Modelling of Precipitation Behaviour of Fe and Si of Commercial Purity Aluminium

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Keywords: Modelling, precipitation, nucleation, growth, hot deformation, commercial purity aluminium

Abstract

A simplified model was applied for the precipitation behaviour of Fe and Si contained in commercial purity aluminium. The model was basically constructed with the nucleation and growth theory. The temperature-time-precipitation curves for Al₃Fe, α -AIFeSi and elemental Si were mainly described in this paper. The present simplified model quantitatively explained the experimental results concerning TTP curves and a slight variation of the content of Fe in solid solution and the total amounts of Fe or Si that existed as constituents and precipitates in commercial purity aluminium.

1. Introduction

Precipitation control through an optimisation of manufacturing process is vitally important for improvement of quality of wrought aluminium alloys. In commercial purity aluminium alloy, it is well known that a small amount of Fe and Si contained as impurities has great effects on formability and mechanical properties such as hardening and softening. These properties are controlled by the amount of solute content, constituents and precipitates for Al₃Fe, α -AIFeSi and elemental Si, but it is very difficult to evaluate the small amount of precipitates quantitatively by the experimental measurement. Therefore a modelling is an effective approach to explain these complicated phenomena of precipitations during the thermomechanical processing, and over the past two decades numerous attempts have been made on the modelling of precipitation [1-4]. Furthermore the basic physical modelling considered strain-induced precipitation has been developed mainly in the field of steel [3,4]. This paper is intended as an investigation of the precipitation behaviour of Fe and Si in commercially purity aluminium using the simplified modelling from the point of view of the application of process modelling to aluminium industry.

2. Experimental Procedures

The chemical compositions of AI-Fe-Si alloy (1100) in the present study are 0.07mass%Si-0.51mass%Fe-0.07mass%Cu(Alloy A) and 0.08mass%Si-0.95mass%Fe-0.01mass%Cu (Alloy B). For the experiment on the kinetics of strain-induced precipitation after hot deformation, Alloy A was used. Cylindrical specimens of 8mm in diameter and 12mm in height were machined from the ingot and then compressed with the true strain of 1.2 at 673K at a strain rate of 10s⁻¹. These specimens were held at the various temperatures from 573K and 823K for various periods (= Deformed specimen). In order to investigate the effect of hot deformation on precipitation kinetics, the precipitation tests without deformation were carried out (= Un-deformed specimen). On the other hand, in order to verify the application to predict the total amount of precipitated Si, Alloy B was used. The specimens machined from the ingot were homogenized at the heating rate of 40K/h at 813K and 673K for 5 hours followed by water quenching. The homogenized specimens were further 80% cold rolled and after that annealed at 523K, 573 and 623K for 3 hours. The content of Fe in solid solution and the total amounts of Fe or Si that existed as constituents and precipitates were quantitatively investigated by chemical analysis of extracted residue with phenol (phenol residue method) and extracted residue with HCl for analysis of elemental Si precipitates using the mesh of pore size of 0.2 μm .

3. The Model

3.1 Nucleation

First of all, the heterogeneous nucleation rate of precipitation is given on the basis of classical nucleation theory expressed as

$$\dot{N}_{het} = v N_{v} \exp\left(-\frac{\Delta G^{*}_{het}}{RT}\right) \exp\left(-\frac{Q_{d}}{RT}\right)$$
(1)

where \dot{N}_{het} is the rate of heterogeneous nucleation, v is a vibration frequency factor, N_v is the total number of heterogeneous nucleation sites, ΔG^*_{het} is the energy barrier against nucleation, Q_d is the activation energy for diffusion in Al (Q_d (Fe)=183kJ/mol, Q_d (Si)=136kJ/mol)), T is temperature(K) and R is the gas constant(8.314J/mol K) [5]. During the early stage of a precipitation reaction, the reaction rate is controlled by the nucleation rate and the time taken to precipitate a certain fraction of the new phase is inversely proportional to \dot{N}_{het} and therefore the time taken to precipitate is basically described through the following equation [1].

$$t^* = \frac{k_1}{N_{\nu}} \exp\left[\frac{k_2}{R} \left(\frac{(T_{eq})^2}{T(T_{eq} - T)^2}\right) + \frac{Q_d}{RT}\right]$$
(2)

Here T_{eq} is the equilibrium dissolution temperature of precipitate and k_1 , k_2 is constant. Parameters in equation (2) related to the shape and position of time-temperatureprecipitation curve (TTP) were fit to the experimental results as follows.

