Thermodynamic modelling of the Y–Zn and Mg–Zn–Y systems

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Abstract

The Mg–Zn–Y alloy system is rich in intermetallic phases and several stable ternary intermetallic compounds including an icosahedral quasicrystal phase (I phase) exist near the Mg–Zn edge, making the system promising for developing Mg-based light metallic alloys with a large variety of candidates of intermetallic reinforcement phases. Detailed information about phase equilibria in the alloy system is critical for cost-effective alloy development. This work attempts for the first time to thermodynamically model the Y–Zn and Mg–Zn–Y system using the CALPHAD method. A full thermodynamic description of the Y–Zn system has been established, and for the ternary system efforts have been focused on regions near the Mg–Zn edge where the important icosahedral phase exists. The resultant thermodynamic database is then applied to case studies of experimentally observed microstructures, showing that the thermodynamic description of the present work offers a valuable working basis for alloy design of advanced magnesium based materials with intermetallic phases as reinforcements.

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1. Introduction

The Mg–Zn–Y alloy system contains a large number of intermetallic phases, with several stable ternary intermetallic compounds existing near the Mg–Zn edge. Recently, this alloy system has attracted intensive attention, following the discovery of a stable icosahedral quasicrystal phase (I phase) [1–3]. Microstructural investigation showed that the I phase was in equilibrium with the hcp (Mg) solid solution phase in the Mg–Zn–Y system [1,2]. The quasicrystal I phase offers attractive properties such as high strength, high thermal conductivity and low friction coefficient. However, due to its innate brittleness like most intermetallic compounds, the I phase could only be effectively used in structural materials as reinforcement for a ductile matrix. The discovery that the I phase can be in direct equilibrium with the hcp (Mg) solid solution makes alloys near the Mg corner of the Mg–Zn–Y system promising candidates as high performance and low density metal-matrix composites for structural applications. The richness of intermetallic phases in the alloy system makes it possible to develop Mg-matrix structural alloys with wide choices for reinforcement phases to target varied properties. Cost-effective alloy development would not be possible without an in-depth understanding of phase equilibria in the alloy system.

The current work aims to model the Mg–Zn–Y system thermodynamically using the CALPHAD (acronym of Calculation of Phase Diagram) method. A full thermodynamic description of the Y–Zn system will be established. For the ternary Mg–Zn–Y system, we will focus on critical assessment of regions near the Mg–Zn edge where the important icosahedral phase exists. The resultant database will then be applied to case studies of solidification microstructures, showing that the present work offers a reliable working basis for alloy design of advanced magnesium based materials with intermetallic phases as reinforcements.

2. Experimental information on phases and phase equilibria in the Mg–Zn–Y system

Experimental data on constituent binary systems, i.e. Mg–Zn, Mg–Y and Y–Zn, have been reviewed and compiled into the current standard phase diagrams [4]. Two of the standard binary phase diagrams, Mg–Y [5] and Mg–Zn [6], were established with the assistance of CALPHAD modelling.
Table 1
Structures of binary and ternary intermetallic phases [1,4,10–12]

<table>
<thead>
<tr>
<th>Phase</th>
<th>Pearson symbol, space group, structure type</th>
<th>Lattice parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(a (\text{nm}))</td>
</tr>
<tr>
<td>(\text{Mg}_2\text{Y}_3(\text{c}))</td>
<td>(c158, \text{I}4\text{3}m)</td>
<td>1.1257</td>
</tr>
<tr>
<td>(\text{Mg}_2\text{Y})</td>
<td>(h\text{P}12, \text{P}6_3/\text{mmc})</td>
<td>0.6037</td>
</tr>
<tr>
<td>(\text{Mg}Y)</td>
<td>(c\text{P}2, \text{I}m\text{3}\text{m}, \text{B}2)</td>
<td>0.3796</td>
</tr>
<tr>
<td>(\text{YZn})</td>
<td>(c\text{P}2, \text{I}m\text{3}\text{m}, \text{B}2)</td>
<td>0.3578</td>
</tr>
<tr>
<td>(\alpha \text{YZn}_2)</td>
<td>(o\text{I}12, \text{I}m\text{ma})</td>
<td>0.4504</td>
</tr>
<tr>
<td>(\beta \text{YZn}_2)</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>(\text{YZn}_3)</td>
<td>(o\text{P}16, \text{P}n\text{ma})</td>
<td>0.6690</td>
</tr>
<tr>
<td>(\text{Y}<em>3\text{Zn}</em>{11})</td>
<td>(o\text{I}28, \text{I}m\text{mm})</td>
<td>0.4388</td>
</tr>
<tr>
<td>(\text{Y}<em>{13}\text{Zn}</em>{48} (\text{Y}_2\text{Zn}_9))</td>
<td>(h\text{P}146, \text{P}6_5/\text{mmc})</td>
<td>1.428</td>
</tr>
<tr>
<td>(\text{YZn}_5)</td>
<td>(h\text{P}36, \text{P}6_5/\text{mmc})</td>
<td>0.8885</td>
</tr>
<tr>
<td>(\text{Y}<em>2\text{Zn}</em>{17})</td>
<td>(h\text{P}38, \text{P}6_3/\text{mmc})</td>
<td>0.8911</td>
</tr>
<tr>
<td>(\text{YZn}_{12})</td>
<td>(t\text{I}26, \text{I}4/\text{mmm})</td>
<td>0.8875</td>
</tr>
<tr>
<td>(\text{Mg}_7\text{Zn}_3 (\text{Mg}<em>5\text{Zn}</em>{20}))</td>
<td>(o\text{I}158, \text{I}m\text{mm})</td>
<td>1.408</td>
</tr>
<tr>
<td>(\text{MgZn})</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>(\text{Mg}_2\text{Zn}_3)</td>
<td>(m\text{C}110, \text{B}2/\text{m})</td>
<td>2.596</td>
</tr>
<tr>
<td>(\text{MgZn}_3)</td>
<td>(h\text{P}12, \text{P}6_3/\text{mmm}, \text{C}14)</td>
<td>0.523</td>
</tr>
<tr>
<td>(\text{Mg}<em>5\text{Zn}</em>{11})</td>
<td>(c\text{P}39, \text{P}n\text{m}3, \text{D}8_\text{c})</td>
<td>0.855</td>
</tr>
<tr>
<td>(\text{W}_{\text{Mg}_3}\text{Y}_2\text{Zn}_3)</td>
<td>(c\text{F}16, \text{F}m\text{3}m)</td>
<td>0.683</td>
</tr>
<tr>
<td>(\text{Z}_{\text{Mg}<em>2}\text{Zn}</em>{65})</td>
<td>(\text{P}6_\text{5}/\text{mmc})</td>
<td>1.458</td>
</tr>
<tr>
<td>(\text{I}_{\text{Mg}_3}\text{Zn}_6)</td>
<td>(\text{F}m\text{53})</td>
<td>(aq = 0.519)</td>
</tr>
<tr>
<td>(\text{H}<em>{\text{Mg}<em>15}\text{Y}</em>{13}\text{Zn}</em>{70})</td>
<td>Hexagonal</td>
<td>0.776</td>
</tr>
<tr>
<td>(\text{X}_{\text{Mg}_12}\text{Y}\text{Zn})</td>
<td>?</td>
<td></td>
</tr>
</tbody>
</table>

