A New Kinetic Mode During the Austenite-to-Ferrite Transformation in Fe–Mn and Fe–Mn–Mo Alloys

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Abstract

The kinetics of isothermal austenite (γ)-to-ferrite (α) transformation at various temperatures in Fe–2Mn and Fe–2Mn–0.5Mo (wt%) alloys is investigated via dilatometry experiments and phase-field modeling. It was interestingly found that Mo addition has a marginal effect on the transformation kinetics. Besides the well-known partitioning and partitionless transformation modes, a new kinetic mode, in which interface migration is controlled by interfacial diffusion, was identified. The phase-field model with considering interfacial segregation could well predict the transformation kinetics and the kinetic mode transition.

Keywords Steel · Austenite · Ferrite · Diffusion · Solute drag

1 Introduction

The austenite (γ)-to-ferrite (α) transformation is one of the most important diffusional solid-state phase transformations in steels processing. The kinetics of $\gamma \rightarrow \alpha$ transformation is in principle controlled by both element diffusion and interface migration [1, 2], while in many cases it is dominated by either element diffusion or interface migration [3–5]. Fe–X alloys (X represents substitutional elements, such as Mn, Ni, Mo, etc.) are ideal model systems for investigating the mechanism of the $\gamma \rightarrow \alpha$ transformation. The kinetics of the $\gamma \rightarrow \alpha$ transformation upon continuous cooling in Fe–X alloys has been widely studied, and it was found there is a kinetic transition from partitioning to partitionless transformation (e.g., massive transformation). Due to the very slow diffusion of X in γ , the partitioning $\gamma \rightarrow \alpha$ transformation is very sluggish. The partitionless massive transformation is fully controlled by interface migration, which has an interface velocity in the order of magnitude about 10^{-6} to 10^{-5} m/s and generally keeps this interface velocity during the transformation [6, 7]. Thermodynamically speaking, the

transition from partitioning to partitionless transformation should occur at the critical temperature T_0 where the Gibbs energy of α phase is equal to that of γ phase with same concentration. However, in fact, the experimental kinetic transition temperature can deviate from T_0 due to the complex interaction between X and interface migration, which was considered to be due to the solute drag effect of X [8–10].

The solute drag effect of X, such as Mn or Mo, has been widely studied in Fe–C–X alloys [11–13]. It is far less studied in interstitial-free Fe–X alloys, even though C was reported to have important effects on the interaction between X and migrating interface [14, 15]. Besides, currently, much effort has been made on studying the $\gamma \rightarrow \alpha$ transformation in Fe–X alloys during continuous cooling from single γ phase region [7, 16, 17]. Nevertheless, the isothermal $\gamma \rightarrow \alpha$ transformation in Fe–X alloys is rarely investigated. It was usually accepted that the kinetic mode of $\gamma \rightarrow \alpha$ transformation could be either fast partitionless mode or the sluggish partitioning mode. However, in this study, we experimentally observed a new kinetic mode in which interface migration was controlled by interfacial diffusion. A phase-field model with considering interfacial segregation was proposed to successfully predict this new kinetic mode.

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2 Experimental

The kinetics of isothermal $\gamma \rightarrow \alpha$ transformation in Fe–2Mn and Fe–2Mn–0.5Mo alloys (all in wt%), as well as the alloying effects of Mn and Mo, will be experimentally and theoretically studied. The chemical composition and T_0 of the two alloys investigated in this study are listed in Table 1.

The standard cylinder specimens with dimensions of 4 mm in diameter and 10 mm in length are prepared for dilatometry experiments. The dilation of the specimens during heat treatment is measured by a Bahr 805A-type dilatometer. The specimens were first heated up to 950 °C for full austenization at a heating rate of 5 K/s and held for 5 min. Then, the specimens were cooled down at a cooling rate of 20 K/s to different holding temperatures for isothermal $\gamma \rightarrow \alpha$ transformation. The kinetics of the isothermal transformation can be derived by lever rule according to the dilation curves. It is worth mentioning that the massive $\gamma \rightarrow \alpha$ transformation during cooling after the isothermal holding cannot be avoided in present experiments, even if the largest cooling rate (> 200 K/s) of the dilatometer has been tried.

