Experimental study and thermodynamic assessment of ternary Mg–Zn–Ce phase relations focused on Mg-rich alloys

Chen-nan Chiu a,b, Joachim Gröbner a, Artem Kozlov a, Rainer Schmid-Fetzer a,*

a Institute of Metallurgy, Clausthal University of Technology, Robert-Koch-Str. 42, D-38678 Clausthal-Zellerfeld, Germany
b Department of Chemical Engineering, National Tsing Hua University, 101, Sec. 2, Kuang Fu Rd., Hsin-Chu 300, Taiwan, Republic of China

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The Mg-rich part of the ternary Mg–Zn–Ce system was investigated by key samples to determine the solubilities, primary crystallization and invariant reactions. Ten alloys were prepared from pure elements and investigated by DTA/DSC and SEM/EDS. A consistent thermodynamic model of the ternary Mg–Zn–Ce system is developed for the first time by using the Calphad method. Phase diagram sections at constant 300 °C, at constant 85 at. % Mg and the liquidus projection of the Mg–Zn–Ce ternary system were calculated and compared with all available experimental data. The thermodynamic description is reasonably well supported by experimental data, especially in the Mg-rich region.

1. Introduction

Improving the mechanical properties and creep resistance of magnesium alloys at elevated temperatures may significantly extend the application limits of such lightweight alloys. In that context Mg–Zn alloys are considered to have great potential, compared to conventional Mg–Al alloys, as reviewed by Bamberger [1]. In order to attain improved creep resistance and strength at elevated temperatures new magnesium alloys with Zn are being developed by adding rare earth (RE) elements (Ce, Gd, and also Y) to form precipitates in these alloys by age hardening [2,3]. Cerium is a major component of misch-metal and thus is considered as the most important part in these industrially used rare earth elements. It has been reported that addition of Ce effects excellent age hardening behavior for the Mg–1.5Zn–0.2Ce (wt.%) alloy [4].

It is evident that the Mg–Zn–Ce ternary alloy system plays a prominent role among the Mg–Zn–RE systems. Precise knowledge of the phase diagram and thermodynamic properties of the Mg–Zn–Ce system are necessary for a better understanding of alloy design. It is also a key system for the construction of a thermodynamic database for multicomponent Mg-based alloys.

The thermodynamic description of the Mg–Zn–Ce ternary system has not been proposed in the literature. In order to exploit the application potential of computational thermodynamics it is essential to not only know the phase diagram but also the corresponding thermodynamic description in a consistent manner. This also leads to the most effective way to study the ternary phase diagram by a combination of selected key experimental work jointly with thermodynamic modeling using the calculation of phase diagrams (CALPHAD) method. This is the aim of the present study on the Mg–Zn–Ce alloy system.

2. Experimental data in the literature

Experimental phase diagram data in the Mg–Zn–Ce system is limited to the isothermal section at 300 °C, at 350 °C and some works in the Mg-rich corner. No complete phase diagram exists in the literature for this system. The ternary phase relations were first investigated by Korol’kov and Sal’dau [5]. The liquidus projection in the Mg-rich corner was drawn based on thermal analysis of alloys at six constant mass ratios (Ce:Zn = 1:10, 1:4.5, 1:2, 1:1, 2:1, and 5:1). A ternary eutectic was reported with liquid composition Mg–47.5wt.%Zn–2.5wt.%Ce (Mg–25.9at.%Zn–0.6at.%Ce) at 341–343 °C without providing explanation [5]. Solvus lines at 20, 200, 300, and 335 °C were also given. It is noted that in their study low purity Ce (96%) was used and the adopted Ce–Mg binary phase
diagram differs from the currently accepted one. Therefore, the combined solubility of Ce and Zn in Mg is considered to be an estimated value. Even though, the results indicate that the solubility of Zn in (Mg) is lowered by the addition of Ce.