The phase diagram data for the Y–Zn system was due to continued efforts of Chiotti, Mason and co-workers [7,8], which were critically reviewed from time to time to form the reference phase diagrams [4,9]. The current Y–Zn phase diagram is based on Mason and Chiotti [8], with the liquidus temperature in the Y end still being tentative.

Although several ternary compounds have been discovered in Mg–Zn–Y alloys (Table 1) [1,4,10–12], experimental phase diagram data on this system is still limited. Tsai et al. studied phase equilibria in Zn-rich Mg–Zn–Y alloys (Zn = 35–70 at%, \(Y = 3–20\) at%) and established partial isothermal sections at 700, 773 and 873 K, with four ternary phases, \(Z\), \(W\), and \(X\), being identified on the basis of electron-probe microanalysis [1]. Padezhnova et al. studied Mg rich alloys and observed the ternary \(X\) phase close to the Mg corner, together with \(W\) and \(Y\) phases [3]. They established a partial isothermal section at 573 K, with the phase labelled as \(Z\) in the work of Padezhnova et al. was later identified as the \(X\) phase by Tsai et al. [1].

In Table 1, crystallographic data of reported ternary Mg–Zn–Y phases are summarized together with binary ones in the constituent binary systems [1,3,4,10,11]. Several crystalline phases in the Mg–Zn–Y system are closely related to the Mg–Y phase. The Mg\(_7\)Zn\(_3\) phase (or Mg\(_5\)Zn\(_{20}\) [6]) was suggested as a 1/1 cubic approximant (\(a = 1.41\) nm) to the Mg–Y phase [12], and the crystalline Z phase Zn\(_{65}\)Mg\(_{28}\)Y\(_5\) (space group P6\(_3\)/mmc, \(a = 1.4579\) nm, \(c = 0.8687\) nm) was related to the I phase as interpenetrating icosahedral clusters [10].

3. Thermodynamic models

There are solution phases, stoichiometric intermetallic compounds and intermetallic compounds with noticeable solubility ranges in this alloy system. All these phases are modelled using the powerful sublattice model [13]. The Gibbs energy of the sublattice model is expressed for a phase \(\phi\) as:

\[
G_\phi = G_\phi^{\text{ref}} + G_\phi^{\text{id}} + G_\phi^{\text{ex}}.
\]

The term \(G_\phi^{\text{ref}}\) defines the Gibbs energy reference surface and is associated with the complete occupation of each sublattice by only one component on it.

\[
G_\phi^{\text{ref}} = \sum_{I} P_{I} (Y) \cdot 0G_{I}
\]

where \(I\) denotes a component array, which defines one component for each sublattice. \(Y\) is the component matrix made of \(y_i^f\), fractions of component/species \(i\) on sublattice site \(s\). \(P_{I}(Y)\) is the product of the site fractions from the \(Y\) matrix corresponding to the component array \(I\). \(0G_{I}\) is the Gibbs energy of the hypothetical compound defined by the array \(I\).