3 Model Description

In this study, a phase-field method, which takes interfacial segregation into account, is proposed to simulate the $\gamma \rightarrow \alpha$ transformation in Fe–2Mn and Fe–2Mn–0.5Mo alloys. The total Gibbs energy of a ternary system is given by

$$G = \int_{\Omega} \left[\frac{1}{V_m} G_m(\phi, x_i) + \frac{1}{2} \varepsilon^2 |\nabla \phi|^2 \right] \cdot dV, \quad (1)$$

where G_m is the molar Gibbs energy. x_i is the mole fraction of component i ($i = 1, 2, 3$). V_m is the molar volume of the system. ε^2 is the gradient coefficient. ϕ is the phase-field variable with value 0 in α phase and value 1 in γ phase. Therefore, the value of ϕ at the interface region between the two phases continuously changes from 0 to 1, and the molar Gibbs energy can be written as

$$G_m(\phi, x_i) = G_m^{\alpha} [1 - p(\phi)] + G_m^{\gamma} p(\phi) + W(x_i)g(\phi). \quad (2)$$

Here, a monotonic function $p(\phi) = \phi^3(10 - 15\phi + 6\phi^2)$ that has $p(0) = 0$ and $p(1) = 1$ reproduces the molar

Gibbs energy of each phase. A double well potential $g(\phi) = \phi^2(1 - \phi)^2$ with its height $W(x_i)$ is adopted within the interface region. Taking Fe–Mn–Mo system as an example, the molar Gibbs energy of each phase can be described by regular solution model as

$$G_m^{\varphi} = \sum_i x_i^{\varphi} G_i^{\varphi} + RT \sum_i x_i^{\varphi} \ln x_i^{\varphi} + \sum_i \sum_j \Omega_{ij}^{\varphi} x_i^{\varphi} x_j^{\varphi} + \Omega_{123}^{\varphi} x_1^{\varphi} x_2^{\varphi} x_3^{\varphi}, \quad (3)$$

where $\varphi = \alpha, \gamma$ represents different phases. G_i^{φ} is the molar Gibbs energy of pure i in standard state in φ phase. x_i^{φ} is the mole fraction of i in φ phase. R is the universal gas constant, and T is the absolute temperature. The term $\Omega_{123}^{\varphi} x_1^{\varphi} x_2^{\varphi} x_3^{\varphi}$ represents the mixing molar Gibbs energy of φ phase. In order to take interfacial segregation into account, $W(x_i)$ should decrease if the solute concentration at interface increases. According to the assumption for GB segregation [18] and interface segregation in binary alloys [10], a linear concentration dependency is introduced in W by

$$W(x_i) = w \left(1 - \sum m_i \cdot x_i \right), \quad (4)$$

where both w and m_i are positive constants. The solute will tend to segregate to the interface to lower the interfacial energy. The coefficient m_i describes the interaction between component i and interface, and determines the binding energy E_0 which can be obtained from first-principle calculations or the commonly used values in the literature.

The temporal evolution equation of non-conserved phase-field variable ϕ is governed by Allen–Cahn equation [19], combining with Eq. (1), we have

$$\frac{\partial \phi}{\partial t} = -M_{\phi} \frac{\delta G}{\delta \phi} = M_{\phi} \left(\varepsilon^2 \nabla^2 \phi - \frac{1}{V_m} \frac{\partial G_m}{\partial \phi} \right). \quad (5)$$

Here, $M_{\phi} = (\sigma/\varepsilon^2)M_{\text{int}}$ is a parameter related to the intrinsic interface mobility M_{int} . σ is the interfacial energy.

The temporal evolution equation of conserved concentration x_i can be obtained according to mass balance equation. Regarding Eq. (1), we have

$$\frac{1}{V_m} \frac{\partial x_i}{\partial t} = -\nabla \cdot J_i, \quad (6)$$

where J_i is the flux of component i . Then, J_i can be obtained from Onsager equation:

$$J_i = - \sum_{j=1}^{N-1} L_{ij}'' \nabla \left(\frac{\delta G}{\delta x_j} \right), \quad (7)$$

L_{ij}'' is a matrix related to diffusion mobility M_i , which can be expressed by [20, 21]:

Table 1 Chemical compositions and T_0 for the two alloys

Alloy	Composition (wt%)			T_0 (°C)
	Mn	Mo	Fe	
Fe–2Mn	2.08	–	Bal.	802
Fe–2Mn–0.5Mo	2.11	0.49	Bal.	809

$$L''_{ij} = \sum_{k=1}^N \sum_{r=1}^N (\delta_{ik} - x_i)(\delta_{jr} - x_j)L_{kr}. \quad (8)$$

Here, if $i = j$, then $L_{ii} = x_i M_i$; if $i \neq j$, then $L_{ij} = 0$. M_i at interface is assumed to be:

$$M_i = (1 - p(\phi))M_i^\alpha + p(\phi)M_i^\gamma, \quad (9)$$

where M_i can be obtained with diffusivity D_i by Einstein's relation $M_i = D_i/RT$.

