Prediction of Bainite Intervened in Ferrite-Pearlite Forging Steel
I. Modeling

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The successive ferrite (α) + pearlite (P) transformations from austenite (γ) were modeled to predict the presence of bainite in as-forged medium-carbon manganese steels. The kinetics of diffusional transformations were calculated based on classical nucleation and growth theory coupled with CALPHAD multi-component thermodynamics. The description of the growth rate of proeutectoid-α includes a time dependence due to the carbon enrichment in the remaining γ. The γ/α interface was assumed to be in negligible-partitioned local equilibrium (NPLE). The kinetics calculation of P nucleating on the α surface was integrated into the α model. Given the transformation temperature range in continuous cooling, the growth rate of P was also expressed in the NPLE constraint for γ/cementite. The concentration of untransformed γ (γU) can be monitored and should be dependent on the extent of the preceding transformations. Thus, the energies available for the nucleation and diffusionless growth of bainitic-α were evaluated from the thermodynamics of the γU single-phase system, which is proposed as a method to predict the inclusion of bainite in the final α + P microstructure.

1. Introduction

Medium-carbon manganese steels (MCMS) are used in large quantities as raw materials for various hot-forged auto parts. Their microstructure consisting of proeutectoid ferrite (α) and pearlite (P) is controlled mostly by the C and Mn content of the steels and the cooling rates. The α/P fraction has a primary effect on the average hardness which should be balanced under the requirement of proof strength and mass productivity. The bainite (B), a mixture of bainitic ferrite (αB) and fine cementite, is comparatively hard and undesired in the α + P microstructure because it degrades machinability in finishing final products. From the standpoint of global production, it is of concern that the fluctuation range of chemical compositions of supplied steels has become larger. In addition, a faster cooling is expected due to space-saving factory design, and even a slightly higher Mn content, which has not been a problem to date, may cause the problem of B in the near future. Thus, a computational prediction of B transformation would be very effective in reducing trial forgings with modified steel compositions and/or cooling schedules.

Many researchers followed the subunit model proposed by Bhadeshia and coworkers1–6 for the description of isothermal B kinetics from austenite (γ) grain boundaries. Still, the fundamentals of the transformation mechanism remain controversial. Apart from the complexity of the kinetics, the energies for the nucleation and growth of bainitic-α (αB) have been interpreted simply, and the criteria for αB formation has been formulated from experimental BS temperatures.1,7 In light of the MCMS grades and practical cooling rates, it is reasonable to assume that the rest of the volume occupied by proeutectoid α and P would result in B. The chemistry of untransformed austenite (γU) is altered by the partitioning during the preceding α transformation. However, the above αB criteria were calibrated for an undercooled γ single phase, and there is no evidence as to whether they can be applied to a detached volume of γU. In order to develop a simple treatment for the B fraction, this first paper aims to build a model that can accurately calculate the evolution of the α + P fraction and the thermodynamic energies for the transformation of γU into αB during continuous cooling.

2. Model and Calculation Methods

2.1 Framework of the model

The inputs for the present model are chemical compositions, γ grain size (dγ) and cooling rate. dγ is strongly related to hot-working conditions and can be estimated using empirical equations.8 Yogo9 proposed a modified expression that accounts for a short holding time in the forging process. Recently, the effect of the distribution of d0 has been incorporated into this kind of kinetic calculations.10 This should have a large effect, which will be discussed in the second paper.

Much effort has been devoted to understanding the kinetics of various phase transformations in steels. There are some integrated models11–14 that can reportedly predict the evolution of α, P, Widmanstätten-α, and B. These models were based on classical nucleation and growth theories (CNGT), developed for low-carbon steel strips, and thus, focused on the prediction of the α grain size which affects significantly the mechanical strength and elongation. For the sake of simplicity of analytical treatment, the present model basically follows the equations in CNGT. In particular, to predict the α/P fractions accurately, the effects of Mn content of MCMS have been studied extensively with respect to the partitioning between the γ and product phases.

