Dissolution kinetics of primary silicon in hypereutectic Al–Si melt

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Abstract

The dissolution process of primary silicon particles in Al–18%wt silicon alloy was studied both by a melt overheating experiment and by theoretical analysis. A dissolution model of primary silicon in the melt was established based on atomic diffusion and taking account to interface reaction and curvature of particles. The results show that the theoretical curve agrees with the experimental curve at an overheating temperature of 1100°C. However, there was some deviation at 700°C due to retained silicon clusters in the melt at lower temperature. Therefore, the model is in accord with experiment when not considering the influence of retained silicon clusters. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

As an important cast alloy, hypereutectic Al–Si alloy is of low linear expansion coefficient and density, good cast performance and wear, and corrosion resistance. Therefore, it is widely used in the aeronautic, astronomic, and in automobile industries. The microstructure of this alloy consists of primary silicon and Al–Si eutectic under normal cast condition. It has been found that some coarse primary silicon is detrimental to the mechanical properties and limits the application of this alloy. In order to refine the primary silicon, comprehensive investigations have been done. One effective method is modification. Since the process of modification is complex and difficult to control, the desired properties cannot be obtained or may even be made worse. Moreover, it would bring about other problems, such as environment pollution, equipment corrosion, etc.

Some previous studies [1–3] showed that the primary silicon could be refined by a proper melt overheating treatment, which thus provide a new method to improve the microstructure and properties of this alloy.

Although a lot of experimental work has been done, there is lack of theoretical analysis to predict the dissolution of primary phase particles in the melt.

In this paper, the dissolution process of primary silicon in an overheat melt is investigated and the correspondent dissolution model is established.

2. Dissolution model

The dissolution of particles in the alloy melt is controlled by two factors, solute diffusion and interfacial reaction. The former is based on the assumption of interfacial equilibrium, i.e. that the interfacial reaction is quick enough and that the dissolution rate depends on long-range diffusion through the melt. The latter assume that the cross-interface atom detachment controls the dissolution rate. Which factors control the process in the dissolution depends on a thermomechanical parameter $\sigma$ [4]:

$$\sigma = \left( \frac{k_0 R}{D} + 1 \right)^{-1},$$

where $k_0$ is the reaction rate constant. $\sigma$ varies between zero and unity. If it is close to zero, the effect of the interface reaction can be ignored. Otherwise, the effect of the interfacial reaction should be considered in the model.

As for a small spherical particle, the curvature also plays an important role on the dissolution.

2.1. Atomic diffusion model

Consider the dissolution of a spherical primary phase particle in the melt (see Fig. 1), where $C_P$ is the concentration inside the primary phase, $C_1$ is the concentration at the solid/melt interface, $C_M$ is the far field composition in the melt, and $R$ is the particle radius.

Assume that the convection in the melt is ignored and atoms transfer into melt isotropically during dissolution.
The diffusion equation from Fick’s law is as follows:

$$\frac{\partial C}{\partial t} = \frac{D}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial C}{\partial r} \right).$$

Subject to the condition:

$$C(r, t = 0) = C_M, \quad (2a)$$

$$C(r = R, t) = C_1, \quad (2b)$$

Eq. (1) can be solved to be:

$$C(r, t) = \frac{(C_1 - C_M)R}{r} \text{erfc} \left( \frac{r - R}{2\sqrt{D}t} \right), \quad (3)$$

where erfc is the error function complement.

It is also necessary to satisfy the independent flux balance:

$$-4\pi R^2 (C_p - C_1) \frac{dR}{dr} = -4\pi R^2 \left( \frac{dC}{dr} \right)_{r=R}. \quad (4)$$

Substitution Eq. (3) into Eq. (4) gives the dissolution rate:

$$\frac{dR}{dr} = -\frac{K}{2} \left( \frac{D}{R} + \sqrt{\frac{D}{\pi t}} \right) \quad (5)$$

with

$$K = 2 \left( \frac{C_1 - C_M}{C_p - C_1} \right). \quad (6)$$

2.2. Interface reaction model

The interface reaction will slow down the speed of the migration of the atoms from the primary phase into the melt. Thus, the actual equilibrium concentration \( C'_1 \) yat the interface will be lower than the local equilibrium concentration \( C_1 \) (see Fig. 2). Define \( \Delta C'_k \) as:

$$\Delta C'_k = C_1 - C'_1, \quad (7)$$

$$C'_1 = C_1 - \Delta C'_k. \quad (8)$$

Assuming that the detachment of atoms from interface is uniform, according to Brice’s hypothesis [5], then

$$\frac{dR}{dr} = -k_0 \Delta C_k$$

with

$$k_0 = \frac{8D \gamma_{ap} V_p C_1}{9R_g T}, \quad (9)$$

where \( \gamma_{ap} \) is the interface energy of solid/liquid, \( V_p \) is the mole volume of primary phase, and \( R_g \) is the gas constant.