The term \(G_\phi^{\text{id}}\) expresses the Gibbs energy arising from the ideal entropy of mixing of the component on each separate sublattice,

\[
G_\phi^{\text{id}} = RT \sum_{s} n_s \sum_{i} y_i^f \ln y_i^f
\]

where \(n_s\) is the number of sites on the sublattice \(s\) per mole of formula units of the phase, and \(y_i^f = n_i^f/\sum_j n_j^f\) with \(\sum_j y_j^f = 1\).

The term \(G_\phi^{\text{ex}}\), the excess Gibbs energy, represents the interaction energies between different components in the same sublattice,

\[
G_\phi^{\text{ex}} = \sum_{Z>0} \sum_{IZ} P_{IZ}(Y) \cdot L_{IZ}
\]
Table 2

14

treated with the three-sublattice model

13
)

reduces to Eq.

Appendix

6

Table 1

Appendix

4

Mg, Y, Zn).

where

x

simplified as:

17

L

of the sublattices contains two components with mixing not

allowed in the remaining sublattices. \( L_{ij} \) is the interaction parameter. For \( Z = 0 \), Eq. (4) reduces to Eq. (2), with

11

\( L_{00} = 0 \) \( G_i \) (in this case mixing is not allowed in any of the

sublattices). A detailed review of the sublattice model can be found in [13]. As an example, for a two-sublattice phase \( \phi \),

\( (A_{\alpha X} B_{\beta Y})_p (A_{\alpha X} B_{\beta Y})_q \) with the subscripts \( p \) and \( q \) refer to total number of sites on each sublattice,

\[
G_\phi^{\text{ref}} = y'_A y'_A G_{A:A}^0 + y'_A y'_B G_{A:B}^0 + y'_B y'_A G_{B:A}^0 + y'_B y'_B G_{B:B}^0
\]

where \( G_{A:B}^0 \) refers to a hypothetical compound \( A_p B_q \) and \( y'_A y'_B \) refers to total mole fraction of component \( i \) e.g. \( L_{AB} \). In this work, a single sublattice is assigned to the liquid. For

3

A

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3

A

solidsolution phases without chemical ordering, such as the hcp

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where \( \phi \) is expressed using Redlich–Kister polynomials for the

interaction parameters [14],

\[
G_\phi = x_{Mg} x_Y \sum_v v L_{Mg,Y}(x_{Mg} - x_Y)^v + x_Y x_{Zn} \sum_v v L_{Y,Zn}(x_Y - x_{Zn})^v + x_{Mg} x_{Zn} \sum_v v L_{Mg,Zn}(x_{Mg} - x_{Zn})^v
\]

where \( v \) \( L_{ij} \) and \( L_{Mg,Y,Zn} \) are the binary and ternary interaction

parameters, respectively.

The Gibbs energy of pure elements \( G_i^0 \) is taken from the

widely accepted SGTE (acronym for Scientific Group for

Thermodata Europe) database [15], which is referred to the

enthalpy for its stable state at 298.15 K.

4. Results and discussion

4.1. Calculation of phase diagrams

CALPHAD modelling involves formulating thermodynamic

models and generating model parameters via optimising

available experimental data. A major advantage of the

CALPHAD methodology lies in its cumulative nature of

database structures, so that the modelling of higher order

systems is built upon the fundamental bricks of constituent

subsystems. This makes the methodology particularly useful

for multi-component alloys for engineering applications [16].

For the optimisation process of this work, we use the PARROT

module in the Thermo-Calc code, which takes various types

of experimental data for the optimisation process [17].

The advantageous features of the PANDAT code [18] for

the calculation of pseudo-binary phase diagram for ternary systems

is also utilised in this work.

Of the three constituent binary systems, the Mg–Zn [6] and

Mg–Y [5] systems were thermodynamically modelled

previously and the data are considered satisfactory. No attempt

was made to thermodynamically model the Y–Zn system

previously. In this work, we model all the intermetallic phases

in the Y–Zn system as stoichiometric ones. The Y–Zn phase

diagram calculated using the thermodynamic data of this work

(see Appendix) is shown in Fig. 2(a). All characteristic features

of the experimental phase diagram [4] are reproduced by the

calculation. The calculated phase boundaries are in very good

agreement with available experimental data [4,7–9], Fig. 2(b).

Calculated enthalpies of formation of intermetallic phases are

compared with experimentally measured data in Table 2, and

the agreement is excellent. The resultant thermodynamic data

(see Appendix) for this system is thus considered satisfactory

and used for modelling the ternary system.

All ternary phases in this system, the \( X, W, H, I \) and \( Z \)

phases (Table 1), are treated with the three-sublattice model

on the basis of available crystallographic information, with

Mg, Y, and Zn being the major elements for each sublattice.