In the following sections, the kinetic equations adopted were originally derived for isothermal conditions. The extension to continuous cooling has been made with the
assumption of the additivity rule. More specifically, the increases in the transformed \( \alpha \) and \( P \) volume were summed for small isothermal time-step along cooling schedules. And the thermodynamic condition was simultaneously evaluated for \( \gamma \) renewed in each time-step.

2.2 Multicomponent thermodynamic calculation

It is important to calculate the thermodynamic effect of Mn on the stability of \( \gamma \), a decisive factor for the phase transformation kinetics of steels. The CALPHAD method is now the standard for calculations in multicomponent thermodynamics. One of the commercial packages, ThermoCalc, was employed in the present modeling work with the aid of the programming interface TQ-i.

Coupled with the database TCFe3 and MOB2, the maximum driving force (\( \Delta G_{\text{max}} \)) for \( \alpha \) precipitation, the equilibrium C composition sets (\( X_{C}^{\gamma/\alpha,\text{PE}} \), \( X_{C}^{\alpha/\gamma,\text{PE}} \)), and the C diffusivities in \( \gamma \) (\( D_{C}^{\gamma/\alpha} \)) are calculated for a required composition in the Fe-C-Si-Mn-Cr system. The para-equilibrium (PE) calculation subroutine in TQ-i was used to get \( X_{C}^{\gamma/\alpha,\text{PE}} \) and \( X_{C}^{\alpha/\gamma,\text{PE}} \). Using other subroutines, we can set and delete diverse equilibrium conditions such as the status of partitioning in a precipitating phase. It has been found that the following procedures successfully yield the interface compositions under negligible-partitioned local equilibrium (NPLE), in this case, with reference to Mn.

1. Calculate the initial \( \gamma + \alpha \) equilibrium for the alloy compositions.
2. Fix the \( \alpha \) status to zero mole. Delete the condition of initial C composition (\( X_{C}^{\alpha} \)).
3. Calculate equilibrium and the new bulk compositions will be on the \( \gamma / (\gamma + \alpha) \) boundary.
4. Set the concentration of non-partitioning elements in \( \alpha \) (\( X_{\text{Mn}}^{\alpha} \)) to the same value as the initial composition (\( X_{\text{Mn}}^{\alpha} \)). Delete the condition of \( X_{\text{Mn}}^{\alpha} \) for bulk.
5. Calculate equilibrium and the new composition set for \( \gamma \) and \( \alpha \) will give the NPLE relation (\( X_{C}^{\gamma/\alpha,\text{NPLE}} \), \( X_{C}^{\alpha/\gamma,\text{NPLE}} \)).
6. Get the activity of the system. Set the same for the activity of \( \gamma \). Delete the condition set in (2) and change the \( \alpha \) status suspended (\( \gamma \) single phase).
7. Calculate equilibrium and the bulk composition moves along the isoactivity line and gives the highest possible C concentration in \( \gamma \) for the \( \gamma \)-to-\( \alpha \) transformation to proceed (\( X_{C}^{\gamma/\alpha,\text{NPlimit}} \)).

Figure 1 is an example of the calculated special \( \gamma / \alpha \) equilibrium interpolated on the Fe-Mn-C isopleth, vertical section of the constant Mn content. The alloy compositions are Fe-0.39%C-1.3%, 1.5%, 1.7%Mn, respectively, and clearly, this small difference in Mn content promotes a larger shift in \( X_{C}^{\gamma/\alpha,\text{NPlimit}} \) than \( X_{C}^{\gamma/\alpha,\text{PE}} \).

