Simulation of the Si Precipitation Process in Mg₂Si Using a Phase-Field Kinetic Model

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The Si precipitation process in an Mg₂Si matrix has been simulated by the phase-field kinetic model, considering the eigen strain at the interface between precipitates and the matrix. We observed that the shape of the precipitate changed during the course of heat treatment from circular to lenticular. As the Si precipitate grew larger, the adjacent precipitate aggregated to form a lamellar microstructure. This microstructure is suitable for thermo-electric materials because the scattering of phonons will frequently occur at the interface between the Si precipitates and the Mg₂Si matrix. Our present simulation suggests drastic improvements of thermo-electric properties of this type of material are possible due to the eigen strain. [doi:10.2320/matertrans.M2015479]

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1. Introduction

The conversion of waste heat into electrical energy plays a key role in current engineering challenges to develop alternative energy technologies that reduce dependence on fossil fuels and lower greenhouse gas emissions. One factor driving the interest in studying nano-composite thermo-electric (TE) materials is the need for safe, clean, and sustainable energy sources. Silicon has been attracting much attention because of its abundance in the earth's crust and its excellent TE properties. Nano-silicon and silicide materials have become competitive TE materials.¹⁾ Mg₂Si has excellent TE properties and it is the only stable compound in the Mg–Si binary system. Therefore, understanding the generation and growth processes of Mg₂Si TE material precipitates is an important step in the study of thermal power systems.

A phase-field kinetic model can be used for simulating phase transition making it a very effective tool in material simulation. The morphology of second phase precipitation in many materials and alloys has been studied.²⁾ For example, the phase-field model was used to simulate martensitic transformations in the polycrystalline phase based on the elasticity theory of Khachaturyan.³⁾

In this study, we simulated generation and growth processes of Si precipitates in Mg₂Si matrix using a phase-field kinetic model. The free energy of the system was expressed as the summation of Landau-type chemical free energy, gradient energy and elastic energy.⁴⁾ Time development equations with respect to a concentration field and the structural order parameter variables were deduced by the variation principle and solved numerically to simulate the microstructure evolution. We confirmed that a single Si particle changed its shape from circular to lenticular under the influence of the eigen strain of Si. We also simulated the microstructure evolution and concluded that finely dispersed Si nano-precipitates would improve the performance of TE materials.

2. Phase-Field Kinetic Model

In the present study, the phase-field simulation was conducted in a 2D space by using two structural field variables, s_1 and s_2 . Both the diffusion and precipitation of Si were considered. The time evolution of a microstructure was determined by solving the time dependent Ginzburg-Landau equations for $s_i(r, t)$, ($i = 1, 2$) and the Cahn-Hilliard diffusion equation for $c(r, t)$ as follows^{5,6)}

$$\frac{\partial c(r, t)}{\partial t} = M \nabla^2 \frac{\delta G_{\text{sys}}}{\delta c(r, t)} \quad (1)$$

$$\frac{\partial s_i(r, t)}{\partial t} = -L_p \frac{\delta G_{\text{sys}}}{\delta s_i(r, t)} \quad (2)$$

where M and L_p are kinetic coefficients characterizing structural relaxation and surface diffusional mobility and G_{sys} is the free energy of the system. In order to solve the time evolution, the free energy of the system must be strictly defined. Details are given in the next section.

2.1 Free energy of the system

The free energy of the system may be expressed as

$$G_{\text{sys}} = G_{\text{chem}} + G_{\text{grad}} + G_{\text{str}} \quad (3)$$

where G_{chem} is the chemical free energy, G_{grad} is the gradient energy, and G_{str} is the elastic strain energy which is discussed in section 2.1.3 within the framework of the theory of elasticity.

2.1.1 Chemical free energy

In the phase-field model, a microstructure is described by a set of spatially dependent field variables. The structure and composition of the precipitate phase (Si) and the parent phase (Mg₂Si) can be studied. These different characteristics can be described by using a composition field variable $c(r, t)$, and the occurrence probability of precipitates, $s_i(r, t)$, where the subscript i ($i = 1, 2$) represents the different kinds of orientation to the matrix.

