

Development of Phase-Field Model of Boronizing Process on Steels

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Abstract Boronizing is a thermo-chemical treatment that has been widely used to improve surface characteristics of metal. However limited study can be found on the detail behavior of phase transformation during this process. Therefore the present research tries to develop phase-field model to simulate the boride phase growth on the iron steels. The phase-field equations were derived from Ginzburg-Landau free-energy functional using Allen-Cahn and Cahn-Hilliard equations. Pre-exponential factor for interface mobility, M_0 , and temperature of process, T , were used as the variable parameter. It was observed, even though the present variations of M_0 does not influence the phase transformation rate, an optimization of this parameter is required in order to meet a good agreement between the phase transformation rate and boron concentration profile, since a slight difference of boron concentration profile was found for the variations of M_0 parameter. On the other hand, it was also observed that as the temperature of process increases from 1000K up to 1300K there is an increasing of phase transformation rate, which is also confirmed by the higher diffusion of boron. These observations agree with the previous finding that higher temperature is required in order to create more Fe₂B phase from austenite phase.

Key words: Phase-field method, Numerical simulation, Boronizing process, Iron steels

INTRODUCTION

Boronizing is a type of thermo-chemical treatment where boron atom is diffused into the metal substrate during high temperature process to form hard boride structure. FeB and Fe₂B are two common types of boride structure that is resulted after the process [1, 2]. The former is considered to be harder than the later but it is more brittle [1, 2]. Normally it is preferable to have single layer of Fe₂B on the substrate rather than having these two carbide phases in the coating layer. The presence of single or mixed layer of boride coating mainly depends on the condition of boronizing process. In most cases FeB phase is considered to form firstly before Fe₂B phase especially for the low temperature process [3]. However, for the case of high temperature process, 950-1100°C, and with the longer boronizing time single Fe₂B boride phase is possible to exist [2].

Beside having higher hardness compared to other types of thermo-chemical treatment products, boronizing product is also believed to offer a better strength to friction wear and abrasion [4-6]. Furthermore, its application in industry has been well accepted for long time such as EKabor boronizing agents that have proved to be very effective in industrial practice for more than 3 decades [7]. However less study on this process can be found in the literature compared to other types of thermo-chemical treatment. Therefore the present study made an effort to study the boronizing process by simulation work, especially on the kinetics of phase transformation and the boron concentration diffusion. Experimentally, this study requires a complex characterization work including the complex of sample preparation and the characterization technique it self. And it is expected, by conducting one dimensional phase-field

simulation, the simpler and easier way to study the kinetics of phase transformation of boride from austenite can be done and therefore the better understanding of this matter will also be obtained.

To the authors knowledge there are only few simulation works on boronizing process can be found in the literature. Among them are simulation works on boronizing process conducted by Brakman *et al.* [8] and Keddad [1]. Brakman *et al.* assume a parabolic growth of boron diffusion during boronizing process and take into account the specific volume difference between FeB and Fe₂B. On the other hand, Keddad works on the simulation of the growth kinetic of Fe₂B, taking into account the thermodynamic properties of the Fe-B phase diagram and adopting diffusivity of boron by Campos *et al.* [9]. In the present study, phase-field method was used to simulate the growth of single Fe₂B phase from austenite phase. This method has been proved to simulate many kinds of phase transformations, such as austenite-ferrite transformation in steel [10]. One important point from this method is the unnecessary of calculating the complex condition of the interface, which might bring difficult problem for the simulation works. In the following section, the construction of phase-field model for simulating the growth of Fe₂B from austenite phase will be presented.