2.3 Kinetics of proeutectoid ferrite

The incubation time (\( \tau \)) of the isothermal \( \alpha \) transformation was calculated in eq. (1) according to the pillbox model.\(^{15}\) The \( \gamma / \alpha \) interfacial energy (\( \sigma^{\gamma/\alpha} \)) and the volume occupied by an iron atom (\( \sigma^{\gamma/\alpha} \)) in \( \alpha \) were assumed to be 0.705 J/m\(^2\) and 8.785 \( \times \) \( 10^{-30} \) m\(^3\), respectively, as in Ref. 16. The average lattice parameter (\( a \)) was estimated from the experimental polynomials\(^{17}\) including the effect of alloying elements. The driving force per unit volume of \( \alpha \) (\( \Delta G_{\text{V}} \)) is equal to the \( \Delta G_{\text{max}} \) divided by the \( \alpha \) molar volume (\( V_{\alpha} \)). \( X_{C}^{0} \) is the initial C content and the other symbols have their usual meanings.

\[
\tau = \frac{12kT\sigma^{\gamma/\alpha}}{D_{C}^{\gamma/\alpha} \cdot \gamma^{2} \cdot \Delta G_{V}}
\]  

The nucleation rate of \( \alpha \) (\( I \)) on the \( \gamma \) grain boundary surface was calculated in eq. 2 following the expression in Ref. 11. The parameter \( K_{1} \): 1.739 \( \times \) \( 10^{36} \) K\(^{0.5} \)/m\(^4\), is related to the density of nucleation sites, and \( K_{2} \): 6.6 \( \times \) \( 10^{8} \) J/mol\(^3\), includes the geometry factor of the nuclei as well as the ratio of the interfacial energies for \( \gamma / \alpha \) and \( \gamma / \gamma \).\(^{18}\) As we discuss later when we examine the C enrichment in \( \gamma \), the \( X_{C}^{\gamma} \) in eq. 4 was recursively input after calculating the volume increment of \( \alpha \) in a previous time-step. The nucleation, however, saturates soon and the enrichment has

- \( a \)
- \( k \)
- \( T \)
- \( \Delta G_{V} \)
- \( D_{C}^{\gamma/\alpha} \)
- \( \gamma^{2} \)
- \( kT \)
- \( K_{1} \)
- \( K_{2} \)
- \( X_{C}^{0} \)
- \( I \)
- \( \sigma^{\gamma/\alpha} \)
- \( \Delta G_{\text{max}} \)
- \( \gamma \)
- \( \alpha \)
- \( V_{\alpha} \)
- \( \Delta G_{V} \)
- \( X_{C}^{\gamma} \)

### Fig. 1
Calculated effect of Mn content on \( \gamma / \alpha \) para-equilibrium (PE) and negligible-partitioned-local-equilibrium (NPLE).
Fig. 2 Calculated free energy change for the nucleation and diffusionless growth of $\gamma$ (see text for symbols) during continuous cooling transformations at 40 K/min. The alloy compositions are Fe-0.39%C-1.3/1.5/1.7%Mn. The results are displayed in two divided figures to show small difference among the alloys.

no significant effect on $I$ compared with the effect on the growth rate.

$$I = \frac{K_1(1-X_d^p)D_C^p}{\sqrt{T}} \exp\left(-\frac{K_2}{RT \Delta G_I}\right)$$

(2)

Assuming carbon-diffusion-controlled growth, the parabolic growth rate constant ($\alpha_1$) was expressed in eq. 3, which can be solved numerically. Interfacial C compositions ($X_C/C^{a/\gamma}$, $X_C/C^{a/\gamma}$) are conventionally estimated under PE for the transformations of low-carbon steels. Recently, the issue has reemerged and non-constant interface compositions have been proposed even those operating in isothermal transformations. The authors have reported that the calculated kinetics of $\alpha$ under the PE condition was far beyond the experimental fraction in 0.37%C-1.45%Mn steel isothermally transformed at 973 K. A transition model from the PE to NPLE can be fitted to the experimental result, but no criteria for the transition to occur has been found for Fe-C-Ni alloys.