An isothermal section at 300 °C in the Mg–MgZn2–CeMg–CeZn region was given by Mel'nik et al. [6]. They inspected this region from 150 alloys annealed for 240 h by using X-ray diffraction analysis. The result shows that most of Ce–Mg binary phases extend with a solid solubility into the ternary system. CeMg and CeZn form a continuous solid solution, and both crystallize in the same CsCl structure. Large solubilities of Zn in CeMg3 and CeMg12 at 300 °C were found, 29 at.% and 8 at.% Zn, respectively. Four ternary compounds, CeMg2Zn12, Ce2(Mg0.5–0.85Zn0.5–0.15)3, CeMg2Zn5, and Ce2Mg3Zn3, were discovered at 300 °C. The crystal structure of Ce2Mg17 is Th2Ni17 structure type by Mel'nik et al. [9]. The structures of Ce2Mg17 and Ce12Mg3Zn3, were discovered at 300 °C by Kolitsch et al. [7]. The structures of Ce2Mg17 and Ce12Mg3Zn3, were discovered at 300 °C by Kolitsch et al. [7]. The structures of Table 1 are also found in their study, and they labeled t2 as CeMg(Mg0.5–0.9Zn0.5–0.1)10.1.

Kevorkov and Pekguleryuz [12] recently studied the Mg-rich corner of the Mg–Zn–Ce phase diagram at 350 °C by using a diffusion couple technique. They examined the solid solubilities of binary and ternary solutions by EDS and EPMA. In addition to the four ternary phases reported previously [6], two new ternary phases, Ce2Mg53Zn45 and CeMg(8–15)Zn(86–79), were found in their work. The decagonal quasicrystal reported in many of the Mg–Zn–RE systems was not observed in the Mg–Zn–Ce system [13]. Pavlyuk et al. reported a Heusler-type alloy with the composition CeMgZn2 [14] and a cubic phase Ce29Mg19Zn31 [15]. Crystallographic data and compositions of all ternary phases accepted in the present study are summarized in Table 1. True ternary phases, not originating at a binary edge, are labeled T1–T5. To avoid confusion, phase designations used by Refs. [7,12] are also given.

3. Experimental procedures

The present experimental work focuses on missing key data for thermodynamic modeling, and is also guided by such calculations with preliminary data sets as detailed later. The Mg–Zn–Ce ternary alloy samples were prepared from cerium ingot (99.9 wt.%, Santoku America Inc., Phoenix, USA), magnesium pieces (99.99 wt.%, Zink GmbH, Goslar, Germany), and Zn rods (99.98 wt.%, Harzer Zink GmbH, Goslar, Germany). Typical weight of these samples was 500 mg. In order to prevent the vaporization of Mg and Zn, the samples were not prepared by arc-melting method, since the significant loss of these metals leads to substantial change of the compositions. The weighted elements were pressed carefully to pellets which were sealed under argon atmosphere by welding in

<table>
<thead>
<tr>
<th>Phase name</th>
<th>Phase description</th>
<th>Prototype</th>
<th>Pearson symbol/space group</th>
<th>Zn–solubility [at.%] at 300 °C</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce(Mg,Zn)</td>
<td>Ce(Mg,Zn)12</td>
<td>CsCl</td>
<td>cP2/Fm-3m</td>
<td>0–100</td>
<td>[6]</td>
</tr>
<tr>
<td>CeMg2</td>
<td>Ce(Mg,Zn)12</td>
<td>MgCu2</td>
<td>cF24/Fd-3m</td>
<td>–</td>
<td>[6]</td>
</tr>
<tr>
<td>CeMg4</td>
<td>Ce(Mg,Zn)12</td>
<td>BiF3</td>
<td>cF16/Fm-3m</td>
<td>0–29</td>
<td>[6]</td>
</tr>
<tr>
<td>CeMg12</td>
<td>Ce(Mg,Zn)12</td>
<td>ThMn12</td>
<td>tI26/J4/m</td>
<td>0–8</td>
<td>[6]</td>
</tr>
<tr>
<td></td>
<td>Phase 3 after [12]</td>
<td></td>
<td></td>
<td>0–48</td>
<td>[12]</td>
</tr>
<tr>
<td></td>
<td>Phase 1 after [12]</td>
<td></td>
<td></td>
<td>0–40</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>t2 after [7]</td>
<td></td>
<td></td>
<td>9.1–45.5</td>
<td>[8,9]</td>
</tr>
<tr>
<td>T1</td>
<td>CeMg2Zn12</td>
<td>hexagonal</td>
<td>Not known</td>
<td>stochiometric</td>
<td>[6]</td>
</tr>
<tr>
<td>T2</td>
<td>CeMg53Zn45</td>
<td>Not known</td>
<td>Not known</td>
<td>stochiometric</td>
<td>[12]</td>
</tr>
<tr>
<td>T3</td>
<td>CeMg3Zn5</td>
<td>Not known</td>
<td>Not known</td>
<td>stochiometric</td>
<td>[6]</td>
</tr>
<tr>
<td>T4</td>
<td>CeMg2Zn12</td>
<td>Not known</td>
<td>Not known</td>
<td>79–86</td>
<td>[12]</td>
</tr>
<tr>
<td>T5</td>
<td>CeMg2Zn2</td>
<td>Heusler-type alloy</td>
<td>cF4/Fm-3m</td>
<td>Not known</td>
<td>[14]</td>
</tr>
</tbody>
</table>