PHASE-FIELD MODEL

Phase-field model for the evolution of boride phase during boronizing process was derived from Ginzburg-Landau free energy functional that take into account the chemical free energy and gradient energy as

$$G = \int_V \left[g(\phi, X_B, T) + \frac{\varepsilon^2}{2} |\nabla \phi|^2 \right] dV, \quad (1)$$

where ϕ is the phase field variable which varies smoothly across the interface from $\phi = 0$ in the austenite phase to $\phi = 1$ in the boride (Fe₂B) phase, X_B is the mole fraction of boron, T is the absolute temperature and ε is the gradient energy coefficient. The chemical free energy density $g(\phi, u_B, T)$ is expressed as

$$g(\phi, u_B, T) = p(\phi)G_m^{Fe_2B} + (1 - p(\phi))G_m^\gamma + Wq(\phi), \quad (2)$$

where $G_m^{Fe_2B}$ and G_m^γ are the chemical free energies of pure Fe₂B and austenite phases, respectively. $p(\phi)$ is an interpolating function expressed as $p(\phi) = \phi^3(10 - 15\phi + 6\phi^2)$ and $q(\phi)$ is a double well function with $q(\phi) = \phi^2(1 - \phi)^2$. W is the potential height defined as a function of interface energy (σ) and interface thickness (δ) as in the following equation

$$W = \frac{6\sigma b}{\delta}, \quad (3)$$

where b is the constant which is defined as $2 \tanh^{-1}(1 - 2\lambda)$ and λ is constant that is set at 0.1. Since phase field is a non-conserved order parameter, its time evolution equation can be derived from the above functional with the assumption that the total free energy decreases monotonically with time following the Allen-Cahn equation as follows,

$$\frac{\partial \phi}{\partial t} = -M_\phi \frac{\delta G}{\delta \phi} = M_\phi \left\{ \varepsilon^2 \nabla^2 \phi + 4W\phi(1 - \phi) \left(-\frac{15}{2W} \phi(1 - \phi) \Delta g + \phi - \frac{1}{2} \right) \right\}, \quad (4)$$

where M_ϕ is the kinetic parameter related to the mobility of the austenite-boride interface M as

$$M_\phi = \frac{\sqrt{2W}}{6\varepsilon} M. \quad (5)$$

On the other hand the interface mobility value, M , that will be used in the present research will follow the similar approach that is used by Mecozzi *et al.* [11] and Krielaart [12], where they defined interface mobility has a simple exponential dependence on temperature,

$$M = M_0 \exp(-E / RT), \quad (6)$$

where the activation energy, E , was taken from the experimental data conducted by Hasan *et al.* [13]. Pre-exponential factor, M_0 , will be used as the variable or fitting parameter as also performed by Mecozzi *et al.* and Krielaart. Vooijs *et al.* [14] proposed that the expected order of magnitude of M_0 can be predicted using the following equation

$$M_0 = \frac{kd}{hR}, \quad (7)$$

where d is the real interface thickness, h , R and k is the Planck's, gas and Boltzmann's constants, respectively. However the reliability of this approach requires further investigation, therefore Krielaart used a wide variation value in order to optimize this parameter, even though their prediction on this value is around 0.8 m/Js as calculated by Eq.7 using real interface thickness of 3 angstrom. For the present simulation work the optimization of M_0 values was done and it was varied at 0.8, 1,1.2, 1.4, 1.6 and 1.8 mol m/Js.

In Eq. 4, Δg is the chemical driving force and is defined as $\Delta g = G_m^{Fe_2B} - G_m^\gamma$. Where $G_m^{Fe_2B}$ and G_m^γ are the molar Gibbs free energy for boride and austenite respectively, and is also used as the value for chemical free energy of boride and austenite in the Eq.2. The molar Gibbs free energy in austenite phase, G_m^γ , was derived using CALPHAD method for two-sublattice model as

$$G_m^\gamma = y_{Fe}y_B {}^oG_{Fe:B}^\gamma + y_{Fe}y_\diamond {}^oG_{Fe:\diamond}^\gamma + RTy_B \ln y_B + RTy_\diamond \ln y_\diamond, \quad (8)$$

where y_{Fe} and y_B is the site fraction for iron and boron, respectively. ${}^oG_{Fe:B}^\gamma$ is the reference energy term for boron austenite and ${}^oG_{Fe:\diamond}^\gamma$ is the reference energy state for vacancy in austenite. In stead of using site fraction, molar fraction (X_{Fe} and X_B , molar fraction for iron and boron respectively) is used in the present research. The site fraction is defined by molar fraction as

$$y_B = \frac{a}{c} \frac{X_B}{(1-X_B)}, \quad (9)$$

where a is equal to c since we consider the fcc austenite Fe. On the other hand y_{Fe} is set as 1 since there is no other alloying element in the matrix.