We also investigated the isothermal $\alpha$ transformation behaviors in a series of 0.39%C-Mn, and revealed the large effect of a small fluctuation in Mn content on the evolution of $\alpha$ fraction. To explain the experimental results we relied on Fig. 1, which clearly shows that the Mn content in the range of interest alters the $X_C/C^{a/\gamma}$, especially when the $\gamma$-Fe is the NPLE condition was adopted in the model.

$$2 \sqrt{\frac{D_C^p}{\pi}} \frac{X_C^{a/\gamma} - X_C^{a/\gamma}}{X_C^{a/\gamma} - X_C^{a/\gamma}} = \alpha_1 \exp\left\{\frac{\alpha_1^2}{4D_C^p}\right\} \text{erf}\left(\frac{\alpha_1}{2\sqrt{D_C^p}}\right)$$

(3)

The soft impingement effect (SIE) is rather pronounced in medium-carbon steels and has to be properly modeled for $\alpha$ growth. The regressive, mean-field approximation has been implemented to calculate C enrichment by the growth of film-like $\alpha$ from the $\gamma$ grain boundary. In eq. 3, the C content away from the interface ($X_C^{a/\gamma}$) is conveniently represented by the average C content in $\gamma$ ($X_{\text{Charm}}$). Accordingly, $\alpha_1$ is constantly updated with a new volume fraction of $\alpha$ ($V_1$) using the relation in eq. 4. This makes $\alpha_1$ time-dependent, and in this sense, other parameters such as $I$ and $D_C^p$ are also recalculated by inputting the new $X_{\text{Charm}}$.

$$X_C^{\alpha} \approx X_C^{\gamma} = \frac{X_C^{\alpha(0)} - V_1 X_C^{a/\gamma}}{1 - V_1}$$

(4)

The volume fraction of proeutectoid-$\alpha$ ($V_1$) was calculated in the following manner.

$$R_i^2(T_n, T_k) = \sum_{i=1}^{n} \left[ \alpha_1^{n}(T_i) \cdot \Delta t \right]$$

(5)

Usually the $\alpha$ grains are assumed to be ellipsoidal hemispheres having a three times longer axis along the $\gamma$ grain boundary. Consider a parallel plane at a distance of $y$ from the $\gamma$ grain boundary. The extended area of the cross-section ($y_{\text{ex}}$) of $\alpha$ hemispheres and the plane is expressed in eq. 6. Thus, the $V_1$ at $T_n$ can be calculated by the integral of $y$ from 0 to the maximum $R$ value multiplied by the $\gamma$ grain boundary area per unit volume ($S_y$).

$$y_{\text{ex}} = 0 \quad \text{for} \quad y > R(T_n, T_k)$$

$$= \sum_{i=1}^{n} \left[ I \cdot \Delta t \cdot \pi \sum_{i=0}^{n} \left( 9R_i^2(T_n, T_k) - y^2 \right) \right]$$

(6)

$$V_1(T_n)/V_1^{eq}(T_n) = 1 - \exp\left[-2S_y \int_{0}^{R(T_n, T_k)} \{1 - \exp(-y_{\text{ex}})\}dy\right]$$

(7)

$S_y$ is related to $d_0$, and is estimated to be 2.37$/d_0$ for truncated octahedron grains. Finally, $V_1$ must be normalized with respect to the equilibrium fraction $V_1^{eq}$ defined by the lever rule.
2.4 Kinetics of pearlite

Before the start of P transformation, the \( \gamma \) grain boundaries in MCMS are in most cases covered with the preceding \( \alpha \). Thus, \( P \) kinetics have been modeled following the comprehensive work by Capdevila et al.,\(^{24}\) in which \( P \) nodules are predominantly formed from \( \gamma \) attached to the \( \alpha \) grains. In general, as a thermodynamic condition, the \( P \) transformation is possible from \( \gamma \) with \( X_{\text{bar}} \gamma \) higher than the \( \gamma/(\gamma + \theta) \) boundary;

\[
X_{\gamma}^{\gamma/\theta} \leq X_{\text{bar}}^{\gamma/\theta}
\]  

(8)

The present model determines the start of \( P \) when the additional kinetic condition is fulfilled. \( P \) nodules to form on the surface of growing \( \alpha \) grain, the velocity of the migrating \( \gamma/\alpha \) interface \( (v^{\gamma/\alpha}) \) should be low enough to allow the nucleation of cementite \( (\theta) \) particle. The critical velocity has been analyzed by Aaronson et al.\(^{25}\)