Among these, the \( H \) and \( X \) phases are treated as stoichiometric

ones, and for the remaining three phases, mixing between

the sublattices of Mg and Zn are considered. On the basis of

experimental findings of phase compositions and available

crystallographic data, the sublattice configurations for the \( I, W \)

and \( Z \) phases are decided to be:

\( I: \) (Mg)$_3$(Y)$_1$(Mg, Zn)$_6$

\( W: \) (Mg, Zn)$_{0.4}$(Y)$_{0.2}$(Mg, Zn)$_{0.4}$

\( Z: \) (Mg)$_{28}$(Y)$_7$(Mg, Zn)$_{65}$. 

where

\[ x_{Mg} x_Y x_{Zn} L_{Mg,Y,Zn} \]
Table 2
Enthalpies of formation of intermetallic phases in the Y–Zn system

<table>
<thead>
<tr>
<th>Phase</th>
<th>Enthalpy of formation (kJ per mole of atoms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work (CALPHAD)</td>
<td></td>
</tr>
<tr>
<td>Experimental data [8] (±2)</td>
<td></td>
</tr>
<tr>
<td>Estimated [23]</td>
<td></td>
</tr>
<tr>
<td>YZn</td>
<td>−47.0 −48 −54</td>
</tr>
<tr>
<td>αYZn$_2$</td>
<td>−48.0 −52 −51</td>
</tr>
<tr>
<td>βYZn$_2$</td>
<td>−46.0 −49 −51</td>
</tr>
<tr>
<td>YZn$_3$</td>
<td>−41.50 −43 −42</td>
</tr>
<tr>
<td>Y$_3$Zn$_11$</td>
<td>−38.743 −40 −36</td>
</tr>
<tr>
<td>Y$<em>{13}$Zn$</em>{58}$</td>
<td>−36.0 −37 −32</td>
</tr>
<tr>
<td>YZn$_5$</td>
<td>−34.333 −33 −25</td>
</tr>
<tr>
<td>Y$<em>2$Zn$</em>{17}$</td>
<td>−28.0 −30 −18</td>
</tr>
<tr>
<td>YZn$_{12}$</td>
<td>−23.070 −23 −13</td>
</tr>
</tbody>
</table>

* SGTE data for pure elements are used to transfer the original data to the current reference states.

Fig. 1. Calculated binary phase diagrams of the (a) Mg–Y and (b) Mg–Zn systems, using data of Refs. [5] and [6] respectively.

The similarity in sublattice mixing in the Z and I phases is attributed to their close crystallographic relationship. For CALPHAD optimisation of the Mg–Zn–Y system, the experimental input on ternary equilibria is based on the work of Tsai et al. [1] and Padezhnova et al. [3]. Thermodynamic data for the binary Mg–Zn and Mg–Y systems are from Refs. [6] and [5] and the data for Y–Zn are from this work. In Fig. 3, we show isothermal sections at 873, 773, 700 and 573 K, which are calculated using the resultant database of this work. The characteristic features of these calculated isothermal sections are consistent with the experimental work of Tsai et al. [1], so that three-phase fields
Fig. 3. Comparison of calculated isothermal sections at (a) 873 K, (b) 773 K, (c) 700 K, and (d) 573 K. Experimental data of phase compositions from the literature [1,3] are superimposed together with phase compositions measured in this work. The dotted lines refer to experimental tie lines and phase boundaries [1,3]. The crosses denote compositions of alloys that contained three phases in the microstructures [1].

such as \((L+I+Z)\) and \((Mg+I+Z)\) exist near the Mg–Zn edge, and \((W+I+H)\) and \((I+Z+H)\) equilibrium occurs in alloys of high Zn and Y contents. In the course of this work, we also studied phase equilibria in the Mg-rich Mg-30at%Zn-2.5at%Y alloy, to provide additional information to the work of Tsai et al. (whose work was for Zn-rich alloys). In the as-cast alloy ingot, the \(I\) phase composition varies in the ratio of Zn and Mg, with Y content largely constant [19], being supportive to our choice of sublattice mixing. Interestingly, when the alloy was annealed in the temperature ranges from 673 to 773 K for one to four hours, the composition of the \(I\) phase was stabilised to contain 1 at% more of Y without evident correlation to annealing temperature. The composition of the \(W\) phase in our annealed samples was found to be close to that reported by Padezhnova et al. [3] but contained evidently less Zn than those reported by Tsai et al. [1] (Fig. 3(a)–(d)). It is worth pointing out that the alloys investigated by Tsai et al. were close to the Zn-rich corner of the Mg–Zn–Y system instead.

These calculated isothermal sections are compared with experimentally observed data of phase compositions and tie lines, as well as alloy compositions with three-phase equilibria from the work of Tsai et al. [1]. Compositions of the \(W\) and \(I\) phases in the Mg-30at%Zn-2.5at%Y alloy of the current work and the data from the 573 K isothermal section of Padezhnova et al. [3] are also shown on these isothermal sections to compare. Overall, the calculated phase diagrams (Fig. 3(a)–(d)) are in reasonably good agreement with experimental data. However, the wide scatter in the \(W\)-phase compositions from three of the samples of Tsai et al., annealed at 773 and 700 K [1], are not sufficiently covered by the present choice of model. In the work of Tsai et al., all the alloys were homogenized at 873 K for 24 h before subsequent annealing at lower temperatures (i.e. 700 and 773 K), though no details
were given for the periods of annealing time \cite{1}. Also, no microstructure details were given about phase equilibria involving the W and H phases \cite{1}. The reported W phase compositions after annealing at 773 and 700 K approached the middle of the $W + H + I$ three-phase fields of the calculated phase diagrams. It might be possible that the prior W phase decomposed into mixtures of different intermetallic phases, and equilibria were not completed in those alloys that consisted mainly of intermetallic compounds (and hence slow transformation kinetics). Actually, it seems that none of the available experimental data concerning ternary phase equilibria can be considered as to be fully equilibrated with confidence. More detailed experimental work will be useful for phase equilibria, particularly for those involving the W and H phases, so that further refinement in the models, if necessary, can be followed.