${}^oG_{Fe:B}^\gamma$ is obtained from Fe-B thermodynamic optimization value by Van Rompaey *et al.* [15] as follow

$${}^oG_{Fe:B}^\gamma = H_B^{ser} + H_{Fe}^{ser} + 45496 - 77.534T, \quad (10)$$

where H_{Fe}^{ser} and H_B^{ser} is the enthalpy at reference state for iron and boron respectively and is obtained from SGTE database for pure elements [16]. On the other hand, the reference energy state for vacancy in austenite, ${}^oG_{Fe:\diamond}^\gamma$, in Eq.8 is obtained from Per Gustafson [17] and defined as

$${}^oG_{Fe:\diamond}^\gamma = H_{Fe}^{SER} - 237.57 + 132.416T - 24.6643T \ln T - 0.00375752T^2 - 5.89269E^{-8}T^3 + 77358.5/T \quad (11)$$

In order to allow a solubility range in the Fe_2B phase, the chemical free energy of Fe_2B is considered having a parabolic function of composition, X_B , following the similar approach by Huh *et al.* [18]

$$G_m^{Fe_2B} = 2. \times 10^5 (X_B - 0.33)^2 + {}^oG^{Fe_2B}, \quad (12)$$

where ${}^oG^{Fe_2B}$ is the reference energy term for the stoichimetric composition of Fe_2B and is obtained from optimization value by Van Rompaey *et al.* [15] as follow

$${}^oG^{Fe_2B} = H_B^{ser} + 2H_{Fe}^{ser} - 93363 + 481.992T - 79.04999T \ln T - 0.007071T^2 + 731991T^{-1}, \quad (13)$$

From Ginzburg-Landau free energy functional in Eq. 1, the nonlinear diffusion equation can also be derived by following the Cahn-Hilliard equation as follow

$$\frac{\partial X_B}{\partial t} = \nabla \left\{ M_B(\phi, X_B, T) \left(\frac{\partial^2 g}{\partial X_B^2} \nabla X_B + \frac{\partial^2 g}{\partial X_B \partial \phi} \nabla \phi \right) \right\}, \quad (14)$$

where M_B is diffusion coefficient of boron, and is defined as a function of diffusion coefficient of boron in austenite, M_B^γ , and boride, $M_B^{Fe_2B}$.

$$M_B(\phi, X_B, T) = (M_B^{Fe_2B})^{p(\phi)} (M_B^\gamma)^{(1-p(\phi))}. \quad (15)$$

Both M_B^γ and $M_B^{Fe_2B}$ has a temperature dependence function as

$$M_B^i = K \exp(-E / RT), \quad (16)$$

where M_B^i is the diffusion coefficient of boron in austenite or boride ($i = \gamma$ or Fe_2B), and K is the pre-exponential parameter of diffusivity. K values for boron in austenite and boride are set at $4.4 \times 10^{-8} \text{ m}^2/\text{s}$ and $1.13 \times 10^{-6} \text{ m}^2/\text{s}$ from Ref. [1].

COMPUTATIONAL MODEL

We performed one dimensional finite difference simulations of Eqs. 4 and 14. The computational domain is divided into 100 finite difference grids. Initial boron concentration was set at $X_B(i) = 0.5 - 0.001i$, for i less than 10, where i is the grid point number from left end, and at $X_B(i) = 0.3 - 0.0018i$ for the subsequent grids. On the other hand, initial phase-field variable was set as one dimensional equilibrium profile with origin at $i = 10$. Both of initial phase-field and boron concentration profile are illustrated in the Fig. 1. The size of computational domain is $100 \text{ }\mu\text{m}$ and Zero Neumann boundary condition is applied at both ends of computational domain. The interface thickness δ is set at $\delta = 12\Delta x = 12 \text{ }\mu\text{m}$ where Δx is grid size, whereas the interface energy, $\sigma = 1.0 \text{ J/m}^2$.

