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Transformation character of ferrite formation by a ledge mechanism under a mixed-control model

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Abstract: A mixed-control model was developed to study the transformation character of ferrite formation by a ledge mechanism. A numerical two-dimensional diffusion-field model was combined to describe the evolution of the diffusion field ahead of the migrating austenite/ferrite interface. The calculation results show that the bulk diffusion-controlled model leads to a deviation from experimental results under large solute supersaturation. In the mixed-control model, solute supersaturation and a parameter Z together determine the transformation character, which is quantified by the normalized concentration of carbon in austenite at the austenite/ferrite interface. By comparing with experimental data, the pre-exponential factor of interface mobility, M_0, is estimated within the range from 0.10 to 0.60 $\mathrm{mol\cdot m\cdot J^{-1}\cdot s^{-1}}$ for the alloys with 0.11wt%-0.49wt% C at 700-740°C. For a certain Fe-C alloy, the trend of the transformation character relies on the magnitude of M_0 as the transformation temperature decreases.

Keywords: iron carbon alloys; modeling; ferrite; ledge mechanism; diffusion; interfaces

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1. Introduction

In the case of the isothermal transformation $\gamma \to \alpha$ (austenite→ferrite) in low carbon Fe-C alloys, the bulk diffusion of carbon in austenite necessarily occurs because of a much lower solubility of carbon in ferrite than that in austenite. Besides, the interface process occurs simultaneously, which is responsible for the lattice change from fcc(γ) to bcc(α) structure. In literatures, the growth kinetics of ferrite is often considered to be controlled by the bulk diffusion of carbon, assuming the interface reaction processes infinitely fast. This is the so-called bulk diffusion-controlled kinetics [1-5]. In this case, the thermodynamic equilibrium conditions occur at the γ/α interface. In addition, interface-controlled kinetics was proposed by Christian [6] as an opposite extreme to diffusion-controlled kinetics. In this kinetics, the bulk diffusion of carbon in austenite is assumed to be infinitely fast and then the interface process is rate-determining.

Recently, a number of studies regarding the mixed-control model, which considers the transformation as a bulk diffusion and interface migration coupled process, have been reported [7-12]. These studies arose from the difference between experimental data and the results of both bulk diffusion-controlled models and interface-controlled models mentioned above. However, these studies are mainly based on the Zener's approach for the growth of planar surfaces, cylinders, spheres, *etc*. In this work, a ledge mechanism [1], which is widely applied to Widmanstätten ferrite and bainitic ferrite, is developed to a mixed-control mode. Meanwhile, a numerical two-dimensional diffusion-field model proposed by Enomoto [4-5] is employed here to describe the evolution of the diffusion field ahead of the migrating γ/α interface.

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2. Theory and modeling procedure

Assume ferrite nucleates at the austenite grain boundary and then penetrates into the adjacent austenite grains. Usually, for ferrite growing by the ledge mechanism, the impact of trailing steps on the leading step can be neglected, except for the case where steps can readily nucleate at the ferrite terrace. Consequently, only ferrite of a single ledge, presented in Fig. 1, is concerned here. Note that the ledge terrace of the coherent or semi-coherent structure provides a barrier for growth in the normal direction, while the ledge riser, which is of a disordered boundary with the matrix, can readily migrate [1]. Thus, here the interface velocity of ferrite is identical with the so-called lengthening rate. Meanwhile, according to observations, ledge risers are reasonably assumed to stay planar during the motion, that is, all points along each riser migrate at the same instantaneous velocity [4-5, 13].

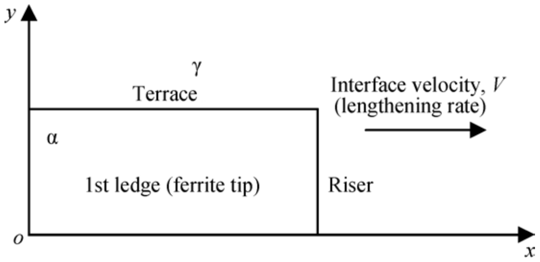

Fig. 1. Schematic diagram showing the ledge geometry of γ/α transformation.