The calculated 573 K isothermal section (Fig. 3(d)) is consistent with the corresponding isothermal section of Padezhnova et al., except for the missing of the Z-phase in the experimental work of the latter. The absence of the stable Mg$_2$Zn$_3$ in the latter could suggest that equilibration was not completed in the experimental work. As was pointed out by Tsai et al., the samples of Padezhnova et al. \cite{3} were not fully equilibrated and their data are largely representative of furnace cooled ingots \cite{1}. In Fig. 4, we compare our calculated Mg–X pseudo-binary phase diagram with differential thermal analysis (DTA) data of Padezhnova et al. \cite{3}, showing excellent agreement. The minor intermetallic phases (W or I) were suspended for the calculation of Fig. 4, since their low equilibrium quantity (<1%) would not have been detected due to the limitation of thermal analysis \cite{3}.

Overall, the results of the current CALPHAD modelling are considered fairly satisfactory, particularly in promising alloys for structural applications near the Mg–Zn edge. The resultant thermodynamic database can then be applied to study various phase-equilibrium related materials problems. In Fig. 5, we present a calculated partial liquidus projection of Mg–Zn–Y. Being in agreement with the tentative suggestion by Tsai et al., the H phase is predicted to have higher melting temperature than the I phase, so that the latter could form via peritectic reactions from the H phase \cite{1}, i.e., $L + H \rightarrow I + (Y_2Zn_{17})$ or $L + H \rightarrow (W) + I$ (Tsai et al. did not consider the phases in the brackets in their hypothetical pseudo-binary diagrams, though). Besides, the calculated liquid surface projection also shows that in alloys of lower Zn content, the W phase could precede the I phase as primary phase during solidification. Such a prediction could be verified by studying the solidification process in alloys lying in the compositional region for primary W phase solidification.

4.2. Case studies

4.2.1. Application to solidification microstructure of Mg-30at%Zn-2.5at%Y

A Mg-rich alloy of the composition of Mg-30at%Zn-2.5at%Y lies close to the uni-variant eutectic valley $L \rightarrow H + W$. The solidification path of this alloy can be calculated using the present database under both equilibrium and Scheil \cite{20} conditions, to generate the lower and upper segregation patterns respectively (Fig. 6). According to the calculation, the alloy starts solidification with the crystallisation of a small amount of the primary W phase, followed by the solidification of the quasi-crystal I phase before the occurrence of the hcp (Mg) solid solution phase. Thermodynamically, the W phase tends to disappear via the peritectic reaction $L + W \rightarrow I + (Mg)$. An invariant peritectic reaction, $L + I \rightarrow (Mg) + Z$, occurs at a $\sim 659$ K (386 °C) to turn the primary I phase into Z, when there is hardly any Y left in the liquid phase. Heavier segregation under the Scheil condition makes this happen at a lower fraction of the solid phases.

The microstructure of the as-cast ingot of the Mg-30at%Zn-2.5at%Y alloy (copper-die casting) were studied in detail using both scanning and transmission electron microscopy (SEM and TEM) and phases were identified by electron diffraction under TEM and quantitative energy dispersive X-ray analysis. A
Fig. 6. Evolution of liquid phase compositions (a)–(c) and melt temperature (d) against molar fraction of solid, calculated under Scheil and equilibrium conditions respectively.

Fig. 7. SEM backscattered-electron image of polished Mg-30at%Zn-2.5at%Y die-cast ingot. Notice the macroscopic symmetric features of the labelled primary \( I \) phase particles. The eutectic domain, "E", has \( I \) phase in the outer peripheral region. The \( \text{Mg}_2\text{Zn}_3 \) compound in the inner eutectic region has lower atomic number than that of the \( I \) phase. A block arrow indicates the initiation of the eutectic \( I \) phase from a primary one. A \( W \) phase particle within a primary \( I \) phase particle is also indicated.

W phase was observed within some of the primary \( I \) phase particles (indicated in Fig. 7). Being in agreement with the thermodynamic prediction, the \( W \) phase was the first phase to appear during solidification, which then acted as prior nucleation sites for the following \( I \) particles. The immediate appearance of the \( \text{(Mg)} \) matrix around the primary \( I \) phase particles is consistent with the prediction that \( \text{(Mg)} \) starts solidification via \( \text{L} + \text{W} \rightarrow \text{I} + (\text{Mg}) \) followed by \( \text{L} \rightarrow \text{I} + (\text{Mg}) \).