a The phases CeMg3 and t4 from the assessment of Kolitsch et al. [7] were simplified to one phase, CeMg5.
b The phases CeMg2 and t2 from the assessment of Kolitsch et al. [7] were simplified to one phase, CeMg12.
c The phase T4 is not modeled in this work, since no formation temperature is available for this phase. The phases T5, CeMgZn2, and Ce29Mg19Zn31 reported by Refs. [14,15] were not considered in this work, focusing on the Mg-rich region.
d At 350 °C.
thin-walled tantalum crucibles to avoid evaporation and oxidation. No reactions between the crucibles and the samples were observed.

After testing the tightness of the tantalum crucibles in a separate furnace, the samples 4, 6, 7, 9, and 10 were measured by DTA in a Netzsch DTA 404S apparatus. The heating/cooling rates applied were 1 K/min and 5 K/min. The overall uncertainty of DTA measurements was estimated to be less than ±4 K. The measurement of the phase transformation temperatures of the samples 1–3, 5 and 8 were carried out by differential scanning calorimetry (DSC) in a heat-flux cylindrical Calvet-type calorimetric system Multi HTC 96 (Setaram, Caluire, France). The equipment was calibrated using high purity Ag, Al, In, Mg and Pb. Helium at 2 l/h flow rate was applied as analysis chamber gas. The reference Ta-capsule was also sealed by welding, and a sapphire cylinder was used as reference material. The sapphire mass was 492.5 mg, which is a good balance for the heat capacity of the sample. The scanning program comprised cycles 100–850–100 °C at heating/cooling rates of 3 K/min and 5 K/min. The results are consistent and reproducible. The difference between heating and cooling peaks was below 4 K. The overall uncertainty of DSC measurements for temperature determination was estimated as ±3 K.

After DTA and DSC measurements, tantalum crucibles were cut to take out the samples, and the alloys were ground and polished immediately under ethanol to avoid oxidation. Then, the microstructures of the investigated alloys were observed by scanning electron microscopy (SEM), and the composition of the phases was determined by energy dispersive X-ray spectroscopy (EDS) analysis.

The compositions of the ten Mg–Zn–Ce ternary alloys, which were investigated in this work are shown in Table 2. The compositions are mainly chosen, using preliminary thermodynamic calculations, to measure ternary invariant but also liquidus temperatures. Especially the formation temperatures of the ternary phases, that is the thermal stability limit of the single phase region – irrespective of the formation reaction (congruent, peritectic...) – are not reported in the literature. Additionally, the ternary solubilities of binary phases are in the focus of the present work.

### 4. Development of the Mg–Zn–Ce ternary thermodynamic description

The thermodynamic parameters of the constituent binary systems are taken from the previous works of Cacciamani et al. [10] (Ce–Mg), Wang et al. [16] (Ce–Zn), and Agarwal et al. [11] (Mg–Zn) and these thermodynamic data sets are considered to be fairly satisfactory.

The Gibbs energy function, \( G_i^\theta(T) = G_i(T) - T \Delta_f \text{SER} \), for the element \( i \) (i= Ce, Mg, and Zn), in any phase \( \phi \) is described by the equation of the following form,

\[
G_i^\theta(T) = a + bT + cT^2 + dT^3 + eT^4 + fT^5 + gT^7 + hT^9,
\]

where \( H_i^{\text{SER}} \) is the molar enthalpy of the element \( i \) at 298.15 K and 1 bar in its standard element reference (SER) state, which is fcc for Ce, hcp for Mg, and hcp for Zn. \( T \) is the absolute temperature. The Gibbs energy function of the element \( i \) in its SER phase, \( \phi = \text{SER} \), is often denoted as \( G_i^{\text{SER}} \).

\[
G_i^{\text{SER}} = G_i^0 \text{SER}(T) \tag{2}
\]

The Gibbs energy functions for Ce, Mg and Zn are taken from the SGTE (Scientific Group Thermodata, Europe) compilation by Dinsdale [17].