In the matrix, the excess amount of carbon for ferrite will transfer from the γ/α interface into the bulk of austenite. This long-range diffusion obeys Fick's second law:

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2}\right) \tag{1}$$

where c is the carbon concentration, and D is the diffusion coefficient of carbon in austenite. In Eq. (1), D is considered to be a constant independent of concentration. However, the diffusion coefficient of carbon in austenite varies significantly with carbon concentration. In order to take into account the concentration dependence, a weighted average diffusion coefficient proposed by Trivedi *et al.* [14] is introduced here to estimate the value of D. Given by integrating D_c, a diffusion coefficient as a function of carbon concentration [15], from the interface to the matrix with the original composition [2, 14], the average diffusion coefficient could apply to the whole diffusion field, expressed by

$$D = \frac{1}{c^{\gamma/\alpha} - c^{\gamma}} \int_{c^{\gamma}}^{c^{\gamma/\alpha}} D_c \mathrm{d}c \tag{2}$$

Note that the interface velocity of ledged ferrite will approach a steady value [2-3, 5]. This implies that a steady diffusion field has been already built up ahead of the migrating γ/α interface, accompanied with a steady carbon concentration of austenite at the interface. The possible interpretation for this steady process is that the carbon diffusion along the Y direction transports almost all carbon ejected from the forming ferrite through the riser, so the concentration field in front of the advancing interface can, to a great extent, remain steady.

Thus, at the interface this steady diffusion field must satisfy the following flux balance condition:

$$\left(c^{\gamma/\alpha} - c^{\alpha}\right) v_{\mathrm{d}} = -D\left[\frac{\partial c}{\partial x}\right]_{\mathrm{interface}} \tag{3}$$

where v_d represents the interface velocity and c^{α} is the carbon concentration of ferrite in equilibrium with austenite in the phase diagram, while $c^{\gamma/\alpha}$ is the steady carbon concentration of austenite at the interface, but not necessarily equal to the equilibrium concentration.

For numerical simulation, the above parameters should be normalized as follows: $U=(c-c^{\gamma})/(c_e^{\gamma/\alpha}-c^{\gamma})$, $T=Dt/a^2$, $V=av/D$, $X=x/a$, and $Y=y/a$, in which a is the height of a single ledge, c^{γ} the carbon concentration in the matrix far from the interface, $c_e^{\gamma/\alpha}$ the carbon concentration of austenite in equilibrium with ferrite in the phase diagram, t, v and (x, y) represent the reaction time, interface velocity, and coordinates respectively, U, T, V and (X,Y) represent the normalized carbon concentration, reaction time, interface velocity, and coordinates respectively. For simplification, a is assigned the uniform value of 0.066 μm [3, 16]. By normalization, Eqs. (1) and (3) can be rewritten as

$$\frac{\partial U}{\partial T} = \frac{\partial^2 U}{\partial X^2} + \frac{\partial^2 U}{\partial Y^2} \tag{4}$$

$$V_{\mathrm{d}} = -\Omega \cdot \left[\frac{\partial U}{\partial X}\right]_{\mathrm{interface}} \tag{5}$$

where $\Omega = (c_e^{\gamma/\alpha} - c^{\gamma}) / (c^{\gamma/\alpha} - c^{\alpha})$, and V_d is the normalized interface velocity. Under bulk diffusion-controlled conditions, the carbon concentration of austenite at the interface, $c^{\gamma/\alpha}$, is assumed to be a constant value of $c_e^{\gamma/\alpha}$. Thus, $\Omega_0 = (c_e^{\gamma/\alpha} - c^{\gamma}) / (c_e^{\gamma/\alpha} - c^{\alpha})$ is defined, which is the so-called solute supersaturation. In the case of the mixed-control model, the normalized carbon concentration of austenite at the interface, that is, $U_{in} = (c^{\gamma/\alpha} - c^{\gamma}) / (c_e^{\gamma/\alpha} - c^{\gamma})$, can be used to quantify the mixed-control character of the transformation. U_{in} has a value ranging from 0 to 1: for $U_{\mathrm{in}}=0$ the transformation is interface-controlled, while for $U_{\mathrm{in}}=1$ the transformation is bulk diffusion-controlled. Subsequently, the DuFort-Frankel finite difference method is introduced to discretize Eqs. (4) and (5), followed by the implementation of numerical calculation. The detailed information on this process is referred to Refs. [4-5].

