Title: Microstructure Simulation for Solidification of Magnesium–Zinc–Yttrium Alloy by Multi-phase-field Method Coupled with CALPHAD Database

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1. Introduction

In order to realize high strength of the Mg–Zn–Y alloy using the precipitation hardening by intermediate phases (the X (Mg₁₂Zn₁₋₁Y₁) phase and W (Mg₃Zn₃₋₂Y₂) phase) in Mg solid solution (the α phase), a control of the precipitation formation is required in order to obtain good mechanical properties. In this study, experimental observations of microstructures of the Mg–Zn–Y system have been performed. Then we have focused on developing CALPHAD (CALculation of PHAse Diagrams) thermodynamic database to obtain the Gibbs free energy to draw phase diagram of the system and to understand the precipitation behavior of the intermediate phases. In order to understand the formation of microstructures, we have performed simulations of solidification of the alloy with use of multi-phase-field method. At the beginning the solidification process has been calculated for a large area, then the zoomed in region of the lamellar structures of the α phase and the W phase have been analyzed. Resulting optimum lamellar spacing reproduce experimental one well.

KEY WORDS: magnesium alloy; CALPHAD; solidification; phase field method.

2. Experimental Procedure

2.1. Sample Preparations and Observations

A master ingot of the 97.0Mg–1.3Zn–1.6Y (at%) alloy was prepared from high-purity raw materials; 99.95% Mg bar, 99.5% Zn sheet and small pieces of 99.99% Y. These metals were melted in a 31 mm diameter graphite crucible using a high-frequency induction furnace under high-purity argon atmosphere, and the as-cast ingot size was 20 mm thick × 50 mm wide × 52 mm high (mm). The sample for examination of the liquid–solid coexistence region was cut into 20 mm thick × 4 mm square (mm) piece and was encapsulated in lidded 6 mm diameter graphite crucible, in consideration of the dangers of molten Mg alloy during water-quenching. And again, a sample for the examination of the liquid–solid coexistence region was encapsulated in quartz tube with high-purity argon gas for an isothermal heat treatment. The isothermal heat treatment was carried out using a vertical furnace.
3. Calculation Methods

The assessment of CALPHAD thermodynamic database based on experimental data was performed with ThermoCalc software package. Then the multi-phase-field simulations coupled with the revised CALPHAD thermodynamic database were carried out with MICRESS software package.

3.1. CALPHAD Technique

Phase equilibrium is able to be calculated by means of CALPHAD approach by calculating minimization of the Gibbs free energy for many phases. The total Gibbs free energy of structure \( \phi \) can be described as,

\[
G^\phi_w = \sum_i x_i^0 G_i^\phi + RT \sum_i x_i \ln x_i + \phi^0 G^\phi_w \tag{1}
\]

where \( x_i \), \( G_i^\phi \), \( R \) and \( T \) are the mole fraction of element \( i \), the Gibbs free energy of \( i \) with structure \( \phi \), the gas constant, and the temperature in Kelvin, respectively. The first term on the right hand side is a linear combination of the pure Gibbs free energy. The second term is the ideal entropy of mixing. The third term is the excess Gibbs energy which is given by the following equation in an \( A-B \) system,

\[
\phi^0 G^\phi_w = x_A x_B L_{A,B}^\phi \tag{2}
\]

where \( L_{A,B}^\phi \) is the interaction parameter between the elements \( A-B \) in \( \phi \) phase. It is written in the form of Redlich–Kister polynomials,

\[
L_{A,B}^\phi = \sum_{v=0}^{n} v L_{A,B}^\phi (x_A - x_B)^v \tag{3}
\]

where \( n \) is taken as an arbitrary degree, \( v L_{A,B}^\phi \) depending on temperature, which is described as follows,

\[
v L_{A,B}^\phi = v a + v b \times T + \cdots \tag{4}
\]

where \( v a, v b \) are constants at the degree is \( v \), which should be determined to yield experimental results.

3.2. Multi-phase-field Approach

The phase field modeling is well described in Ref. 10). The pair-wise interaction of phase \( i \) with all other phases \( j \) in case of a double obstacle potential are considered. The numerical methods of multi-phase-field approach coupled with CALPHAD thermodynamic database are summarized. The microstructure evolves according to a decrease of total free energy. A set of multi-phase field equations could be derived based on thermodynamic principles,

\[
\frac{d \phi_i}{dt} = \sum_j \mu_{ij} \left( \phi_i \nabla^2 \phi_j - \phi_j \nabla^2 \phi_i - \frac{\pi^2}{\eta \eta_{ij}} (\phi_i - \phi_j) \right) + \frac{\pi}{\eta_{ij}} \phi_i \phi_j \Delta G_{ij} \tag{5}
\]

where \( \phi \) denotes phase field parameter, \( \eta \) is interface thickness, \( \Delta G \) is the driving force, \( \sigma \) is interface energy and \( \mu \) is interface mobility.

