1. Introduction

Grain refinement by inoculation, which can be achieved by the addition of master alloys (inoculants) to the melt, is an important technique used to improve the mechanical properties of aluminum alloys.\(^1,2\) The most widely used inoculants for \(\alpha\)-Al are based on compounds of the Al–Ti–B systems, where TiB\(_2\) particles function as the effective grain refiners. Easton and StJohn\(^3,4\) reported the effect of Ti and B solute compositions on the refinement of 99.97% pure aluminum. They observed that the main factors determining the degree of refinement are the TiB\(_2\) particles, which act as nucleation site, and the concentration of Ti which is the solute in liquid. Murty\(^5\) reported an identical tendency in commercial pure aluminum. Some models describing the refinement mechanism have been proposed.\(^1,6\) The strength of the refinement effect of the solute composition is evaluated by the growth restriction factor (GRF), which is represented for a binary system as,

\[
GRF = m_L(kL - 1)C_0
\]

where \(m_L\), \(k\) and \(C_0\) are the liquidus slope, partition coefficient and bulk solute content, respectively. The GRF value of Ti is much higher than that of the other solute elements. Quested\(^7\) recently performed GRF modeling for aluminum alloys by coupled with phase-diagram calculations using CALPHAD method.\(^8\)

Some numerical models describing the grain refinement in aluminum alloys have been proposed. Quested proposed an analysis for population variance in the size distribution of the inoculant particles in an Al–Ti–B alloy. Some cell-automaton methods have been applied to simulate the influence of the solute content on grain refinement during the equiaxed solidification of Al alloys.\(^9,10\) Steinbach and Apel\(^11\) successfully simulated the rapid crystallization of silicon on a substrate by using a faculty of multigrain nucleation in the multi-phase field method (MPFM). Boettger et al.\(^12\) showed that the combination of a MPFM and a nucleation model for multielement systems is valuable in simulating the refinement process during the equiaxed solidification of an Al alloy. However, the authors are not aware of any literature reporting on quantitative analysis of the influence of the Ti content on grain refinement and comparison with experimental measurements during the equiaxed solidification of Al alloys.

In this paper, a MPFM, the CALPHAD approach and a nucleation model are used together to estimate the grain sizes during equiaxed solidification in the Al–Ti–B and Al–Si–Ti–B systems. The nucleation model consists of the seed density distribution, which is defined by the distribution of number density versus the radius of the nuclei. This model is called the seed density model (SDM) in the present MPFM study. The distribution of SDM for the Al–Ti–B system is calibrated by comparison with experimental measurements for two different Ti contents and one B content. Finally, the calculated grain sizes during the equiaxed solidification of an Al–Ti–B alloy are rigorously compared with the experimental measurements for various Ti contents. Furthermore, the refinement effect of Ti content is confirmed for Al–Si–Ti–B system by using a MPFM and SDM.

2. MPFM and CALPHAD

Steinbach et al.\(^13,14\) proposed the multiphase field method as an advanced formulation for multiphase or multigrain systems that employed the phase field method for two-phase system. Thus, a MPFM is very suitable for microstructure simulation for industrial materials. However, it is not easy to estimate the driving force for interface
movement in the MPFM equation because industrial materials are usually multicomponent systems. Currently, the CALPHAD approach is most promising method to create Gibbs energy descriptions of industrial materials, as assessed by experiments. Consequently, a numerical method involving the combination of a MPFM with the CALPHAD method was developed by Steinbach et al. and released as a software package, MICRESS, now distributed by ACCESS eV. Eiken et al. summarized the numerical methods of MPFM coupled with CALPHAD data. They described a numerical procedure for detailed thermodynamic analysis of multiphase and multicomponent systems. The multicomponent diffusion equation for the interface regions was also presented in basis of consideration of the diffusion data base Dictra coupling.

3. SDM

The use of SDM in the MPFM was proposed by Boettger et al. SDM data are defined by the distribution of number density versus radius of the nuclei, as shown in Fig. 1(a). The numerical procedure for modeling nucleation using the SDM is briefly explained as follows: First, when setting the initial conditions, the seeds are virtually distributed over the liquid domain at random positions according to the distribution data, as shown in Fig. 1(b); at this stage, no seeds nucleate. Next, after starting heat extraction from the domain, it is checked whether each virtually distributed seed can nucleate by comparing the temperature at its position with the amount of undercooling estimated by classical nucleation theory. Then, the area of the nucleated seed in the liquid domain is taken in solid phase. Finally, the newly formed solid region (of the size of the seed) is taken into account in the phase field calculation procedures.

As the nucleated particle starts growing and releasing latent heat, it immediately affects other virtually distributed seeds waiting to nucleate. Boettger et al. explained not only the SDM, but also a numerical treatment for the recrystallization phenomenon, which is caused by the release of the latent heat and is a very important factor influencing nucleation during the equiaxed solidification of an Al alloy.

4. Calculation for the Al–Ti–B Alloy

4.1. Simulation Conditions

At hypoperitectic levels of Ti and B, all the B content exists in the form of TiB₂ at temperatures greater than over 665°C (i.e. above the liquidus line), as shown in Fig. 2. Thus, in this system, it is sufficient for the residual Ti content in the liquid phase to be considered as a solute in the solidification process. Consequently, calculation and physical conditions were set to liquid and α-Al phases. TiB₂ particles are completely wetted by Al, making them very effective inoculants for α-Al grain refinement. Thus, grain refinement is controlled not only by the density of inoculant particles but also by the particle size distribution. Consequently, the SDM data are defined using the density-radius distribution of nuclei, as shown in the schematic illustration of Fig. 1(a).