The growth of Si precipitates is driven by the difference in

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chemical free energy and the volume fraction of Si precipitate. In the present model, we described the chemical free energy density approximately using a Landau-type of free energy polynomial as²⁾

$$G_{\text{chem}}(c, s_1, s_2) = \frac{A_1}{2}(c - C_1)^2 + \frac{A_2}{2}(c - C_2)(s_1^2 + s_2^2) - \frac{A_3}{2}(s_1^4 + s_2^4) + \frac{A_4}{2}(s_1^6 + s_2^6) + A_5 s_1^2 s_2^2 + A_6(s_1^4 s_2^2 + s_1^2 s_2^4) \quad (4)$$

where C_1 and C_2 are the constants close to Si concentration in the Mg₂Si matrix and of the Si phase, respectively, and their values were chosen as $C_1 = 0.33$ and $C_2 = 1$. For the present case of Si precipitation in the matrix, the coefficients in eq. (4) were chosen as $A_1 = 148$, $A_2 = -8$, $A_3 = 118.5$, $A_4 = 2.7$, $A_5 = A_6 = 0.2$. The process to determine these parameters is as follows.

The temperature 973 K was chosen because an actual experiment has already been done at this temperature.¹⁾ At this temperature, the Gibbs free energy of pure Mg₂Si and Si was calculated by utilizing Gibbs energy function for pure substance and we found that $\Delta(G_{\text{Si}} - G_{\text{Mg}_2\text{Si}}) = 5493 \text{ J/mol}$.^{7,8)} The unknown Gibbs free energies of the Mg₂Si and Si phases as a function of silicon concentration, c , should have the minimum at $c = 0.333$ and $c = 1$, respectively. For the Gibbs free energies of the Mg₂Si and Si phases as a function of silicon concentration, the two simple quadratic forms, which have the energy difference $\Delta(G_{\text{Si}} - G_{\text{Mg}_2\text{Si}}) = 5493 \text{ J/mol}$ and common tangent at $c = 0.333$ and $c = 1$, were assumed. The parameters in eq. (4) were determined to reproduce the quadratic Gibbs free energies of the Mg₂Si and Si phases as a function of silicon concentration by using a mathematical fitting tool.

From eq. (4), the variation of G_{chem} with respect to s_i is given by

$$\frac{\delta G_{\text{chem}}}{\delta s_i} = s_i \{A_2(c - C_2) - A_3 s_i^2 + A_4 s_i^4 + 2A_5 s_j^2 + 2A_6(2s_i^2 s_j^2 + s_i^4)\} \quad (i \neq j). \quad (5)$$

2.1.2 Gradient energy

According to the Spinodal decomposition theory, the gradient energy density term, G_{grad} can be expressed as^{9,10)}

$$G_{\text{grad}} = \frac{1}{2} K_s \int_{\text{r}} [(\nabla s_1)^2 + (\nabla s_2)^2] dr + \frac{1}{2} K_c \int_{\text{r}} (\nabla c)^2 dr \quad (6)$$

where K_s , K_c is the coefficient of the gradient energy. The variation of G_{grad} with respect to s_i and c is given by

$$\frac{\delta G_{\text{grad}}}{\delta s_1(\text{r})} = -K_s \nabla^2 s_1, \quad \frac{\delta G_{\text{grad}}}{\delta s_2(\text{r})} = -K_s \nabla^2 s_2, \quad \frac{\delta G_{\text{grad}}}{\delta c(\text{r})} = -K_c \nabla^2 c. \quad (7)$$