The primary \( I \) phase particles are surrounded by leafy eutectic domains ("E" in Fig. 7) that share the same \( \text{(Mg)} \) matrix. The intermetallic phase in the outer peripheral regions of the eutectic domains shows the same contrast as that of the primary \( I \) phase in the back-scattered electron image, and electron diffraction under TEM showed that this intermetallic phase in the peripheral eutectic regions does have the icosahedral structure. A typical selected-area electron diffraction (SAD) pattern at the 5-fold axis of the primary \( I \) phase is shown in Fig. 8(a), and a micro-area diffraction (MD) pattern at the 5-fold axis from the \( I \) phase in the peripheral eutectic region is shown in Fig. 8(b). The inner eutectic region is made of the \( \text{(Mg)} \) solid solution phase and the binary \( \text{Mg}_2\text{Zn}_3 \) compound, with both phases containing negligible amounts of \( Y \). There are nano-precipitates of equilibrium \( \text{MgZn} \) phase in the \( \text{(Mg)} \) matrix (Fig. 8(c)). Fig. 9 are X-ray maps covering the immediate neighbourhood of a primary \( I \) phase particle, showing branching of the primary \( I \) phase (indicated as “A”) and the initiation of \( \text{Mg}_2\text{Zn}_3 \) in the \( \text{(Mg)} \) matrix (indicated as “B”), with both being intermetallic phases in the outer and inner
regions of leafy eutectic domains respectively (see Fig. 7 for a larger field of view).

In spite of careful TEM investigation, the Z phase was not observed in the solidification microstructure. Thus, the equilibrium process \( L + I \rightarrow Z + (Mg) \) was suppressed during solidification. Instead, the metastable eutectic solidification \( L \rightarrow (Mg) + Mg_2Zn_3 \) occurred in a later stage of solidification to form the inner eutectic region (Fig. 7), when the remaining liquid was nearly free of Y. The appearance of \( Mg_2Zn_3 \) is attributable to peritectic reactions at lower temperature, and in the binary Mg–Zn system (the liquid is almost free of Y in the last stage of solidification), by the route of the peritectic reaction \( L + (Mg) \rightarrow Mg_7Zn_3 \) (see Fig. 1(b)).

It is worth pointing out that the equilibrium Z phase has not been observed either in furnace cooled [3] or as-cast Mg-rich Mg–Zn–Y alloys [2,24,25]. The absence of the Z phase from the solidification microstructures in Mg-rich alloys could be attributed to slow transformation kinetics of crystallisation of the Z phase via the peritectic reaction \( L + I \rightarrow Z + (Mg) \). From a crystallographic point of view, the Z phase could be related to the C14 Laves MgZn₂ by introducing basal plane

chemical ordering (compare the lattice parameters of the two phases in Table 1 to see that \( c_Z \approx c_{MgZn_2} \) and \( a_Z \approx 3a_{MgZn_2} \)). Singh et al. analysed a relationship between the Z phase and \( I \) phase, suggesting the correspondence between a 2-fold \( I \)-phase axis and the 6-fold Z-phase axis [21]. They showed that the hexagonal symmetry of the Z phase could be obtained by rotating the 2-fold axis of the \( I \) phase twice accompanied by a slight distortion, so that the Z phase originates from interpenetrating \( I \) phase clusters with sequential chemical ordering [21]. Either of such chemical ordering processes could be rather sluggish kinetically, as ordering of \( I \)-clusters would be similar to ordering molecular species, and the Laves structure are notorious for slow diffusion due to a strict requirement for atomic size ratios [22]. Probably due to such kinetic sluggishness in ordering, Padezhnova et al. did not observe the \( Z \)-phase formation in their slowly-cooled Mg–Zn–Y alloys that were subsequently annealed at 573 K. Indeed, they only found the \( L + I \) two-phase equilibrium near the Mg corner [3], which would suggest rather low thermodynamic driving force for turning the \( I \) phase into the Z structure via the peritectic reaction \( L + I \rightarrow Z + (Mg) \). Indeed, this is reflected in the thermodynamic database of this work (see Appendix), which shows that the Z phase even has a smaller enthalpy of formation than the I phase.

### 4.2.2. The role of Zn/Y ratio on alloy microstructures

It has been noticed that the phase constituency in Mg–Zn–Y alloys are largely dependent on the Zn/Y ratio [26]. Experimentally observed phases in alloys of different Zn/Y ratios are superimposed on a partial 673 K isothermal section (Fig. 10), which is calculated using the resultant thermodynamic database of this work. It is seen that the Zn/Y ratio is indeed a controlling parameter for phase constituencies, and alloys of Zn/Y ratios around 6 are largely located in the \( (Mg) + I \) phase region, being in excellent agreement with experimental findings, bearing in mind that none of these experimental microstructures were in equilibrium [24–26]. It is

Fig. 10. The 673 K isothermal section calculated using the data of this work, superimposed with experimentally observed phases in as-cast ingots and thermo-mechanically processed materials [24–26]. The phase constituency is determined by the atomic ratio of Zn/Y.
also noticed that the best agreement is with alloys that were thermo-mechanically processed at about 673 K, as they were in states closer to equilibration. The resultant thermodynamic database can therefore be considered to be a solid working basis for designing (Mg)-based metal matrix composites using intermetallic phases near the Mg–Zn edge as reinforcements.

5. Conclusions

The Y–Zn and Mg–Zn–Y systems are thermodynamically modelled for the first time using the CALPHAD method. A full thermodynamic description of the Y–Zn system has been established, and for the ternary system efforts have been focused on regions near the Mg–Zn edge where the important icosahedral phase exists. The calculated phase diagrams are in reasonable agreement with available experimental data.