In the following, a two-phase system with evenly distributed solute is considered, and the interface is assumed to be 1 nm thick. All the thermodynamic data used in the simulations are obtained from Thermo-Calc with TCFE7 and MOB2 database. The governing equations, i.e., Eqs. (5) and (6), are solved in their dimensionless forms using Fourier spectral method [22]. The length is normalized as $\tilde{z} = z/h$, where $h = 0.2$ nm is the grid size. The time is normalized as $\tilde{t} = t \cdot D_0/h^2$, where $D_0 = M_i^\alpha RT$ is chosen as a reference diffusivity. The reference energy is obtained as RT . The values of simulation parameters are given as $V_m = 7 \times 10^{-6}$ m³/mol, $\epsilon^2 = 4 \times 10^{-10}$ J/m, $\sigma = 0.3$ J/m², $w = 3 \times 10^4$ J/mol. The α/γ interface mobility is expressed as $M_{\text{int}} = 2.7 \times 10^{-6} \exp(-145000/RT)$ m⁴/(Js) [7]. The binding energies of Mn and Mo are set to be 8 and 22 kJ/mol, respectively, which are comparable with those reported in the literature for Mn [2, 23] and Mo [24, 25].

4 Results and Discussion

The measured kinetics of isothermal $\gamma \rightarrow \alpha$ transformation in the Fe–2Mn and Fe–2Mn–0.5Mo alloys at different temperatures is shown in Fig. 1. It can be seen that there is almost no transformation within 200 s at 760 °C for both alloys. However, when the temperature is down to 700 °C, the transformation almost finishes within 30 s for the Fe–2Mn alloys and transforms about 80% in 60 s for the Fe–2Mn–0.5Mo alloys.

Using Eq. (10), the α/γ interface velocity can be estimated from the transformation curves (linear stage) in Fig. 1 according to Refs. [6, 7, 17]:

$$v_{\alpha/\gamma} = \frac{df_\alpha/dt}{3(N^* \cdot g)^{1/3} (1 - f_\alpha^2) \operatorname{arctanh}^{2/3}(f_\alpha)}. \quad (10)$$

Here, $v_{\alpha/\gamma}$ is the α/γ interface velocity; f_α is the fraction of ferrite; N^* is the density of nuclei per volume (it can be estimated as d^{-3} , and d is the average grain size of ferrite); and g is the geometrical factor ($g = 1$ for cubic growth and $g = 4\pi/3$ for spherical growth).

Then, in Fig. 2a, the experimental interface velocity is compared with the PFM prediction as a function of temperature. The PFM predicts three kinetic modes for

Fig. 1 Ferrite (α) fraction as a function of time during isothermal holding at various temperatures in **a** Fe–2Mn, **b** Fe–2Mn–0.5Mo alloys

the $\gamma \rightarrow \alpha$ transformation at different temperatures, which generally agrees with the experimental results. The Mn profiles at three typical temperatures are shown to demonstrate the kinetic modes. In Fig. 2b, there is evident Mn partitioning from α to γ when the temperature is relatively higher (e.g., 780 °C), which is a partitioning transformation (denoted as mode I). The kinetics of interface migration in mode I is controlled by Mn diffusion in γ . Besides, in Fig. 2d, Mn hardly diffuses between the two phases nor segregates to the interface at relatively lower temperature (e.g., 700 °C) during the transformation, which is a partitionless massive transformation (denoted as mode III). Transformation kinetics in mode III is interface-controlled. The partitioning and partitionless transformation modes have already been predicted and experimentally detected during the $\gamma \rightarrow \alpha$ transformation upon continuous cooling [3, 7, 26].