The Gibbs energies for liquid, bcc, fcc, and hcp solution phases are described by the substitutional solution model as follows,

\[
G_i^\theta = \sum_i x_i^j G_i^\theta_j + RT \sum_i x_i^j \ln x_i^j + \sum_i x_i^j \sum_j x_j^i \ln x_j^i A_i^j + B_i^j x_i^j - \sum_i x_i^j \ln x_i^j \ln x_i^j, \tag{3}
\]

where \( x_i^j \) (\( y_i^j \)) represents the mole fraction of element \( i \) (\( j \)) with \( i \neq j \), \( R \) is the gas constant \( (R = 8.314 \text{ J/mole K}) \) and \( A_i^j \) and \( B_i^j \) are the Redlich-Kister parameter representing the interaction between elements \( i \) and \( j \) [18]. This interaction parameter, \( A_i^j \) may be linearly temperature dependent and is usually expressed as \( A_i^j = A_i^{j0} + B_i^{j0} T \). In eq. (3), the first and the second terms represent the Gibbs energies for mechanical mixture of elements and ideal mixing, respectively, and the third term corresponds to the excess Gibbs energy of mixing.

As mentioned in Section 2, the binary phases CeMg and CeZn form a continuous solid solution. This phase is modeled with two sublattices and a substitutitional solution on the second sublattice, Ce(1)[Mg,Zn]1. Similarly, the other ternary solution phases are modeled as Ce(1)[Mg,Zn]n. The Gibbs energy of the phase Ce(1)[Mg,Zn]n (per mole of atoms) is expressed in the Compound Energy Formalism (CEF) [19] by

\[
G_i^{\text{Ce}(1)[Mg,Zn]n} = \left. \frac{dG_i^{\theta}}{dT} \right|_{Mg} y_{Mg} + \left. \frac{dG_i^{\theta}}{dT} \right|_{Zn} y_{Zn} = \left. \frac{dG_i^{\theta}}{dT} \right|_{Ce} y_{Ce} + \left. \frac{dG_i^{\theta}}{dT} \right|_{Zn} y_{Zn} + \left. \frac{dG_i^{\theta}}{dT} \right|_{Mg} y_{Mg} (1 - \sum_{n} y_{Ce}^{(1)[Mg,Zn]n}) \tag{4}
\]
in which \( y_{\text{Mg}} \) and \( y_{\text{Zn}} \) are the site fractions of Mg and Zn on the second sublattice. \( \theta_{\text{Ce}(\text{Mg},\text{Zn})_{12}} \) and \( \phi_{\text{Ce}(\text{Mg},\text{Zn})_{12}} \) represents the interaction parameters, describing essentially the interaction within the sublattice, optimized in the present work. The parameters \( G_{\text{Ce:Mg}}^{0}\text{Ce:Mg} \) and \( G_{\text{Ce:Mg}}^{0}\text{Ce:Mg} \) are the Gibbs energies of the end-member phases. The end-member phases are formed when the second sublattice is occupied only by one kind of species; they can be either real or hypothetical. The Gibbs energies of CeMg and CeZn phases are real and taken directly from the binary description can be either real or hypothetical. The Gibbs energies of CeMg and CeZn phases are real and taken directly from the binary description.

The ternary phases T1, T2 and T3 are modeled as stoichiometric compounds referred to the stable elements in the system optimized in this work. The parameters \( A \) and \( B \) are the enthalpy and entropy of formation of T1. The software package “Pandant” [20] is utilized for all calculations and the thermodynamic parameters for the ternary system optimized in this work are listed in Table 3.

The phase T4 reported by Ref. [12] is not modeled in this work, since no formation temperature is available for this phase. The composition lies far outside the Mg-rich area which was focused on in this work. Also the phases CeMgZn2 (T5) and Ce27Mg18Zn81 reported by Refs. [14,15] were not considered in the present modeling.

5. Results and discussion

5.1. Experimental results

Temperatures obtained by thermal analysis as extracted from the DTA/DSC signals are given in Table 2. Each heating/cooling signal is based on at least 2 repeated cycles of a single sample. Invariant reactions were recognized from the peak shape. The interpretations of the experimental temperatures in the last two columns are based on the thermodynamic calculation. The corresponding microstructures of slowly solidified samples are given later and discussed in detail jointly with the calculated temperatures in vertical phase diagram sections.