The expression of the time evolution of concentration field is described by diffusion equation,

\[
\frac{D}{\eta} \frac{\partial c}{\partial t} = \sum_i \phi \phi_i \nabla c \tag{6}
\]

where \( D \) is interdiffusion matrix.

4. Results and Discussion

4.1. Experimental Results

The backscattered electron image (BEI) of the casted Mg alloy is shown in Fig. 1. Dark region is the \( \alpha \) phase, bright area is a region of coexistence of the \( X \) phase and lamellar (the \( \alpha \) phase and the \( W \) phase) structure.

A magnified image of Fig. 1 is shown in Fig. 2. The coexistence of the \( \alpha \) phase and the plate-like \( X \) phase is clearly observed.

4.2. CALPHAD Thermodynamic Parameters

In the calculations we used previous reported thermodynamic parameters based on first-principles calculations and the thermodynamic data for the intermetallic com-

Fig. 1. The backscattered electron image observed by EPMA for the Mg-Zn-Y alloy.

Fig. 2. The coexistence of the \( \alpha \) phase and the plate-like \( X \) phase.
pounds of the $X$, $W$ and $I$ phases are based on the another literature data. However the sublattice model for the $W$ phase was rebuild based on the experimental results. The $W$ phase normally denotes the Mg$_3$Zn$_2$Y$_3$ with L$_2^1$ crystal structure. Though the previous CALPHAD thermodynamic parameter has a 20 at% Y constant line, one of authors have revealed that the crystal structure of the $W$ phase is basically L$_2^1$ which has a 25 at% Y constant line and in this study sublattice model of the phase are modeled based on L$_2^1$ crystal structure and this phase is treated as a non-stoichiometric compound. Therefore we revised a model that 25 at% Y constant line and Mg and Zn solubility are taken into account.

The Mg$_{12}$Zn$_1$Y$_1$ is denoted by the $X$ phase with a long periodic stacking ordered structure (LPSO), which contributes to the high mechanical strength. The thermodynamic model of the $X$ phase is build as a stoichiometric compound.

4.3. The Phase Field Modeling

We performed two types of phase field simulations, one is macro area analysis to understand overall picture of the microstructures, and another is micro scale area analysis in order to understand the growth of the lamellar structures.

4.3.1. Diffusivities and Interface Energies

Diffusivity data of the elements in the $\alpha$ phase were taken from MOB2 kinetic database. Because the diffusivity data of the Y in the $\alpha$ phase were not available in the literature, the diffusivity of the La in the $\alpha$ phase was applied as substitutes.

The interface energies were obtained by empirical calculations or experimental results. An interface energy $\sigma$ between $\alpha$ phases was obtained by following equation:

$$\sigma_{\alpha-\alpha} = \frac{3}{2} \left(\frac{N_A}{V_m}\right)^{2/3} \left(\frac{\Delta H_m}{N_A}\right)$$

where $N_A$ is the Avogadro number, $V_m$ molar volume, $H_m$ latent heat of melting.

An interface energy between the $\alpha$ phase and the $X$ phase was obtained from a dihedral angle between the $\alpha$ phase and the $X$ phase at the triple point at 723 K shown as following expression:

$$\sigma_{\alpha-X} = \sigma_{\alpha-\alpha} \frac{1}{2\cos(\theta/2)}$$

where $\theta$ is a dihedral angle of 85° between the $\alpha$ and the $X$ at the triple point of $\alpha-\alpha-X$ at 723 K based on our experiments.

<table>
<thead>
<tr>
<th>Interface</th>
<th>Energy [J/m$^2$]</th>
<th>$\epsilon$</th>
<th>$k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_{\text{liquid}}$</td>
<td>1.0×10$^{-1}$</td>
<td>0.0057</td>
<td>6$^{(20)}$</td>
</tr>
<tr>
<td>$\sigma_{\text{liquid}}$</td>
<td>1.2×10$^{-1}$</td>
<td>0.0067</td>
<td>2</td>
</tr>
<tr>
<td>$\sigma_{\text{liquid}}$</td>
<td>1.2×10$^{-1}$</td>
<td>0.0133</td>
<td>4</td>
</tr>
<tr>
<td>$\sigma_{\alpha-\alpha}$</td>
<td>2.2×10$^{-1}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\sigma_{\alpha-X}$</td>
<td>1.5×10$^{-1}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\sigma_{\alpha-W}$</td>
<td>1.5×10$^{-1}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2. The interface energy $\sigma_{ij}$ [J/m$^2$] between $i$ and $j$ phase applied in the simulations. The $\epsilon$ and $k$ are anisotropy parameters in interface energy and mobility, respectively. An anisotropy is expressed as $\sigma(\theta) = (\cos^2\theta + 0.1\sin^2\theta)\sigma_{ij}(1 + \epsilon \cos(k\theta))$.