Besides, the normalized interface velocity V can also be expressed by the mechanism of interface migration [6]:

$$V_{\mathrm{in}} = M \cdot \Delta G_2 \cdot a / D \quad (6)$$

where M is the interface mobility, and ΔG_2 is the driving force for interface migration [12]. For simplification, ΔG_2 can be assumed to be proportional to the concentration difference from the equilibrium concentration. This proportionality is given by the following equation [12]:

$$\Delta G_2 = \chi \cdot (c_{\mathrm{e}}^{\gamma/\alpha} - c^{\gamma/\alpha}) \quad (7)$$

where χ is the proportionality factor. In view of χ being a weak function of temperature and carbon concentration, a constant value of 99 J/(at%·mol) is adopted in this work. The value is obtained from the Thermo-Calc software under an assumption that the total driving force at the interface is the sum of ΔG_2, the driving force for interface migration, and ΔG_1 (the driving force for carbon diffusion ahead of the interface) [11-12]. The temperature dependence of M can be described by an Arrhenius-type expression:

$$M = M_0 \exp\left(-\frac{E}{RT}\right) \quad (8)$$

For the activation energy E, a value of 140 kJ/mol is usually used, but the value of the pre-exponential factor M_0 is still controversial, ranging from 0.058 to 5000 mol·m·J^{-1}·s^{-1} [7]. Thus, in this work M_0 is considered as an unknown parameter in advance and then determined by comparison with experimental data.

Definitely, under the same condition the two resultant interface velocities mentioned above should be identical, that is

$$V_{\mathrm{d}} = V_{\mathrm{in}} \quad (9)$$

Therefore, the basic calculating procedure used in this work is presented as follows. First, Ω_0 is obtained on the basis of bulk composition and transformation temperature. Then, after assigning an arbitrary value between 0 and 1 to U_{in}, the corresponding lengthening rate V_{d} can be obtained from the implementation of numerical calculation. Subsequently, by combining Eqs. (6)-(9), one can readily determine the specific M_0 value corresponding to the assigned U_{in}. Consequently, after assigning a series of values from 0 to 1 to U_{in}, the relationship between M_0 and U_{in} can be obtained, as well as the variation of transformation kinetics with M_0.

Obviously, the method used in this work cannot correctly describe the initial stage of the transformation, that is, from the nucleation of ferrite to the building up of the steady diffusion field. Fortunately, reasonable results have been obtained for this stage in Refs. [10, 12]. Then, the purpose of this work is to investigate the effect of solute supersaturation and transformation temperature on the growth kinetics of ledged ferrite and the transformation character during the steady stage.

3. Results and discussion

3.1. Bulk diffusion-controlled conditions

In the case of the bulk diffusion-controlled model, that is, U_{in} being invariably set to 1 in the numerical simulation, only solute supersaturation affects the interface velocity. Fig. 2 shows the calculated relation between the normalized interface velocity and the solute supersaturation. From the figure, one can directly note that V approaches infinity as Ω_0 approaches 1, which is evidently unreasonable in reality. In such a case, interface reaction cannot be considered to be infinitely fast but does play a role in growth kinetics. Neglecting the role of interface migration will lead to a deviation from experimental results, especially under the condition of large supersaturation.