For the Zn-rich samples 6, 7, 9 and 10 the interpretation of DTA signals proved to be difficult. The microstructure of the alloys solidified slowly under DTA condition shows local inhomogeneities of the formed phases. During polishing a powdering of Zn-rich samples was observed. Therefore no artifact-free photos of the solidified samples was observed. Therefore no artifact-free photos of the formed phases. During polishing a powdering of Zn-rich regions could be obtained.

5.2. Thermodynamic calculation of phase equilibria

Ternary parameters for the solid phases were adjusted on the one hand to meet the measured ternary invariant and liquidus temperatures. Additionally, the assessed data from literature for the homogeneity ranges of CeMg12 and CeMg and tie-line triangulation at 300 °C and own EDS measurements were used. The phases CeMg12 and \( t_2 \) from the assessment of Kolitsch et al. [7] were treated as one phase starting from the binary CeMg12 phase and dissolving up to 40 at.% Zn. The CeMg3 and \( t_4 \) phases from that assessment [7] were also unified into a single phase starting from the binary CeMg3 phase and dissolving as a line-compound up to 48 at.% Zn by substituting Mg. Although Mehl'nik et al. [6] described different crystal structures for the corresponding phases, we treat them as one phase. This not only simplifies the calculation, moreover [12] did not find any two-phase field between these phases and draw the CeMg12–\( t_2 \)-phase as one line and the CeMg3–\( t_4 \)-phase with dashed triangle in their figures. The maximum Zn-solubility of CeMg3 is set to the value reported by Ref. [12] (about 48 at.% Zn at 350 °C) and reproduced by the calculation as 48.1 at.% Zn (350 °C) and 47.9 at.% Zn (300 °C), respectively. The maximum Zn-solubility of CeMg12 is set to 40 at.% Zn at 300 °C based on our own samples. At 350 °C a value of 41.5 at.% Zn is calculated, which is lower than the value reported by Ref. [12] (about 49 at.% Zn).

The liquidus temperatures of these phases from the thermal analysis (DTA/DSC) are also used to determine the thermodynamic parameters. The Zn-solubilities of CeMg2 phase is measured and modeled at 1 at.% Zn, which gives an excellent fit to the measured liquidus temperature of sample #5, which is also very close to the transition reaction U1. The compositions of the ternary phase reported by Refs. [6,12] in Table 1 are confirmed for the phases T1, T2 and T3 by own EDS measurements. Their parameters are selected to reproduce both their solid state equilibria and the measured formation temperatures in Table 2: 735 °C for T1 in sample #9, 562 °C for T2 in sample #6, and 680 °C (P2) for T3 in sample #10. The invariant reaction at about 680 °C measured in samples #8 and #10 can be allocated to two different reactions, E2 and P2. These reactions are calculated closely spaced at 681 and 680 °C, respectively. Depending on the solidification path the alloy will pursue, P2 is passed under equilibrium condition but E2 under Scheil condition.

Fig. 1a shows the calculated liquidus projection of the Mg–Zn–Ce system based on the proposed thermodynamic description. It is dominated by the three binary Ce–Mg phase with large Zn-solvability: Ce(Mg,Zn), CeMg3 and CeMg12. Beside the numerous Ce–Zn phases in the Zn-rich part, larger primary fields are only visible for the (Mg) and the ternary T1 phase. The CeMg14 and especially CeMg12 phases show only small primary fields, which is also due to their small solid solubility of Zn. For the Ce-poor region of the liquidus projection a magnification of the Mg–Zn-rich edge is

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**Table 3**

Ternary thermodynamic parameters for the Mg–Zn–Ce.