Table 1. The re-evaluated thermodynamic parameters for the intermetallic compounds. The thermodynamics parameters for other phases were applied with another Ref. 7). The same sublattice models in Ref. 5) were used except for the sublattice for the $W$ phase, (Mg)$_{0.25}$(Y)$_{0.25}$(Mg,Zn)$_{0.5}$.
Fig. 3. The ternary isothermal phase diagram of the Mg–Zn–Y system at 833 K (top: overall phase diagram, bottom: magnified image at Mg-rich region). The black solid circles indicate the stoichiometric compounds of the $X$ phase. The bold solid line indicates the non-stoichiometric compounds of the $W$ and $I$ phase.

Fig. 4. The liquidus surface projection of the Mg–Zn–Y system. The red lines in the figure are monovariant lines, and the letters on red lines are $Z$ values shown above equation expressing temperature in Kelvin.

Fig. 5. The microstructure calculated with MICRESS software. The green rectangle in the picture of 6.5 s is a reference area to evaluate the compositions of the liquid phase, which is used in the zoomed in analysis.

Fig. 6. The calculation model and boundary conditions.

Fig. 7. The bright field image observed by TEM for lamellar microstructure.

Fig. 9. The stable lamellar growth at 0.050 s. In case that the initial interval length of the $W$ phase, $b$, is larger than 0.3 μm, the lamellar spacings keep the initial interval length.

Fig. 10. The microstructure calculated by MICRESS software (left: the overall picture for the analysis) (right, top: final solidificated areas, after 10 s) (right, bottom: initial stage of the solidification, after 0.05 s).
The interface energies are listed in Table 2. The \( k \) for \( \sigma_{\text{liquid}-W} \) was determined by the assumption that the \( W \) phase has cubic crystal structure and the same value for the interface energy for \( \sigma_{\alpha-X} \) and \( \sigma_{\alpha-W} \) were applied.

4.3.2. Formation of Microstructure
Solidification Process

The simulation was started from a liquid state and then the \( \alpha \) phase was nucleated in the liquid phase. The multiphase-field simulation conditions are listed in Table 3.

As cooling down the temperature the particles of the \( \alpha \) and \( W \) phase were appeared in the liquid phase, before the \( X \) phase appeared as shown in Fig. 5, which is in good agreement with the experimental observations shown in Fig. 2. The solidification path derived from phase field calculation was the same as that from CALPHAD approach.

Then particular focus is placed on the formation behavior of the \( X \) phase. The microstructure formation that liquid phase was changing into the \( X \) phase.

4.3.3. Multi Phase Field Modeling
Zoomed in Analysis

As results of experimental measurement, a strong anisotropy of the \( X \) phase has been observed on basal plane of matrix shown in Fig. 2. Thus the initial liquid composition of Mg–1.3at\%Zn–1.6at\%Y alloy were set for the analysis of zoomed in area (the value in the green box in Fig. 2 at 6.5 s (833 K)). The same amount of cooling rate compared to experimental conditions has been obtained by the heat extraction rate condition for the simulations. The calculation conditions are listed in Table 4.

Lamellar microstructures consisting of the \( \alpha \) phase and the \( W \) phase formed from a liquid phase were observed in the experiments as shown in Fig. 7.

The composition of the liquid phase for lamellar microstructure simulation was evaluated from the solidification simulation. The liquid composition at 833 K in the simulation was started from a liquid state and then the \( W \) phase was nucleated in the liquid phase. The multi-phase-field simulation conditions are listed in Table 3.

The size dependency of growth rate of the \( W \) phase has been evaluated by means of experimental, CALPHAD technique and multi-phase-field method.

The experimental measurement of the solubility of the Mg and Zn elements in the \( W \) phase has been carried out, and calibrated for the CALPHAD modeling to implement the thermodynamic model into the multi-phase-field method. The microstructures obtained by the multi-phase-field method coupled with revised CALPHAD thermodynamic database well explain the experimental measurements in the Mg–Zn–Y system. A result for lamellar microstructure simulation by the initial \( W \) phase interval of 0.2 \( \mu \)m has been evaluated by means of experimental, CALPHAD technique and multi-phase-field method.

5. Conclusions

The microstructure formation of the Mg–Zn–Y system has been evaluated by means of experimental, CALPHAD technique and multi-phase-field method.

The experimental measurement of the solubility of the Mg and Zn elements in the \( W \) phase has been carried out, and calibrated for the CALPHAD modeling to implement the thermodynamic model into the multi-phase-field method. The microstructures obtained by the multi-phase-field method coupled with revised CALPHAD thermodynamic database well explain the experimental measurements in the Mg–Zn–Y system. A result for lamellar microstructure simulation by the initial \( W \) phase interval of 0.2 \( \mu \)m, the lamellar spacing in the simulation is about 0.33 \( \mu \)m, and experimental one is about 0.32 \( \mu \)m, which is in good agreement. The optimum lamellar spacing which gives the maximum steady growth velocity in the lamellar
microstructure simulation quantitatively agrees with the lamellar spacing obtained by the experimental measurement.

REFERENCES