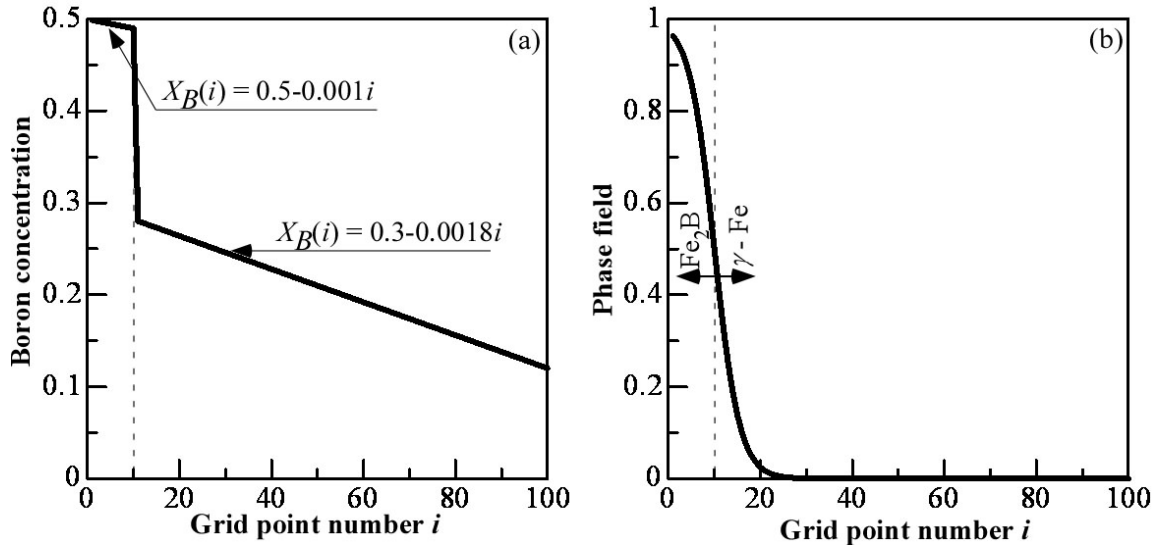


Fig. 1 Initial profiles for boron concentration (a) and phase field (b)

SIMULATION RESULTS

Figure 2 shows the typical boride layer that is growth on the steel substrate after boronizing process. Before this boride phases forms on the steel substrate, certain amount of boron has been diffused into certain depth of thickness inside the steel substrate as also explain by Xu *et al.* [2]. Here, the initial boron concentration profile is assumed to have a linier function on the depth of thickness and is set as $X_B(i) = 0.5 - 0.001i$, for i less than 10, and at $X_B(i) = 0.3 - 0.0018i$ for the subsequent grids, as has been explained in the previous section. The grid points here, i , is a representation of the depth of profile of boron inside the steel substrate.

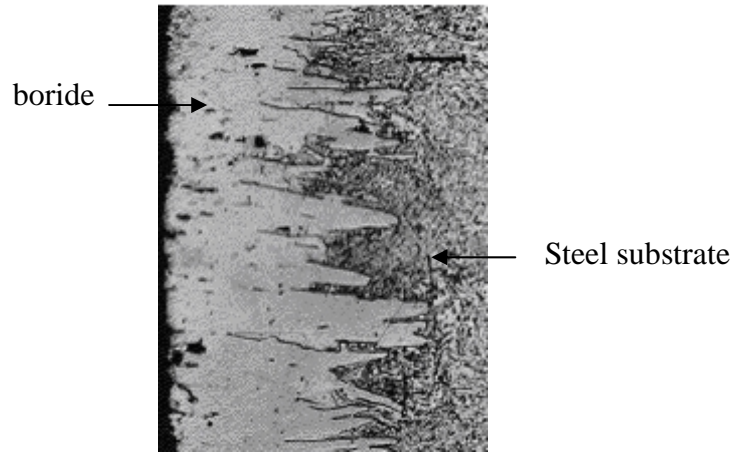


Fig. 2 Typical boride growth on steel substrate [19]