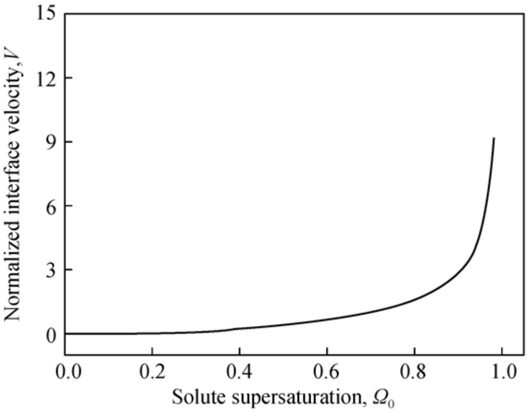

Fig. 2. Variation of normalized interface velocity with solute supersaturation under the bulk diffusion-controlled model.

3.2. Variation of transformation character with M_0 and solute supersaturation

Three Fe-C alloys with a composition of 0.3at%C, 1.0at%C, and 2.0at%C transforming at 720°C are adopted for subsequently investigating the mixed-control mode. The equilibrium concentration is calculated from the Thermo-Calc software and the resultant supersaturations (Ω_0) of the three alloys are 0.94, 0.75, and 0.46, respectively. By implementing the calculating procedure mentioned above, the variation of interface velocity with the assigned interface concentration U_{in} is first obtained, as seen from Fig. 3. As U_{in} increases, the interface velocity increases approximately linearly, especially at low supersaturation. For high supersaturation, the relationship between the two tends to a parabolic type. Nevertheless, in the following calculation the approximately linear relationship is utilized to avoid tedious numerical simulation. As the procedure continues, M_0 corresponding to the assigned U_{in} will be obtained. However, to analyze the effect of M_0 on the transformation character, resultant M_0 is inversely considered as an independent variable and then U_{in} as a function of M_0 is shown in Fig. 4. The figure shows that U_{in} increases dramatically with increasing M_0, but subsequently a sluggish increase follows until M_0 approaches infinity, where U_{in} reaches 1. In other words, as M_0 increases, the transformation character changes dramatically from the interface-controlled mode to the bulk diffusion-controlled mode, and then a sluggish change follows until M_0 approaches infinity, where a completely bulk diffusion-controlled condition occurs. Additionally, from Fig. 4 one can find that as for a certain value of M_0, U_{in} increases with decreasing supersaturation, indicating the trend to the bulk diffusion-controlled mode. Therefore, a conclusion can be drawn that as for traditional models, bulk diffusion-controlled conditions seem more suitable for the case of low supersaturation, while interface-controlled conditions seem more suitable for the case of high supersaturation.

A comparison of the calculated kinetics with experimental data from Refs. [2-3] is carried out to estimate the range of M_0 for Fe-C alloys, and the resultant M_0 is summarized in Table 1. It shows that the reversely calculated M_0 varies from 0.10 to 0.60 mol·m·J^{-1}·s^{-1} for the alloys with 0.11wt%-0.49wt% C at 700-740°C. Then, a value of 0.3 mol·m·J^{-1}·s^{-1} is adopted for M_0 to investigate the effect of temperature on the transformation kinetics and character.

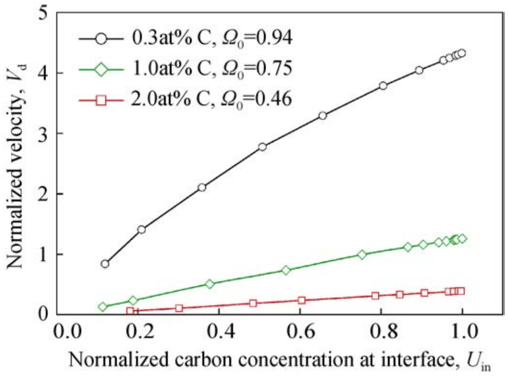

Fig. 3. Variations of normalized interface velocity with normalized carbon concentration in austenite at interfaces for three Fe-C alloys.