The resultant thermodynamic database is applied to case studies, showing that the present thermodynamic description of the Mg–Zn–Y system is reliable as a working basis for computer-assisted design of advanced magnesium based materials with intermetallic phases as reinforcements.

The transformation of prior $I$ phase into the crystalline $Z$ phase in Mg-rich alloys via the peritectic reaction, $L + I \rightarrow Z + (Mg)$, is a sluggish process, due to slow transformation kinetics and low thermodynamic driving force.

Appendix

Summary of the optimised thermodynamic parameters for the Mg–Y–Zn system. Values are given in SI units for molar formula of phases. Lattice stabilities of pure elements are from [15].

**Liquid**, sublattice model: (Mg, Y, Zn)

\[
\begin{align*}
0 L_{Mg,Y} &= -25 802.51 + 4.30042 T \\
1 L_{Mg,Y} &= -19 229.76 + 3.20497 T \\
0 L_{Mg,Zn} &= -77 729.24 + 680.52266 T - 95 T \ln T + 0.04 T^2 \\
1 L_{Mg,Zn} &= -3674.72 + 0.57139 T \\
2 L_{Mg,Zn} &= -1588.15 \\
0 L_{Y,Zn} &= -128 000 + 4.2 T \\
1 L_{Y,Zn} &= +56 000 \\
0 L_{Mg,Y,Zn} &= -16 000 \\
\end{align*}
\]

*bcc_A2*, sublattice model: (Mg, Y, Zn) (Va)$_3$

\[
\begin{align*}
0 L_{Mg,Y,Va} &= -38 570 + 15 T \frac{2}{3} \\
1 L_{Mg,Y,Va} &= -8204.21 \\
0 L_{Mg,Zn,Va} &= -10 000 \\
0 L_{Y,Zn,Va} &= -67 700 + 4 T \\
1 L_{Y,Zn,Va} &= 27 000 \\
\end{align*}
\]

*fcc_A1*, sublattice model: (Mg, Y, Zn) (Va)

\[
\begin{align*}
0 L_{Mg,Y,Va} &= +0.0001 \\
0 L_{Mg,Zn,Va} &= -3056.82 + 5.63801 T \\
1 L_{Mg,Zn,Va} &= -3127.26 + 5.65563 T \\
0 L_{Y,Zn,Va} &= -67 700 + 4 T \frac{2}{3} \\
1 L_{Y,Zn,Va} &= 27 000 \\
\end{align*}
\]

*hcp_A3*, sublattice model: (Mg, Y, Zn) (Va)$_{0.5}$

\[
\begin{align*}
0 L_{Mg,Y,Va} &= -16 582.94 + 4.77482 T \\
0 L_{Mg,Y,Va} &= -7077.87 \\
\end{align*}
\]

0\(_{L_{Mg,Zn,Va}} = -3056.82 + 5.63801 T \]

1\(_{L_{Mg,Zn,Va}} = -3127.26 + 5.65563 T \]

0\(_{L_{Y,Zn,Va}} = -67 700 + 4 T \frac{2}{3} \\
1\(_{L_{Y,Zn,Va}} = 27 000 \\
\]

MgZn\_2 (C14), sublattice model: (Mg, Zn)$_1$ (Mg, Zn)$_2$

\[
\begin{align*}
G_{Mg,Zn} &= 3.0 G_{hcp} + 15 000 \\
G_{Zn,Zn} &= 3.0 G_{hcp} + 15 000 \\
G_{Mg,Zn} &= 0 G_{hcp} - 2.0 G_{hcp} + 65 355.45 - 8.838867 T \\
G_{Zn,Zn} &= 2.0 G_{hcp} - 0 G_{hcp} - 35 355.45 + 8.838867 T \\
1 G_{Mg,Zn} &= +35 000 \\
0 G_{Mg,Zn} &= +35 000 \\
0 G_{Mg,Mg} &= +8 000 \\
0 G_{Zn,Zn} &= +8 000 \\
\end{align*}
\]

Mg\_2Zn\_11: (Mg)$_2$(Zn)$_{11}$$L_{Mg,Zn} = 2.0 G_{hcp} - 1 G_{hcp} + 73 818.32 + 18.45457 T

Mg\_2Zn\_1: (Mg)$_2$(Zn)$_{13}$$L_{Mg,Zn} = 2.0 G_{hcp} - 3.0 G_{hcp} = -54 406.2 + 13.60156 T

Mg\_7Zn\_1: (Mg)$_{15}$(Zn)$_{20}$$L_{Mg,Zn} = 5 G_{hcp} - 20 G_{hcp} - 235 714.54 + 35.5 T

Mg\_Zn\_1: (Mg)$_{12}$(Zn)$_{13}$$L_{Mg,Zn} = 12 G_{hcp} - 13 G_{hcp} = -236 980.84 + 59.24524 T

Mg\_4Y\_5: (Mg)$_4$(Mg, Y)$_5$$L_{Mg,Mg} = 29 G_{hcp} + 44 506.01

Mg\_Y\_4: (Mg)$_4$(Mg, Y)$_5$$L_{Mg,Y} = 24 G_{hcp} - 5 G_{hcp} = -227 282.28 + 36.52985 T

Mg\_2Y\_1: (Mg)$_2$(Y)$_1$$L_{Mg,Y} = 2 G_{hcp} - 0 G_{hcp} = -39 075.78 + 6.51258 T