The two-dimensional finite difference method was used to solve the MPFM and the multi-component diffusion equations. In this study, the grid size was set as 2.0 µm square. The calculation region size was 600 µm square. The equiaxed solidification calculations were performed for Ti contents of 0.005–0.1 wt% and TiB₂ contents of 0.03–0.12 wt%. The heat extraction rate was set as $50 \times 10^4$ J s⁻¹ m⁻³. The values of the physical constants employed are summarized in Table 1, where the interface mobility value that is inherent to the phase field equation was determined by some trial calculations. The diffusion mobility values, which vary with local temperature and composition, were taken from the DICTRA database. The interface mobility value at lower temperatures must be smaller than...
that at higher temperatures because diffusivity is lower at lower temperatures.

### 4.2. Calibration of SDModel Data

The SDM data was calibrated against experimentally measured solidified grain sizes for Ti content of 0.02 and 0.1 wt% and a TiB\(_2\) content of 0.12 wt%.

**Figure 3** shows the calibrated (a) grain sizes and (b) SDM distribution of Seed Density Model in the TiB\(_2\) content of 0.12 wt%: Seed Model A.

We assumed that the same radius distributions existed at TiB\(_2\) content of 0.03 and 0.12 wt%. Thus, the seed density at 0.03 wt\% TiB\(_2\) was divided by four in Fig. 3(b). This distribution for a TiB\(_2\) content of 0.03 wt\% was named Seed Model B.

### 4.3. Calculation Results

**Figure 4** shows temperature history curves for various Ti contents and the addition of 0.12 and 0.03 wt\% TiB\(_2\): Seed Model A and B. It is seen that the absolute undercooling temperature at higher contents of Ti and TiB\(_2\) is smaller than lower them in the same content of TiB\(_2\) and Ti, respectively. These results show that a high content of Ti or TiB\(_2\) will result in a refined grain structure during equiaxed solidification because of high absolute undercooling temperature, which leads to a low nucleation density and high grain growth rate.

**Figure 5** shows the \(\alpha\)-Al grain distributions at cooling times of (a) 4 s and (b) 50 s for Ti contents of 0.1, 0.06 and 0.02 wt\%, and a TiB\(_2\) content of 0.12 wt\%. We see that the \(\alpha\)-Al grain growth to become more dendritic at higher Ti contents in the liquid. The solidified grain sizes in Fig. 5(b) confirm the previous consideration of refinement effect of TiB\(_2\) and Ti in the liquid. **Figure 6** shows the solidified grain sizes for various Ti contents and the additions of 0.12 and 0.03 wt\% TiB\(_2\). Clearly, calculated results are in very good agreement with the experimental measurements. Furthermore, the refinement effect of solute Ti is better at TiB\(_2\) content of less than about 0.02 wt\%.

### 5. Calculation for Al–Si–Ti–B Alloy

The insufficient number of experimental results available...
for this system prevented validation of the calculated results as Fig. 6. Hence, we confirmed the refinement effect of the solutes of Ti and Si only by the present MPFM calculations. Calculations were performed for Ti contents of 0, 0.01, 0.05, 0.1 and 0.15 wt% with a Si content of 2 wt%; and with a Ti content of 0.1 wt% with 0 wt% Si. The same amount of TiB2 (0.12 wt%) was used in all these calculations. Then, Seed Model A of the previous Al–Ti–B alloy was applied to this Al–Si–Ti–B system.

The same region and the grid sizes as in the previous Al–Ti–B simulation were used in these calculations. The physical constants for the Si phase are summarized in Table 2. The constants for the liquid and α-Al phases listed in Table 1 were also applied in these calculations.

Figure 7 shows the solidified α-Al and Si grain distributions in the conditions of Ti contents of 0 wt%, 0.01 wt%, 0.05 wt%, 0.1 wt% and 0.15 wt% with Si content of 2 wt% and in the condition of Ti content of 0.1 wt% with 0 wt% Si.

6. Summary and Conclusion

A Multiphase field method together with the CALPHAD approach was used to simulate grain refinement during the equiaxed solidification of alloys belonging to the Al–Ti–B system.
and Al–Si–Ti–B systems. In these calculations, recalescence and a model of the distribution of nucleating seed density versus the radius were considered. In the Al–Ti–B system, the seed density-radius distribution was calibrated against experimental measurements of the solidified grain sizes for two different contents of Ti and one content value of TiB₂. It was seen that 1) an increase in the Ti or TiB₂ content causes grain refinement and 2) the calculated grain sizes at various Ti contents, two different seed distributions, and different TiB₂ contents quantitatively agreed with the experimentally measured grain size. It is also seen that an increase in Ti or Si content at a constant TiB₂ content causes grain refinement during the equiaxed solidification in Al–Si–Ti–B system. Consequently, it is confirmed that the combination of the multi-phase field method with the CALPHAD approach, together with functions representing recalescence effect and nucleation (on the basis of a seed density-radius distribution model), can be applied to study of complex solidification processes in multiphase and multicomponent systems. However, for a quantitatively accurate simulation, it is important to obtain the seed density data by calibration with the results of solidification experiments.

REFERENCES

1) J. E. C. Hutt, D. H. StJohn, L. Hogan and A. K. Dahl: Mater. Sci. Technol., 15 (1999), 495.