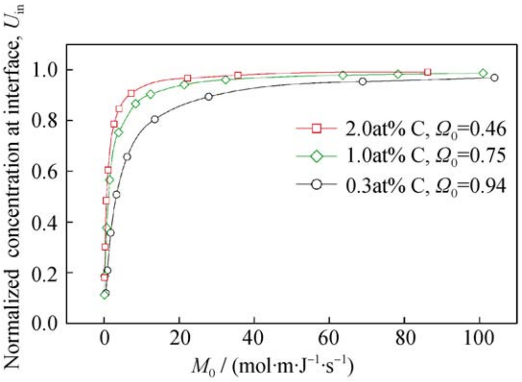

Fig. 4. Variations of normalized carbon concentration in austenite at interfaces with M_0 for three Fe-C alloys with different solute supersaturations.

Table 1. M_0 obtained by comparison with the experimental data

C content in the alloy / wt%	Transformation temperature / °C	Calculated lengthening rate of ferrite / (μm·s^{-1})	Experimental lengthening rate of ferrite / (μm·s^{-1})	Estimated M_0 / (mol·m·J^{-1}·s^{-1})
0.11	740	22.3	1.43-2.38 [3]	0.10-0.18
0.22	720	11.0	1.70-3.40 [3]	0.18-0.43
0.49	700	4.2	2.0 [2]	0.60

Note: the calculated lengthening rates listed are based on the bulk diffusion-controlled model.

3.3. Parameter *Z* determining the transformation character

A fixed supersaturation of 0.75 is adopted to exclude the effect of solute supersaturation in advance. Specifically, at each temperature, a specific alloy composition was chosen so that a supersaturation of 0.75 can be obtained. Fig. 5 shows that as the transformation temperature decreases, U_{in} rises to a maximum and then decreases. Additionally, in this case another parameter, $Z = D / [M(c_e^{\gamma/\alpha} - c^{\gamma/\alpha})]$, can also describe the transformation. In the definition of *Z*, the term

($c_e^{\gamma/\alpha}-c^{\gamma/\alpha}$) quantitatively represents the driving force for interface migration. In contrast to U_{in}, $Z\to\infty$ means that the transformation is interface-controlled; while $Z\to 0$ means that the transformation is bulk diffusion-controlled. Fig. 5 shows that as the transformation temperature decreases, Z declines to a minimum and then rises. Consequently, a conclusion can be drawn from both U_{in} and Z that, in the case of constant supersaturation, as the transformation temperature decreases, the transformation character inclines to the bulk diffusion-controlled mode until a limit value is reached and then inclines to the interface-controlled mode.

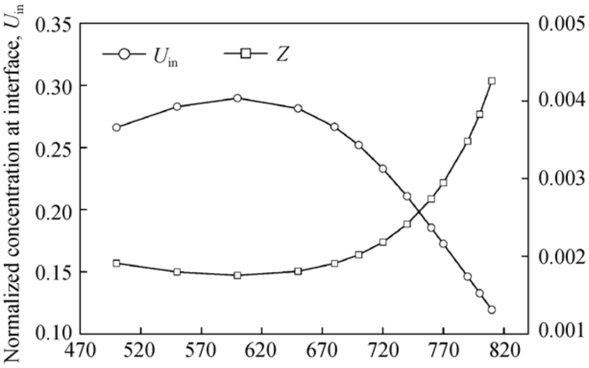

Fig. 5. Variations of normalized carbon concentration in austenite at the interface and parameter Z with transformation temperature under the conditions of Ω_0 =0.75 and M_0=0.3 mol·m·J^{-1}·s^{-1}.