Y\_Zn\_1: (Y, Zn)$_{12}$$L_{Y,Zn} = 0 G_{hcp} - 12 G_{hcp} = -299 910 + 64.137787 T

Y\_Zn\_1: (Y, Zn)$_{17}$$L_{Y,Zn} = 0 G_{hcp} - 17 G_{hcp} = -532 000 + 807 T

Y\_Zn\_1: (Y, Zn)$_{15}$$L_{Y,Zn} = 0 G_{hcp} - 5 G_{hcp} = -206 000 + 23.7497 T

Y\_Zn\_1: (Y, Zn)$_{13}$$L_{Y,Zn} = 0 G_{hcp} - 3 G_{hcp} = -166 000 + 16.3022017 T

Y\_Zn\_1: (Y, Zn)$_{12}$$L_{Y,Zn} = 0 G_{hcp} - 2 G_{hcp} = -138 000 + 9.7 T

Y\_Zn\_1: (Y, Zn)$_{11}$$L_{Y,Zn} = 0 G_{hcp} - 11 G_{hcp} = -542 400 + 55.5617 T

Y\_Zn\_1: (Y, Zn)$_{13}$$L_{Y,Zn} = 0 G_{hcp} - 3 G_{hcp} = -166 000 + 16.3022017 T

Y\_Zn\_1: (Y, Zn)$_{12}$$L_{Y,Zn} = 0 G_{hcp} - 2 G_{hcp} = -138 000 + 9.7 T

Y\_Zn\_1: (Y, Zn)$_{11}$$L_{Y,Zn} = 0 G_{hcp} - 11 G_{hcp} = -542 400 + 55.5617 T

Y\_Zn\_1: (Y, Zn)$_{10}$$L_{Y,Zn} = 0 G_{hcp} - 3 G_{hcp} = -166 000 + 16.3022017 T

Y\_Zn\_1: (Y, Zn)$_{0}$$L_{Y,Zn} = 0 G_{hcp} - 2 G_{hcp} = -138 000 + 9.7 T

Y\_Zn\_1: (Y, Zn)$_{0}$$L_{Y,Zn} = 0 G_{hcp} - 2 G_{hcp} = -144 000 + 15.06 T
\[ I_{\text{Mg}_3}\text{YZn}_6: \text{sublattice model:} \langle \text{Mg}\rangle_3 \langle \text{Y}\rangle_1 \langle \text{Zn}\rangle_6 \]
\[
G - 3\theta_{\text{hcp}}^{\text{Mg}} - 0\theta_{\text{hcp}}^{\text{Y}} - 6\theta_{\text{hcp}}^{\text{Zn}} = -307\,500 + 86\,T
\]
\[
G - 9\theta_{\text{hcp}}^{\text{Mg}} - 0\theta_{\text{hcp}}^{\text{Y}} = -37\,000 + 38\,T
\]

\[ Z_{\text{Mg}_8\text{Y}_7\text{Zn}}: \langle \text{Mg}\rangle_{28} \langle \text{Y}\rangle_7 \langle \text{Zn}\rangle_{65} \]
\[
G - 28\theta_{\text{hcp}}^{\text{Mg}} - 7\theta_{\text{hcp}}^{\text{Y}} - 65\theta_{\text{hcp}}^{\text{Zn}} = -2719\,000 + 900\,T
\]
\[
G - 93\theta_{\text{hcp}}^{\text{Mg}} - 7\theta_{\text{hcp}}^{\text{Y}} = -326\,810 + 390\,T
\]

\[ H_{\text{Mg}_5\text{Y}}_{15}\text{Zn}_{90}: \langle \text{Mg}\rangle_{15} \langle \text{Y}\rangle_1 \langle \text{Zn}\rangle_{70} \]
\[
G - 15\theta_{\text{hcp}}^{\text{Mg}} - 15\theta_{\text{hcp}}^{\text{Y}} - 70\theta_{\text{hcp}}^{\text{Zn}} = -3837\,000 + 980\,T
\]

\[ W_{\text{Mg}_3\text{Y}_2\text{Zn}_3}: \langle \text{Mg}\rangle_{0.4} \langle \text{Y}\rangle_{0.2} \langle \text{Zn}\rangle_{0.4} \]
\[
G - 0.4\theta_{\text{hcp}}^{\text{Mg}} - 0.2\theta_{\text{hcp}}^{\text{Y}} - 0.4\theta_{\text{hcp}}^{\text{Zn}} = -3446 + 11.9\,T
\]
\[
G - 0.2\theta_{\text{hcp}}^{\text{Y}} - 0.8\theta_{\text{hcp}}^{\text{Zn}} = -37\,000 + 4.1\,T
\]

\[ X_{\text{Mg}_{12}\text{Zn}}: \langle \text{Mg}\rangle_{0.86} \langle \text{Y}\rangle_{0.08} \langle \text{Zn}\rangle_{0.96} \]
\[
G - 0.86\theta_{\text{hcp}}^{\text{Mg}} - 0.08\theta_{\text{hcp}}^{\text{Y}} - 0.96\theta_{\text{hcp}}^{\text{Zn}} = -8720 + 3.1\,T
\]

References