Figure 3 shows the effects of pre-exponential factor of interface mobility, M_0 , on the phase-field evolution, where the temperature is set constant at 1300K. In each figure of Fig.3, the growth of phase field is from the solid line (100 steps), followed with the long-dashed line (1000 steps) and ended with the dot line (2000 steps). From these figures, it can be seen that there is no significant differences between one figure to other, which give a suggestion that the present variations of M_0 have no effect on the kinetics of phase transformation. It is quite difficult to explain the reason why there is no effect of

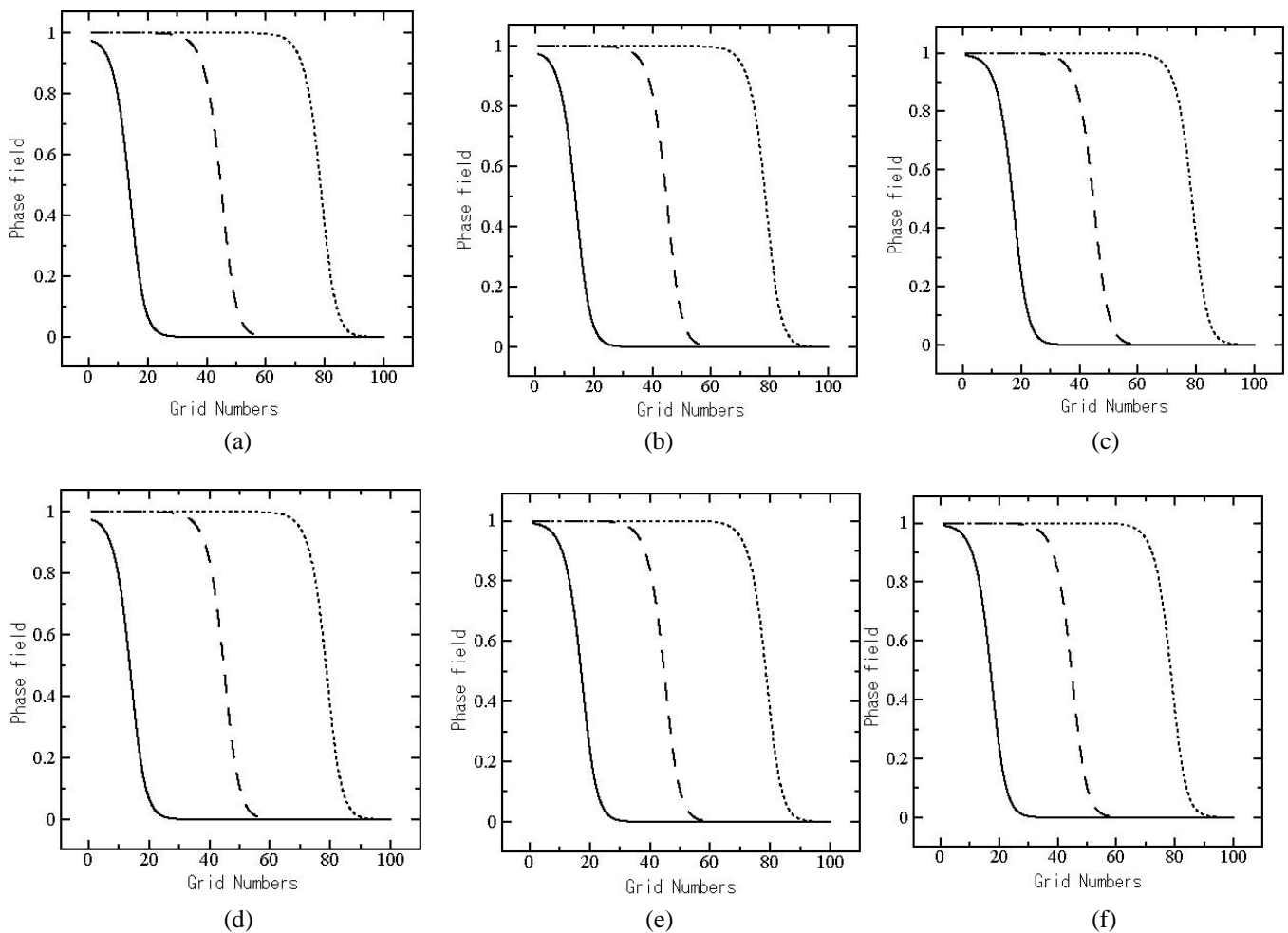


Fig. 3 The effect of pre-exponential factor of interface mobility on the kinetic of phase transformation
 (a) 0.8 mol m/Js, (b) 1.0 mol m/Js, (c) 1.2 m/Js, (d) 1.4 m/Js, (e) 1.6 m/Js and (f) 1.8 mol m/Js

this parameter on the phase transformations. However two explanations may be can be applied on this fact. The first is that the prediction on the order of magnitude of this parameter based on Eq. 7 is quite good and it requires higher order of magnitude of this parameter to change the kinetic of phase transformation. The second explanation is that other setting parameters for this simulation works might suppress the effect of this parameter on the kinetics of phase transformation.