In eqs. 9, \( a^{\gamma} \) is the lattice parameter in \( \gamma \), \( \Delta G^{\alpha/\gamma} \) is the volume free energy change associated with \( \theta \) nucleation given conveniently by eq. 10. \( K \) is a constant that equals \( 1.0 \times 10^{-4} \) and \( \sigma^{\alpha/\gamma} \) is the \( \alpha/\gamma \) interfacial energy for which a value of \( 0.68 \text{ J/m}^2 \) was adopted.

\[
\nu^{\gamma/\theta} \leq \frac{-(a^{\alpha})^3 D^{\gamma/\theta}_{\alpha} (\Delta G^{\theta}_{\gamma})^3}{16(1 - \omega^{\gamma/\theta}/2\alpha^{\gamma/\theta}) \sqrt{\pi k T (\omega^{\gamma/\theta})^2} K}
\]

(9)

\[
\nu^{\gamma/\theta} = \frac{\alpha_1}{2} \sqrt{f}
\]

\[
\Delta G^{\theta}_{\gamma} = 6.914 \cdot 10^8 \cdot (A_1 - T)/A_1, \ 1/\text{m}^3
\]

(10)

The nucleation rate of pearlite \( (I_P) \) was formulated in a manner similar to that proposed by Reed and Bhadheia\(^{26}\) for the \( \alpha \) nucleation from \( \gamma \) grain surfaces, edges, and corners.

A series of papers have discussed the diffusion-controlled growth of \( P \) in the Fe-Mn-C system,\(^{24,27,28}\) and it was proposed that either the growth rate with full partitioning of Mn or the growth rate in NPLE operated depending on the temperature. Considering a narrow temperature range and a small possibility of Mn partitioning at a practical cooling rate, we have taken the NPLE expression for \( P \) growth rate \( (G) \). The \( \gamma/\theta \) interface \( C \) concentrations in eq. 11 should be given in the NPLE calculation as described for the \( \gamma/\alpha \) interface previously. The expressions for lamellar spacing \( S \), \( S_c \), were taken from Ref. 29).

\[
G = \frac{D_C^{\gamma/\theta}}{0.72 S_c S_p} \frac{X_{\gamma}^{\gamma/\theta} - X_{\gamma}^{\gamma/\theta}}{X_{\gamma}^{\gamma/\theta} - \sigma^{\alpha/\gamma}} \left[ 1 - \frac{S_c}{S_p} \right]
\]

(11)

\[
V_{eq}(T_n)/V_P = 1 - \exp \left\{ \sum_{i=1}^{n} G(T_i) \Delta t \cdot f(G, I_P, T_n) \right\}
\]

(12)

In eq. 12, the volume fraction of \( P \) \( (V_P) \) is analyzed assuming a semi-spherical geometry. The \( \alpha/\gamma \) interface area \( (S^{\gamma/\theta}) \) depends on \( V_\gamma \) and can be estimated by a simple expression: \( S_\gamma (1 - V_\gamma)^{2/3} \). The \( \phi \) is an integral constant that equals \( \gamma/G \), where \( \gamma \) is the normal distance from the surface of the parent \( \alpha \). \( V_{eq} \) is the equilibrium fraction of \( P \) defined in the relation\(^{19}\)

\[
V_{eq} = \frac{X_C^0 - X_C^{\alpha/\gamma}(T_n)}{X_C^{\gamma/\theta}(T_n) - X_C^{\alpha/\gamma}(T_n)}
\]

(13)

This expression has been revised in this work and it equals the rest of \( V_{eq} \) at the start and becomes unity at the temperature \( T^* \) where \( X_C^0 = X_C^{\gamma/\theta} \).