3.4. Variation of transformation character with temperature

Based on the individual effect of solute supersaturation and transformation temperature mentioned above, the variation of transformation kinetics of a certain Fe-C alloy, take 1.0at% C for instance, with transformation temperature, is then investigated. In such a case, individual parameter Z, involving the interface mobility, diffusion coefficient and driving force for interface migration, cannot determine the transformation character but should be combined with solute supersaturation. Fig. 6(a) displays U_{in} as a function of transformation temperature and M_0. As a whole, for M_0=1.0 mol·m·J^{-1}·s^{-1} the transformation character tends to the interface-controlled mode as the transformation temperature decreases; for M_0=0.1 mol·m·J^{-1}·s^{-1} the transformation character tends to the diffusion-controlled mode, while for M_0=0.3 mol·m·J^{-1}·s^{-1} a negligible change occurs. Fig. 6(b) shows that as the transformation temperature decreases, the solute supersaturation increases. This implies a tendency to the interface-controlled mode. However, as the temperature decreases, parameter Z decreases. This implies a tendency to the diffusion-controlled mode. Evidently, during the decrease of temperature, the solute supersaturation and parameter Z have opposite effects. Note that, as M_0 decreases in the range of 0 to around 10 mol·m·J^{-1}·s^{-1}, the effect of solute supersaturation on U_{in} declines, as indicated in Fig. 4. Therefore, the possible reason for the trend of transformation character is that, as for large M_0, solute supersaturation, rather than Z, dominates the process and then a tendency to the interface-controlled mode occurs; however, as M_0 decreases, the effect of solute supersaturation declines and then Z gradually becomes the predominant factor instead, resulting in a tendency to the diffusion-controlled mode.

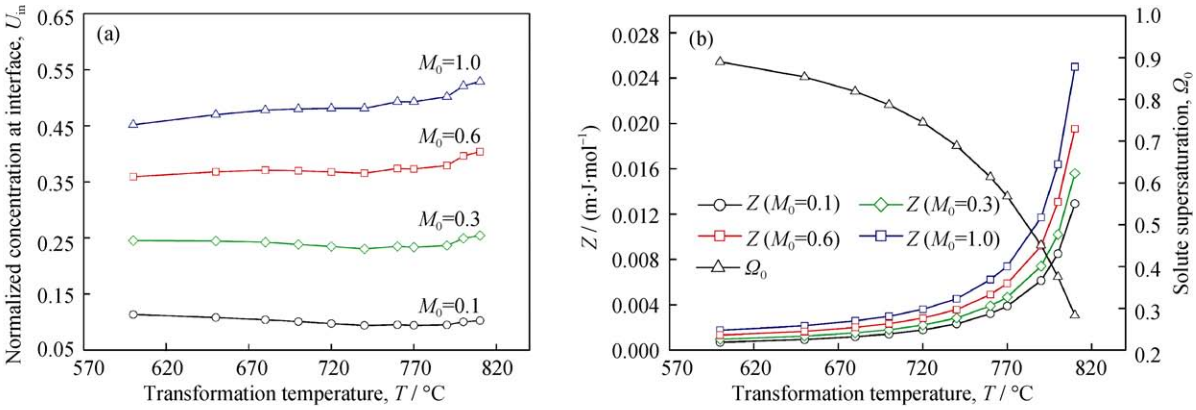

Fig. 6. Variation of normalized carbon concentration in austenite at the interface with transformation temperature in the Fe-1.0at%C alloy for M_0=0.1, 0.3, 0.6 and 1.0 mol·m·J^{-1}·s^{-1}, respectively (a) and the corresponding variation of parameter Z and solute supersaturation (b).

4. Conclusion

In the case of the mixed-control model, it was determined by comparison with the experimental results that M_0 varies from 0.10 to 0.60 mol·m·J^{-1}·s^{-1} for the alloys with 0.11wt%-0.49wt% C at 700-740°C. Solute supersaturation and parameter Z together determine the transformation character. Additionally, in the case of constant solute supersaturation, individual parameter Z can quantify the transformation character. As for a certain Fe-C alloy, the trend of the transformation character relies on the value of M_0 as the transformation temperature decreases. For large M_0, solute supersaturation plays a dominant role over the parameter Z, causing a tendency to the interface-controlled mode, while for low M_0, parameter Z dominates instead, causing a tendency to the diffusion-controlled mode.

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