2.1.3 Elastic energy

The elastic energy is caused by lattice mismatch between the Si-precipitate and Mg₂Si matrix. According to Khachaturyan's theory, the elastic energy can be expressed as follows:

$$G_{\text{st}} = \frac{1}{2} \int_{\text{r}} c_{ijkl}(\text{r}, t) \{ \varepsilon_{ij}^c(\text{r}, t) - \varepsilon_{ij}^0(\text{r}, t) \} \{ \varepsilon_{kl}^c(\text{r}, t) - \varepsilon_{kl}^0(\text{r}, t) \} dr \quad (8)$$

$$\varepsilon_{ij}^c(\text{r}, t) = \varepsilon_{ij}^{-c}(\text{t}) + e_{ij}^c(\text{r}, t) \quad (9)$$

where $c_{ijkl}(\text{r}, t)$ is elastic constant, $\varepsilon_{ij}^c(\text{r}, t)$ is total strain, and $\varepsilon_{ij}^0(\text{r}, t)$ is eigen strain. The spatial mean $\varepsilon_{ij}^{-c}(\text{t})$ and variation $e_{ij}^c(\text{r}, t)$ are included in the total strain. The boundary condition is stress free, so that the system can expand and contract. Then the spatial mean of strain tensor ε_{ij}^{-c} can be obtained from

$$\frac{\delta G_{\text{str}}}{\delta \varepsilon_{ij}^{-c}} = 0. \quad (10)$$

The eigen strain is given by

$$\varepsilon_{ij}^0(\text{r}, t) = \varepsilon_{ij}^0(1) s_1^2(\text{r}, t) + \varepsilon_{ij}^0(2) s_2^2(\text{r}, t) \quad (11)$$

where the eigen strain tensor matrix can be represented as

$$\varepsilon_{ij}^0(1) = \begin{bmatrix} -0.00971 & 0 \\ 0 & 0.0396 \end{bmatrix} \quad \varepsilon_{ij}^0(2) = \begin{bmatrix} 0.0396 & 0 \\ 0 & -0.00971 \end{bmatrix} \quad (12)$$

from the experimental observation of semi-coherent interface between Si and Mg₂Si in the form of a thin film (see Fig. 3 in Ref. 11)). According to the observation, the semi-coherent interface was such that Si (111) // Mg₂Si (110), Si [1 $\bar{1}$ 0] // Mg₂Si [1 $\bar{1}$ 0] and Si [11 $\bar{2}$] // Mg₂Si [00 $\bar{1}$]. In addition, every seven Si {2 $\bar{2}$ 0} atomic planes, there were six Mg₂Si {2 $\bar{2}$ 0} planes. From the lattice parameters of Mg₂Si ($a = 0.635 \text{ nm}$) and Si ($a = 0.539 \text{ nm}$), we estimated the mismatch strains at the interface as -0.971% in the Si [1 $\bar{1}$ 0] direction and 3.96% in the Si [11 $\bar{2}$] direction. Then we set the x and y directions as the Si [1 $\bar{1}$ 0] // Mg₂Si [1 $\bar{1}$ 0] and Si [11 $\bar{2}$] // Mg₂Si [00 $\bar{1}$] directions, respectively. The values of the elastic constants of Mg₂Si are $C_{11} = 121.37 \text{ GPa}$, $C_{12} = 20.28 \text{ GPa}$, and $C_{44} = 46.78 \text{ GPa}$ for the normal crystal orientation.¹²⁾ By the transformation from the normal orientation to the present orientation, we used the values as $C_{11} = 138 \text{ GPa}$, $C_{12} = 61 \text{ GPa}$, and $C_{44} = 116 \text{ GPa}$. In the present study, we used only the elastic constants of Mg₂Si to simplify the calculation; this approach has been used in the case of the precipitation of θ' phase in Al matrix⁴⁾. Si precipitate is harder than Mg₂Si matrix by about 20–30%. According to the simulation of Hu *et al.*¹³⁾, such difference does not alter the obtained conclusion (see Fig. 12 in Ref. 13)). From eq. (8), the variation of G_{str} with respect to s_p is given by

$$\frac{\delta G_{\text{str}}}{\delta s_p} = 2s_p(c_{ijkl}(\text{r}, t)\varepsilon_{ij}^0(\text{p})\varepsilon_{kl}^0(\text{r}, t) - c_{ijkl}(\text{r}, t)\varepsilon_{kl}^0(\text{p})\varepsilon_{ij}^c(\text{r}, t)) \quad (\text{p} = 1, 2). \quad (13)$$