2.5 Start condition of bainite

The energetic criteria for the start of \( B \) from undercooled \( \gamma \) are:

1. The driving force \( (\Delta G_{\max}) \) for \( \alpha \) nucleation becomes larger than the function \( G_N \) irrespective of the steel composition, and
2. The free energy change associated with diffusionless growth \( (\Delta G^{\gamma->\gamma+\alpha}) \) exceeds the stored energy of bainite.

In the course of \( \alpha \) and \( P \) kinetics calculation, the average composition in the remaining \( \gamma \) is constantly monitored from the change in \( X_{\text{bar}} \gamma \). If \( \alpha \) growth so far results in a high \( V_\gamma \), the carbon swept by \( \alpha \) enriches in the remaining \( \gamma \) and the \( \Delta G_{\alpha} \) for \( \alpha \) nucleation should be small. This prevents the formation of \( \theta \) from \( \gamma \) and helps avoid \( B \) formation. Thus, these criteria have been applied to the \( \gamma \) single-phase system having the enriched \( C \) composition of \( X_{\text{bar}} \gamma \).

The \( G_N \) recently reviewed by Mateo\(^{3}\) for high-carbon steels was considered appropriate for the above purpose of predicting \( B \) from \( \gamma \). In his work, these energies were evaluated using MTDATA, and the chemical free energy change \( (\Delta G^{\gamma->\gamma+\alpha}) \) was used conveniently to avoid the complexity of the numerical analysis of \( \Delta G_{\max} \). We have interpreted \( \Delta G^{\gamma->\gamma+\alpha} \) as the difference between the free energy of the \( \gamma \) single phase with all the other phases suspended and of the \( \gamma + \alpha \) system in PE. \( \Delta G^{\gamma-\alpha\beta} \) could be calculated by taking the difference in free energies of \( \gamma \) and the forced \( \alpha \) single-phase system. These changes of phase status were controlled by \( TQ-i \).

3. Calculation Test

A test calculation was designed to see if the present combination of kinetic models reveals the difference in the energies concerning the \( \alpha \) \( \gamma \) from \( \gamma \). The compositions of the model alloys are Fe-0.39%C-1.3%, 1.5%, 1.7% Mn, which lets us focus on the effect of small Mn fluctuations. The histories of the energies are compared in Fig. 2 for continuous cooling at a rate of 50 K/min. The calculation starts at each Fs temperature of the alloy and terminates when the total transformed fraction becomes unity.

The chemical free energy change \( \Delta G^{\gamma->\gamma+\alpha} \) decreases with decreasing temperatures and coincides with the \( G_N \) function at around 793 K. Among the alloys, little difference
is predicted at this critical temperature. On the other hand, $\Delta G^{\alpha\rightarrow\alpha B}$ is positive at the start of transformation and diffusionless transformation becomes possible below around 873 K. Initially, 1.7%Mn steel has the highest positive energy and, as $\alpha$ transformation proceeds, the order of $\Delta G^{\alpha\rightarrow\alpha B}$ reverses owing to the difference in C enrichment. As a result, the entire volume transforms into $\alpha + P$ in 1.3%Mn steel before the criteria of $-400\,\text{J/mol}$ is reached. In contrast, the 1.5%Mn and 1.7%Mn steels fulfill the second criteria at around 798 K. On the basis of this result alone, it cannot be expected that these energy calculations on $\chi_1$ would provide an accurate $B$ fraction; however, at least it demonstrates the possibility of $B$ formation depending on the composition and cooling rate.

4. Conclusions

The model for $B$ formation from $\chi_1$ has been proposed, in particular for continuous cooling of MCMS. New treatments including the time-dependent growth rate and NPLE at the $\gamma/\alpha$ interface are intended a Mn-content-sensitive description of the preceding $\alpha$ transformation kinetics. This has been enabled by the recursive evaluation of C enrichment in $\gamma$ and a direct link with CALPHAD thermodynamic calculations. The energy criteria for nucleation and diffusionless growth of $\alpha_B$ were applied to $\chi_1$ during $\alpha + P$ transformations. This method showed the ability to predict the different possibility of $B$ caused by minor fluctuations in Mn content.

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