$$k_1/N_v = 5 \times 10^{-10}$$
, $k_2 = 83.14$ in equation (2) for TTP(Al₃Fe) and TTP(elemental Si)
 $k_1/N_v = 5 \times 10^{-12}$, $k_2 = 83.14$ in equation (2) for TTP(α -AlFeSi)

Figure 1 shows the equilibrium phase diagram for Alloy A obtained by the thermodynamic calculation (Thermo-Calc)[6]. The initial content of Fe in solid solution in the ingot was approximately 0.04 % analyzed by phenol residue method and most of Fe addition existed as the form of constituents. Accordingly precipitation behaviour in matrix can be assumed to occur on the dot line in Figure 1. The equilibrium dissolution temperature of each precipitate, $T_{eq}(Al_3Fe)$ =843K, $T_{eq}(\alpha - AlFeSi)$ =734K and $T_{eq}(Si)$ =567K can be estimated.



3.2 Simplified Description of Effects of Strain-Induced Precipitation

Some basic descriptions of effects of strain-induced precipitation have been proposed [3,4,7], but it is difficult to apply the theoretical model as it is because there are many values of the physical parameters that have not been clarified in aluminium alloy. However, the interaction between precipitation, recovery and recrystallization can be ignored in commercial purity aluminium because the retardation of recrystallization by strain-induced precipitation is not observed clearly in this alloy due to such a slight variation of precipitates that hardly work as a pinning force. Therefore the modelling of strain-induced precipitation can be simplified in this work. A stored energy term, which was related to recovery and recrystallization, was added to the nucleation rate equation, through the following assumption [8].

$$t^*_{dynamic} = B \times t^*_{static}$$
(3)

$$B = k_3 / \rho \tag{4}$$

Here t^*_{static} is time taken to precipitate without deformation, $t^*_{dynamic}$ is time taken to precipitate with deformation, ρ is the dislocation density, k_3 is constant. The parameter B, which value is inversely proportional to the dislocation density, is expressed as the acceleration parameter of the strain-induced precipitation, B = 1 when in the undeformed specimen. As a further assumption the flow stress can be substituted for the estimate of dislocation density, since the dislocation density ρ has the relation of $\sigma \propto \sqrt{\rho}$ to the flow stress of the material σ [9].

3.3 Recovery and Recrystallization

Flow stress during hot deformation is expressed as

$$\sigma_{def} = a D_0^{\ \alpha} \varepsilon^{\beta} \dot{\varepsilon}^{\gamma} \exp(b/T_{def})$$
(5)

where σ_{def} is the flow stress(kgf/mm²), D_0 is the initial grain size(μm), ε is true strain, $\dot{\varepsilon}$ is the strain rate, T_{def} is the deformation temperature and a, b, α , β , γ are the fitting parameters [10,11]. Next, the description of recrystallization is modified using the parameter σ_{def} based on the Johnson-Mehl-Avrami type equation as follows [8,11].

$$X_{v} = 1 - \exp\left(-0.69\left(t/t_{0.5}\right)^{k}\right)$$
, $X_{v} = 0.5$ when $t = t_{0.5}$ (6)

$$t_{0.5} = d\sigma_{def}^{\delta} \exp\left(Q_{rex}/RT_{rex}\right)$$
(7)

Here X_{v} is the fraction of recrystallization, t is the time after deformation, T_{rex} is the temperature, Q_{rex} is the activation energy for recrystallization, and k, δ is the fitting parameter. And then, the description of the variation of the average dislocation during the recovery process is defined using the parameter of flow stress as follows.

$$\sigma_{recovery} = \sigma_{def} - (\sigma_{def} - \sigma_0) \times X_v$$
(8)

Here $\sigma_{recovery}$ and σ_0 are the residual stress of recovered and recrystallized specimen, respectively. Parameters in equation (5), (6) and (7) were determined by experimentally measuring the flow stress of the compression test and the softening curve during recovery and recrystallization as shown the following values [11].

$$a = 4.2, b = 1133, \alpha = -0.27, \beta = 0.25, \gamma = 0.07$$
 in the equation (5)
 $k = 0.7, d = 1.02 \times 10^{-8}, \delta = -1.03, Q_{rex} = 128000$ (J/mol) in the equation (6) and (7)

3.4 Growth

Volume fraction of precipitates at an arbitrary time can be also estimated in a general form: $X = 1 - \exp\left(-(t/\tau)^n\right)$. In case of the early stage of a precipitation reaction, the reaction rate is controlled by the nucleation rate [1]. For instance, the fraction of precipitated Fe to form Al₃Fe and/or α -AlFeSi, X_{Fe} is represented by the right hand side of the following equation.