As for Al–18%Si alloy, \( \sigma \approx 1 \), it is necessary to take the interface reaction into account.

2.3. The effect of curvature on the dissolution kinetics

It can be shown from Gibbs–Tompson relation that the equilibrium melt composition at the curved solid/liquid interface \( (C'_1) \) varies with particle radius \( R \), modified as follows [6]:

$$C'_1 = C_1 \exp \left( \frac{\gamma_{ap} V_p}{R_g TRC_p} \right). \quad (10)$$

The dissolution kinetics model can be established by including Eqs. (6), (9–11) into Eq. (5) to a multinomial:

$$\left( \frac{dR}{dr} \right)^2 + \alpha \left( \frac{dR}{dr} \right) + \beta = 0, \quad (12)$$

where

$$\alpha = -k_0 C_p + k_0 C_1 \exp \left( \frac{\gamma_{ap} V_p}{R_g TRC_p} \right) - \left( \frac{D}{R} + \sqrt{\frac{D}{\pi t}} \right)$$

and:

$$\beta = k_0 \left[ C_1 \exp \left( \frac{\gamma_{ap} V_p}{R_g TRC_p} \right) - C_M \right] \left( \frac{D}{R} + \sqrt{\frac{D}{\pi t}} \right).$$

3. Experiment and comparison

A model (Eq. (12)) has been established which combined interface reaction, curvature with diffusion. In order to
examine whether it fit for experiment, an experiment of overheating for the melt and then quenching is designed using Al–18%Si hypereutectic alloy. The samples were heated to 700–1100°C, kept for a predetermined time, and then quenched at a rate of 10³ K/s. The average size of the retained particles was measured with Leitz-TAS-Plus quantitative metallograph equipment.

Applying the parameters of Al–18%Si alloy [7,8] \( D_0 = 2.08 \times 10^{-7} \text{ m}^2/\text{s}, \quad Q = 25740 \text{ J/mol}, \quad \gamma_{\alpha p} = 352.41 \times 10^{-7} \text{ J/cm}^2 \) to Eq. (12), the numerical solution can be obtained. The calculated kinetics curves and the experimental curves are illustrated in Fig. 3.

It is shown that the calculated curve roughly agrees with the experimental curve at 1100°C. At 700°C, the first half of the curves fit, but the second-half parts deviated obviously. It is considered that the deviation does not result from the model itself but the dissolution characteristic of primary silicon at the lower temperature melt, which will be discussed later.

On the other hand the numerical solution of Eq. (5) is also obtained for the pure diffusion case, which shows that the primary silicon will dissolve completely only within 1 and 0.01 s at 700 and 1100°C, respectively. Compared with the experiment result, the difference is of the order of ten thousand.

Obviously, the model (Eq. (12)) is more precise than the pure diffusion model (Eq. (5)).

4. Analysis and discussion

Fig. 3 shows that the primary silicon phase can dissolve completely when the holding time is over 60 min at 700°C according to the calculated results, whereas experiment reveals that the size of primary silicon particles is kept at about 12 μm and almost without change when the holding time is over 1 h.

A lot of studies [9,10] have suggested that there are atom clusters of silicon in the lower temperature melt of Al–Si alloy. Therefore, they could serve as nuclei and grow into observable silicon particles when the melt is quenched. In order to verify this, the size of these clusters was calculated under the quench condition using a growth model [11]. The radius of growth of primary silicon is 13 μm, which agrees with the second half of the experimental curve at 700°C. Because this kind of silicon particles grow from retained clusters, they are independent of the holding time, and the dissolution curve cannot describe them.

The present model assumes silicon particles of the shape of a sphere with the same size, but this is not true for the real situation. In the melt, there are of different size and different shapes, such as planar, five petal star, etc. Therefore, the model can only approximately describe the process of dissolution.

5. Conclusions

The dissolution kinetics of the primary phase in the melt is established by taking account of diffusion, interface reaction and curvature of particles, which is more precise than the traditional diffusion model.

As for the Al–Si hypereutectic alloy, the primary silicon can dissolve completely at the higher overheating temperature of 1100°C, but at the lower temperature of 700°C, there are silicon clusters in the melt, which can serve as nuclei and grow during the subsequent cooling.

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