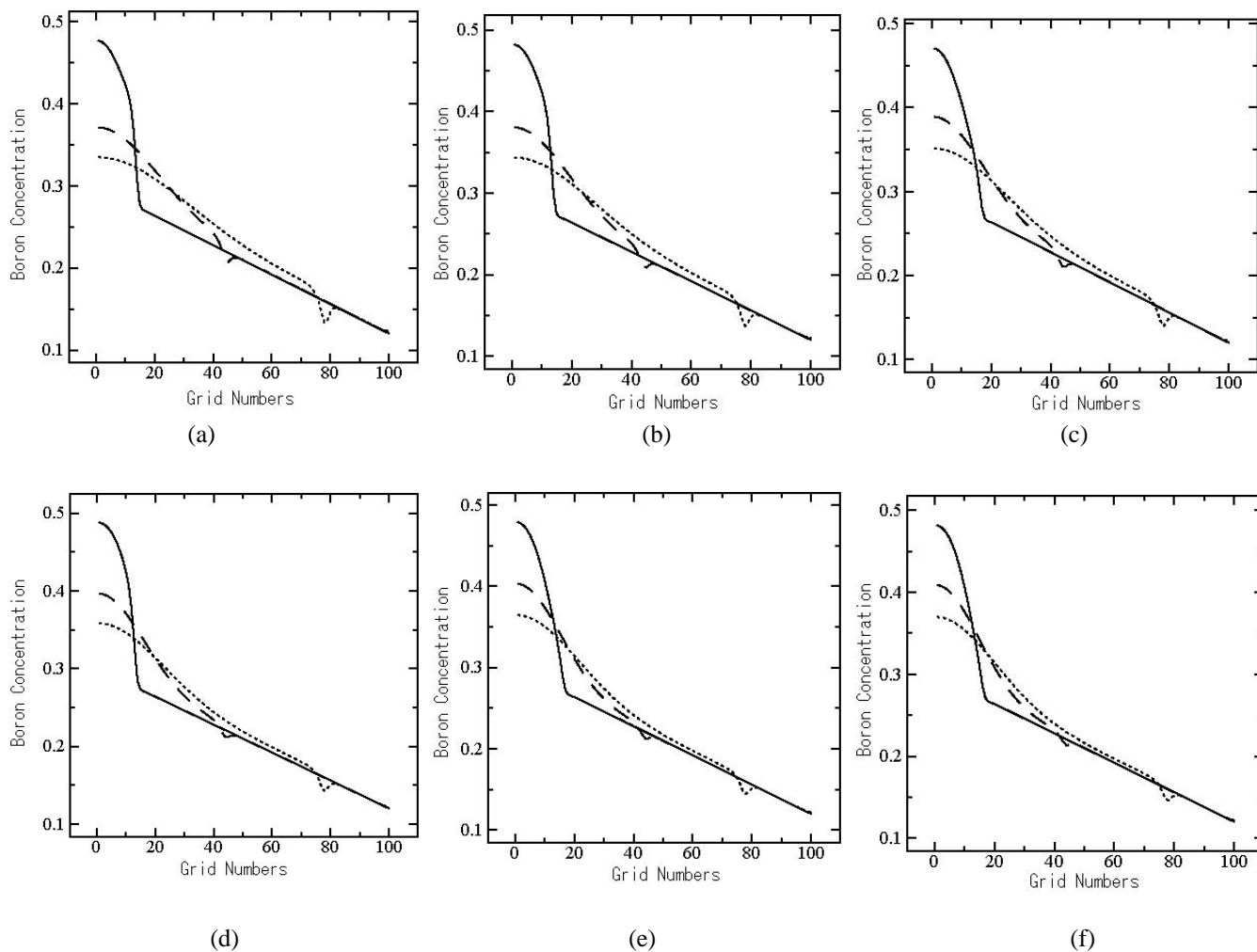
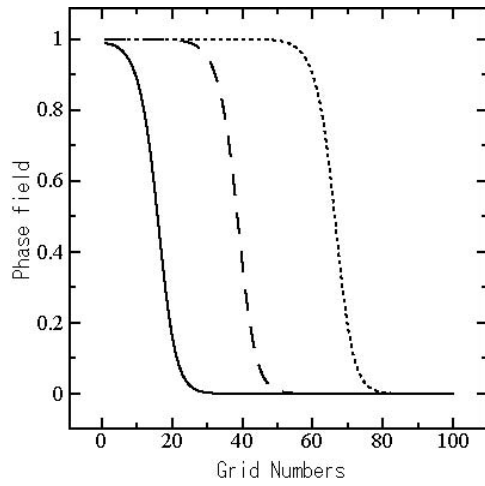
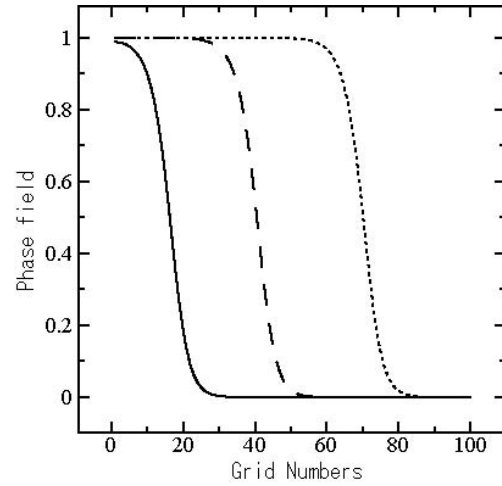


Fig. 4 The effect of pre-exponential factor of interface mobility on the boron concentration profile
 (a) 0.8 mol m/Js, (b) 1.0 mol m/Js, (c) 1.2 m/Js, (d) 1.4 m/Js, (e) 1.6 m/Js and (f) 1.8 mol m/Js