<table>
<thead>
<tr>
<th>Phase name</th>
<th>Model</th>
<th>Parameters ([mol formula unit])</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeMg12</td>
<td>(Ce)  (Mg,Zn)12</td>
<td>( c_{\text{Ce}}^{0}\text{CeMg}) = -280000 + 80 T + ( c_{\text{Mg}}^{0}\text{CeMg} ) + 12( c_{\text{Zn}}^{0}\text{CeMg} )</td>
</tr>
<tr>
<td>CeMg3</td>
<td>(Ce) (Mg,Zn)3</td>
<td>( c_{\text{Mg}}^{0}\text{CeMg} ) = -110000 + 50 T</td>
</tr>
<tr>
<td>CeMg12</td>
<td>(Ce) (Mg,Zn)2</td>
<td>( c_{\text{Mg}}^{0}\text{CeMg} ) = -140000 + 35 T + ( c_{\text{Mg}}^{0}\text{CeMg} ) + 3( c_{\text{Zn}}^{0}\text{CeMg} )</td>
</tr>
<tr>
<td>T1</td>
<td>(Ce)(Mg)2/3(Zn)12</td>
<td>( c_{\text{Ce}}^{0}\text{T1} ) = -92000 + 94 T</td>
</tr>
<tr>
<td>T2</td>
<td>(Ce)(Zn)2/3(Zn)45</td>
<td>( c_{\text{Ce}}^{0}\text{T2} ) = -87000 + 27 T + ( c_{\text{Mg}}^{0}\text{T2} ) + 2( c_{\text{Zn}}^{0}\text{T2} )</td>
</tr>
<tr>
<td>T3</td>
<td>(Ce)(Zn)5</td>
<td>( c_{\text{Ce}}^{0}\text{T3} ) = -332000 + 10 T + 2( c_{\text{Mg}}^{0}\text{T3} ) + 7( c_{\text{Mg}}^{0}\text{T3} ) + 12( c_{\text{Zn}}^{0}\text{T3} )</td>
</tr>
</tbody>
</table>
shown in Fig. 1b. The small primary fields of T2 and MgZn2 and the locations of the invariant reactions U10, U11, U13, U14 and U15 can be seen. The calculated invariant reactions are given in Table 4. They also comprise six more invariant reactions below U15 in the temperature range 415.8–340.99 °C. These six reactions cannot be seen in Fig. 1b since their calculated liquid composition is even below 10^{-5} at.%. That is, they are entirely degenerate to the corresponding six invariant reactions of the binary Mg–Zn system.

Two of them, U17 and E3, are on the Zn-rich side and equilibrate with CeZn11, while the other four, U16, U18, U19 and E4, are on the Mg-rich side and equilibrate with T2. There are only two invariant reactions involving liquid and the (Mg) solid solution phase, U15 and U19, followed very closely by the deepest eutectic, E4.

The calculated isothermal section at 300 °C is given in Fig. 2. Three-phase equilibria proven by experimental data are marked with an asterisk. The Ce-solubility in (Mg), which is only 8 × 10^{-8} at.% Ce in the binary Mg–Ce, is further reduced by addition of Zn to 0.02 × 10^{-8} at.% Ce at the three-phase point (Mg) + CeMg12 + T2. This edge is at 1.3 at.% Zn (3.4 wt.% Zn), which means that (Mg) with less Zn is saturated with CeMg12 while beyond that (Mg) + T2 prevails up to the limit of 2.4 at.% Zn in (Mg) at the (Mg) + T2 + MgZn equilibrium.

The phase diagram section calculated at constant 85 at.% Mg, including the DSC signals from samples #1–#3, is shown in Fig. 3. The strong heating and cooling signal shown by sample #1 at the invariant reaction U8 is most decisive. Also the liquidus temperatures of samples #1 and #2 are well reproduced by the calculation while the liquidus temperature of sample #3, calculated at 639 °C, could not be detected.

![Figure 1](image1.png)

**Fig. 1.** (a) Calculated liquidus projection of the Mg–Zn–Ce system; superimposed are the present sample compositions. (b) Magnified Mg–Zn-rich edge of (a).
5.3. Solidification paths and microstructures of Mg-rich alloys

Microstructures of the samples in the Mg-rich corner were investigated in detail. Samples #1–#3 in fact exhibit the phase sequence and primary crystallizing phases given by the calculation in Fig. 3. The back-scattered electron micrograph (BSE) of sample #1 (Ce13–Mg85–Zn2) solidified at 5 K min\(^{-1}\) is shown in Fig. 4. Primary crystallized dendrites of CeMg\(_3\) (with 3 at.% Zn-solubility) are enlaced by secondary CeMg\(_{12}\) and some Ce\(_5\)Mg\(_{41}\). This microstructure is confirmed by the calculated invariant reaction U8: \(L + \text{CeMg}_3 \rightarrow \text{CeMg}_{12} + \text{Ce}_5\text{Mg}_{41}\) at 617 °C; the calculated phase amounts reveal that this is almost a eutectic reaction (\(L / \text{CeMg}_{12} + \text{Ce}_5\text{Mg}_{41}\)) with only a negligible amount of CeMg\(_3\) being consumed. This finding is further corroborated by the strong thermal signals detected at that temperature by DSC in the same sample, see Table 2 and Fig. 3.