$$X_{Fe} = \frac{C^{0}_{Fe} - C_{Fe}}{C^{0}_{Fe} - C^{e}_{Fe}} = 1 - (1 - X_{c})^{(t/t^{*})^{n}}$$
(9)

Here is $X = X_c (X_c = 0.05)$ when $t = t^*$. C^{e}_{Fe} and C^{0}_{Fe} are the equilibrium and the initial concentration of Fe in solid solution. The input data of *n* was 0.5-0.75, which was determined by Avrami plot of equation (9) with the experiment. From the equation (9) the content of Fe in solid solution C_{Fe} at an arbitrary time *t* is given. In addition, the equilibrium solvus boundaries of Fe and Si in solid solution and the equilibrium dissolution temperature of each precipitate were determined by thermodynamic calculation.

4. Results and Discussion

Figure 2 demonstrates the calculated results of TTP curves for Al₃Fe, α -AlFeSi and the elemental Si precipitates in Alloy A as compared with the experimental results in undeformed and deformed specimens. The existence of Al₃Fe at 773K or more and α - AlFeSi in the range from 573K to 723K was confirmed by TEM observation. As shown in Figure 2, the predicted TTP curves with this model were approximately corresponding with the time equivalent to 5% volume fraction of precipitation from the variation of solute Fe content analyzed by phenol residue method.

Figure 3 presents the comparison between calculated curves and experimental results for the variations in solute Fe concentration during isothermal annealing (a) at 673K and (b) at

773K. These calculated curves are in good agreement with the experimental results both in un-deformed and deformed specimens, although some experimental values may be smaller than the calculations. It seems reasonable that the acceleration of strain-induced precipitation can be expressed by this model and assumption. It follows from Figure 3 that the degree of the acceleration of strain-induced precipitation during annealing at 673K is larger than that at 773K. It indicates that precipitation during hot deformation at higher temperature is less affected by the effect of strain-induced precipitation because recrystallization is completed at the early stage. On the other hand, it should also be added that the precipitation could be accelerated due to the existence of constituents [8]. The start of precipitation in un-deformed commercial purity aluminium occurs earlier than that in high purity aluminium [8]. It is noteworthy that not only grain boundaries and dislocation but also interface of matrix and constituents plays an important role in nucleation site of Al₃Fe and α -AIFeSi precipitates in case of commercial purity aluminium.

Figure 4 shows the prediction of precipitation after homogenization in Alloy B as compared with the experimental results. Although it is difficult to estimate the volume fraction of Al₃Fe and α -AlFeSi precipitates, the calculations are similar to those experimental values of solute Fe content and residue Si content analyzed by phenol residue method.



Figure 2: Calculated TTP curves for Al₃Fe, α -AlFeSi and elemental Si precipitates in Al-Fe-Si alloy compared with experimental results.



Figure 3: Calculated curves for changes in solute Fe concentration of the un-deformed and the deformed specimens during isothermal annealing (a) at 673K and (b) 773K compared with experimental results.

Figure 5 illustrates the variation of the volume fraction of (a) residue Si and (b) elemental Si with annealing temperature as compared with the prediction of this model. The amount of elemental Si in the specimen homogenized at 673K is less than that in the specimen homogenized at 873K due to the decrease in solute Si content after homogenization at 673K as shown in Figure 4 (b). In addition, the increase in elemental Si after annealing at 525K admits of two interpretations. One likely explanation is that the lower temperature is close to the predicted nose of TTP curves of elemental Si and another is that the precipitation of elemental Si depends heavily on dislocation density. As shown in Figure 5 (b), elemental Si hardly precipitates without cold rolling. In this respect a small amount of elemental Si in the specimen annealed at higher temperature can be explained by recrystallization that is completed at the early stage. Thus the modelling of strain-induced precipitation is very important for the prediction of precipitation behaviour of elemental Si. Note that the calculations are sensitive to the dissolution temperatures of precipitates that change by the amount of Fe and Si or the initial solute concentration.



Figure 4: Calculated behaviours of (a) Fe and (b) Si after homogenization compared with the experimental results analyzed by phenol residue method.



Figure 5: Comparison between analyzed and calculated concentration of (a) residue Si and (b) elemental Si. The predicted amount of residue Si is estimated as the sum of constituents and α -AIFeSi precipitates.

5. Conclusions

A simplified model has been applied to express the TTP curves of Al₃Fe, α -AlFeSi and elemental Si in commercial purity aluminium. The calculated precipitation curves were good agreement with the experimental results of a slight variation of the content of Fe in

solid solution and the total amounts of Fe or Si that existed as constituents and precipitates in both un-deformed and deformed specimens.

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