2.1.4 Simulation conditions

We performed the simulations in a 2D space. A 256×256 uniform square grid was used to discretize spatially the field equations. Periodic boundary conditions are applied along the both lateral direction. The gradient coefficients was set to be $K_s = K_c = 1.5 \times 10^{-5} \text{ J} \cdot \text{m}^2/\text{mol}$. The kinetic coefficients in eqs. (1) and (2) were assumed to be constant. M and L_p were chosen to be 0.4. The initial value of $c(\text{r}, t)$ was set to be 0.67. That is, the initial state has the uniform Si concentration but consists of the two phases of Mg₂Si (matrix) and Si (seeds). As the trigger of the precipitation process, the values of s_1 within the seeds were all set to be 1. The numerical calculation was performed in the dimension-less unit for time and length. The actual time and length can be estimated by com-

paring to an actual experiment as shown in the discussion. As the seeds of Si precipitates, 98 circular areas, with a radial 3.5 grid, were randomly chosen and the values of s_1 within the seeds were all set to be 1. It may seem to be curious why only the values of s_1 were set. Our purpose is to obtain a lamellar microstructure in which the scattering of phonons will occur frequently at the interface between the Si precipitates and Mg_2Si matrix for high performance TE material. If s_1 and s_2 were both set to be 1 as nucleus, our preliminary simulation showed that they interrupt each other during the growth process, leading to an undesirable structure. However, in the case of mixed nucleus of s_1 and s_2 , the growth of only s_1 variant can be achieved by utilizing unidirectional stress on the specimen as shown in Ref. 4), that a supersaturated Al-Cu system under unidirectional compressive stress gives the preferential growth of θ' precipitation along the direction of applied stress. Taking into account of this effect, we have chosen only s_1 as nucleus for the first step to the research. The simulation of the case of mixed nucleus of s_1 and s_2 under unidirectional stress will be performed in the subsequent research.

3. Results and Discussion

Figure 1 shows the microstructure evolution of Si precipitates in Mg_2Si matrix: (a) at the 120 time step, (b) at the 1200 time step

time step, (c) at the 3600 time step and (d) at the 6000 time step. We simulated the precipitation process of pure Si in Mg_2Si matrix, and for the Si precipitation, s_1 were set to be 1, while for Mg_2Si matrix, s_1 were set to be 0. The inserted color scale represents the value of s_1 which represents the occurrence probability of Si precipitates. That means, the locations colored by red ($s_1 = 1$) are occupied by pure Si precipitates, and those colored by blue Mg_2Si matrix. The precipitate shape clearly changed during the course of heat treatment from that of circular to lenticular. As the Si precipitate grew larger, adjacent precipitates aggregated to form lenticular shaped precipitates. This was mainly due to the fact that the elastic energy is a crucial factor to decide the morphology of the Si precipitates.

From Fig. 2 we can see how a single circular Si precipitate changed its shape under the influence of eigen strain by comparing it to the case without eigen strain. Figure 2(c) shows the shape change of the Si precipitate from the circular shape presented in Fig. 2(a) to the lenticular shape under the influence of eigen strain, while the case without eigen strain showed no change in shape (Fig. 2(b)). The antisymmetric shape for the case with eigen strain was due to the anisotropy of the elastic energy.

In an actual experiment, Ikeda *et al.* have formed the nano-composite structure of the Mg_2Si -Si system and confirmed

Fig. 1 Microstructural evolution of the Mg_2Si -Si binary system: (a) at the 120 time step, (b) at the 1200 time step, (c) at the 3600 time step and (d) at the 6000 time step. The inserted color scale represents the value of s_1 which represents the occurrence probability of Si precipitates. That means, the locations colored by red ($s_1 = 1$) are occupied by pure Si precipitates, those colored by blue Mg_2Si matrix.