In sample #2 (Ce10–Mg85–Zn5) the microstructure in Fig. 5 reveals again primary dendrites of CeMg\(_3\) (with 9 at.% Zn-solubility) with subsequent crystallization of CeMg\(_{12}\) (with 3 at.% Zn-solubility). This is entirely consistent with the calculated two-phase equilibrium solidus structure of this sample.

The phase diagram section, Fig. 3, indicates that the primary phase changes from CeMg\(_3\) to CeMg\(_{12}\) beyond 6.5 at.% Zn. Indeed, sample #3 (Ce5–Mg85–Zn10) shows primary crystallization of the phase CeMg\(_{12}\) (with 15 at.% Zn-solubility) in Fig. 6. The secondary phase is (Mg) with 1 at.% Zn dissolved and no measurable content of Ce, using SEM/EDS.

Finally the electron micrograph (BSE) of sample #5 (Ce42–Mg56–Zn2) in Fig. 7 shows the primary dendrites of CeMg\(_3\) (with 1 at.% Zn-solubility) with secondary Ce(Mg,Zn). The calculation
Termination of ternary solidification involving (Mg) and secondary phases under equilibrium conditions is given by the reaction L + (Mg) → Mg₂Zn₃ + T₂ (U19) at 341.02 °C. If this transition-type reaction does not go to completion, the final ternary eutectic, L + MgZn₁ + MgZn₃ + T₂ (E₄) at 340.99 °C may be reached. Both invariant reactions are calculated at negligible composition of Ce in the liquid (<10⁻⁵ at.% Ce), and consequently only a negligible amount of T₂ forms and the temperatures are virtually identical (within less than 0.01 K) to those of the corresponding binary Mg–Zn reactions. Therefore, the ternary eutectic temperature reported by Ref. [5] at 342 ± 1 °C may be interpreted only as verification that the invariant reaction E₄ calculated at 341 °C is indeed very close to the binary one. On the same grounds the calculated liquid composition of E₄ (29.0 at.% Zn) is virtually identical to the adjacent binary one. The difference to the reported composition of 25.9 at.% Zn, given by Ref. [5], cannot be due to a shift of the eutectic trough in the ternary. It is probably caused by the experimental uncertainty related to the binary value that is calculated from here lately the thermodynamic assessment of the Mg–Zn system [11].

6. Conclusion

On the experimental side our work focuses on the Mg-rich part of the ternary system. Sample compositions were chosen from 34 to 85 at.% Mg from preliminary calculations indicating these to be most decisive for determination of thermodynamic parameters and verification of invariant liquidus reactions and solid state equilibria up to pure magnesium. The final thermodynamic modeling, however, covers the entire range of the Mg–Zn–Ce system. The Zn–Ce-rich region of the Mg–Zn–Ce system is calculated based on the extrapolation from the thermodynamic descriptions of the edge binary phases. Additional experimental data particularly in the Zn-rich corner are required to establish the phase equilibria of this ternary system completely.

All solid solubilities of Zn in Mg–Ce intermetallic phases are due to substitutional exchange of Mg by Zn. The large Zn-solubilities of the CeMg₁₂ and CeMg₃ phases are treated as two single phases (CeMg₁₂ up to 40 at.% Zn and CeMg₃ up to 48 at.% Zn at 300 °C). This might be considered as simplification since [6] described different crystal structures and two-phase field between these phases. However, these observations could not be confirmed by Ref. [12] and in this work.

It is remarkable that extremely small solubilities of Ce in Mg–Zn liquid alloys are observed beyond which Ce-containing intermetallic phases precipitate. In the present work only as verification that the invariant reaction E₄ calculated at 341 °C is indeed very close to the binary one. On the same grounds the calculated liquid composition of E₄ (29.0 at.% Zn) is virtually identical to the adjacent binary one. The difference to the reported composition of 25.9 at.% Zn, given by Ref. [5], cannot be due to a shift of the eutectic trough in the ternary. It is probably caused by the experimental uncertainty related to the binary value that is calculated here lately the thermodynamic assessment of the Mg–Zn system [11].

References

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