At an intermediate temperature (e.g., 740 °C), significant interfacial segregation of Mn is predicted as shown in Fig. 2c. The Mn spike is about 1 nm thick, which is inside the interface, and there is no obvious Mn partitioning (denoted as mode II). Correspondingly, interface velocity in mode II at 740 °C is somewhat between that in mode I and mode III. To the authors' best knowledge, a new type of transformation mode between sluggish partitioning transformation and fast massive transformation is found here. Different from mode I, there is only interfacial segregation of Mn but no Mn partitioning between γ and α in

Fig. 2 Austenite (γ)-to-ferrite (α) transformation in an Fe-2Mn alloy, **a** the experimental α/γ interface velocity compared with PFM predictions at different temperatures, and the predicted Mn profiles at **b** 780 °C, **c** 740 °C, **d** 700 °C

mode II. The kinetics of interface migration is controlled by interfacial diffusion of Mn when the transformation is in mode II.

Similar PFM simulations have also been carried out for the Fe-2Mn-0.5Mo alloys. As shown in Fig. 3a, compared with the experimental results, the kinetic transition from 780 to 700 °C has also been predicted by PFM simulations. The Mn and Mo profiles at different typical temperatures are shown in Fig. 3. In Fig. 3b, there is evident Mn partitioning from α to γ phase as well as interfacial segregation of both Mo and Mn when the temperature is relatively higher (e.g., 780 °C, mode I), which is a partitioning transformation mode (denoted as mode I). In Fig. 3d, neither Mn nor Mo diffusion occurs at relatively lower temperature (e.g., 700 °C), which is a partitionless massive transformation mode (denoted as mode III). At an intermediate temperature (e.g., 740 °C, mode II), significant segregation of both Mn and Mo is predicted to occur, which is within the interfacial region, while there is no solute partitioning between γ and α , as indicated in Fig. 3c. Therefore, an intermediate type of $\gamma \rightarrow \alpha$ transformation kinetics between sluggish partitioning transformation and fast partitionless transformation is also experimentally found in Fe-2Mn-0.5Mo alloys. Based on PFM predictions, the distribution of Mn at different

temperatures in Fe-2Mn-0.5Mo alloys is similar to that in Fe-2Mn alloys.

Mo is widely added to retard $\gamma \rightarrow \alpha$ transformation, and it has been reported in the literature that even 0.5 wt% Mo addition has great influence on the kinetics of $\gamma \rightarrow \alpha$ transformation in carbon-contained steels [13, 27]. However, in our study, comparing the experimental results of two interstitial-free steels in Fig. 4, it is interestingly found that the addition of 0.5 wt% Mo has a marginal effect on the transformation kinetics. In mode I (e.g., 780 °C), i.e., the partitioning mode, the kinetics of interface migration is controlled by the diffusion of Mn and Mo in γ , which is extremely sluggish. In mode II (e.g., 740 °C), the kinetics of interface migration is controlled by the interfacial diffusion of Mn and Mo. The difference between interfacial diffusion of Mn and Mo could be negligible, which could explain why interface velocities for Fe-2Mn and Fe-2Mn-0.5Mo alloys in mode II are similar. In mode III (e.g., 700 °C), i.e., the partitionless mode, the kinetics of interface migration is controlled by the intrinsic interface mobility and chemical driving force for the $\gamma \rightarrow \alpha$ transformation. Mo addition will not affect the intrinsic α/γ interface mobility. Besides, the chemical potential of Mo in α is quite comparable to that in γ , and thus Mo has a small effect on chemical driving force [28, 29] (T_0 changes only 7 °C with

Fig. 3 Austenite (γ)-to-ferrite (α) transformation in an Fe–2Mn–0.5Mo alloy, **a** the experimental α/γ interface velocity compared with PFM predictions at different temperatures, and the predicted solute profiles at different time at **b** 780 °C, **c** 740 °C, **d** 700 °C (the arrows on the axis indicate the positions of interface)

Fig. 4 Experimental α/γ interface velocity during $\gamma \rightarrow \alpha$ transformation in an Fe–2Mn alloy and an Fe–2Mn–0.5Mo alloy

0.5 wt% Mo addition according to Table 1). Therefore, Mo addition hardly changes the transformation kinetic modes of Fe–2Mn alloys.

5 Conclusions

In summary, the isothermal $\gamma \rightarrow \alpha$ transformation at various temperatures in the Fe–2Mn and Fe–2Mn–0.5Mo alloys has been studied. Mo addition is experimentally found to have a marginal effect on the transformation kinetics. It is also found that the transition from partitioning to partitionless transformation is not sharp. There can be a new kinetic mode, e.g., interfacial diffusion-controlled mode, in which the interface migrates at an intermediate velocity between sluggish partitioning transformation and fast partitionless transformation. The complex transition of kinetic modes could be well predicted by a phase-field model with considering interfacial segregation.

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