Fig. 2 Time change of the shape of a Si precipitate from a circular one: (a) at the 0 time step, (b) at the 6000 time steps without eigen strain and (c) at the 6000 time steps with eigen strain. The inserted color scale is the same as in Fig. 1.

that the spherical Si particles dispersed in the entire region by field-emission scanning electron microscopy and transmission electron microscopy (see Fig. 3 in Ref. 1)). From the comparison of the actual experiment, a time step can be estimated to be 0.4 second and the length of the system shown in Figs. 1 and 2 is about 600 nm and 150 nm, respectively.

Our simulation result suggests that the lamellar microstructure can be obtained in this system by utilizing effectively the eigen strain, leading to more efficient TE material. The performance for thermoelectric energy conversion is characterized by the figures of merit $ZT (\equiv S^2 \sigma T / \kappa)$, where S is Seebeck coefficient, σ the electrical conductivity, T the absolute temperature and κ the thermal conductivity. In this study, it can be considered that the precipitated Si particles formed semi-coherent interface under the influence of the eigen strain. Due to the semi-coherent interfaces, the phonon scattering enhances while electron scattering remain almost unchanged, leading to that κ decreases and σ stays unchanged in the figures of merit ZT . Thus, the lamellar microstructure could improve the thermoelectric properties of the Mg₂Si materials.

At the present study, the comparison with experimental work is done only in the respect of the form of the precipitated particles. We have focused on the effect of eigen strain on the form of the precipitated particles and have found that the precipitated particles in the actual experiment are round shaped and stress-free. Therefore we propose that the lenticular shaped precipitation can be achieved by utilizing eigen strain at the interface between Si precipitation and Mg₂Si matrix. This is crucial, however, it should be noticed that the structure shown in Fig. 1 was obtained assuming that Si precipitation with fixed orientation in single crystal of Mg₂Si. To utilize the eigen strain effect in actual experiment, we propose the sintering under hot press with free boundary condition for pre-sintered specimen. We will report such experiments in the subsequent paper.

Figure 3 shows the time change of the ratio of interface area with and without eigen strain. The definition of interface area is as follows. We use a 256×256 simulation uniform square grid and every grid has a value of s_1 . The value of the pure Si precipitate is 1 and that of pure Mg₂Si matrix is 0. It should be noted that the s_1 values at interface change continuously between 0 and 1, so we defined the value of s_1 for the interface area as 0.4–0.7. The ratio of the number of grids at interface to the total number of grids 256×256 is the inter-

Fig. 3 Time change of the ratio of interface areas with and without eigen strain.

Fig. 4 Region around a Si precipitate arbitrarily selected from the system: (a) at the 590 time step (A in Fig. 3) and (b) at the 650 time step (B in Fig. 3). The inserted color scale is the same as in Fig. 1. The red zone is Si, the blue zone is the Mg₂Si matrix, and the zone with intermediate color between red and blue is the interface of Si precipitates and Mg₂Si matrix.

face area ratio.

When the system had eigen strain, larger fluctuation of the ratio of interface area was seen, with the maximum value being 2.79%. The interface growth rate gradually decreased with time because of the lack of Si atoms. Figures 4 (a) and

(b) show the regions around a Si precipitate arbitrarily selected from the system at two time steps, 590 and 650. We consider that the large fluctuation of the interface area for the case with eigen strain is crucial, not caused by numerical error. From Fig. 4, the origin of high fluctuation of the interface area is due to the oscillation of growth front along s_1 variant, i.e. the origin of apexes of lenticular precipitate.

4. Conclusion

We simulated the Si precipitation process in Mg_2Si matrix by the phase-field method, considering the eigen strain at the interface between precipitates and the matrix. We observed that the shape of the precipitate changed during the course of heat treatment from circular to lenticular. As the Si precipitation grew larger, the adjacent precipitates aggregated to form a lamellar microstructure. This is mainly due to the fact that the elastic energy is a crucial factor to decide the morphology of the Si precipitates. This microstructure is suitable for TE materials because the scattering of phonons will occur frequently at the interface between the Si precipitates and Mg_2Si matrix. Our present simulation suggested drastic improvements of TE properties of this type of material would be possible because of the eigen strain.

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