This is the first attempt to construct the ternary phase diagrams of the Mg–Mn–Sn and Mg–Mn–Sr systems using the MQM for the liquid.

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7 References