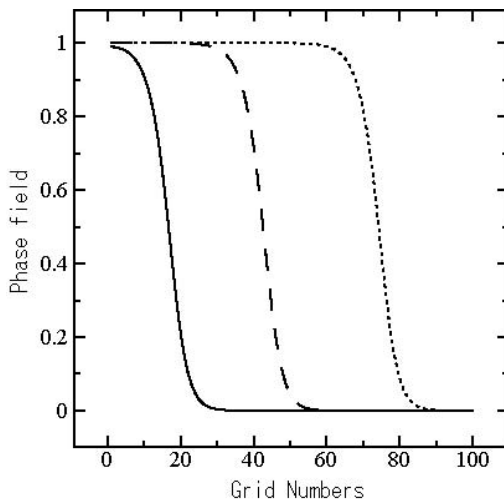
On the other hand, Fig. 4 shows the effect of M_0 on the boron concentration profile. The solid line, long-dashed line and dot line in these figures indicate the boron concentration profile after 100, 1000 and 2000 steps respectively. Generally, all figures show that there is a depletion of boron concentration at the grid numbers less than 10 which may correspond with the near-surface of boron in the real boronizing process. On the other hand, there is an increasing of boron concentration at the subsequent grid numbers. This observations give a suggestion that the near-surface boron diffuse into the inner part of substrate to form the thicker layer of boride as also confirm in the Fig. 3. This finding is also in a flow with the observation by Xu *et al.*[2] that the growth of boride structure is accompanied with the depletion of boron concentration on the surface. In addition, by relating Figs. 3 and 4, it can be seen that generally, boride phase in the inner part of substrate has a lower boron concentration compared with the boride phase in the near surface depth of profile. This situation is also observed by Keddad [1], where his calculation on the boron concentration profile resulted a linier decreasing of boron concentration in the area of boride phase as the depth of thickness increases.



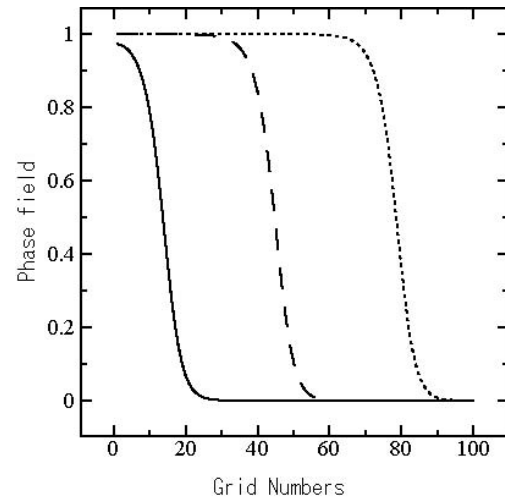
(a)



(b)



(c)



(d)

Fig. 5 The effect of Temperature of process on the kinetics of phase transformation (a) $T = 1000K$, (b) $T = 1100K$ (c) $T = 1200K$ and (d) $T = 1300K$

By comparing each figure in the Fig. 4, it can also be observed that a slight difference of boron concentration profile exists with the present variations of M_0 . It can be seen that as the M_0 value increases from 0.8 up to 1.8, there is a decreasing of diffusion of boron which is represented by the slower changing of boron profile from the black line up to the dot line. This condition indicates that higher value of interface mobility might inhibit the role of diffusivity on the phase transformation and optimization of this value is important in order to get the correct relation between the phase transformation kinetics and the diffusion of boron. Therefore it can be concluded that even though the present variations of M_0 does not have significant effect on the kinetics of phase transformation, however the determination of the correct value of this parameter is important in order to get the correct relation between the kinetics of phase transformation and the boron concentration profile.

Figure 5 shows the effect of temperature of process on the kinetics of phase transformation where M_0 value is set at 0.8 mol m/Js. It can be observed from this figure that there is an increasing of kinetics of phase transformation as the temperature of process increases. This condition is considered due to the increasing of kinetics of transformation as the temperature of process increases as also observed by Keddad [1]. This observation is also in a flow with the observation by Xu *et al.* [2], that single phase of Fe_2B may be exist by higher temperature of boronizing process in the range of 950-1100°C. This observation is also confirmed by the Fig. 6 that there is a slight difference of boron concentration profile

with the present variations of temperature. It can be seen from this figure that as the temperature of process increases, a higher diffusion of boron is observed. One point to be noted here is, since the present simulation works used similar value of pre-exponential diffusivity (K) for all temperature due to the unavailability data of K value of boron in boride for temperature other than 1300K, it is supposed that by implementing precise value of K for each temperature, a better understanding on the effect of temperature on the kinetic of phase transformation will be obtained.

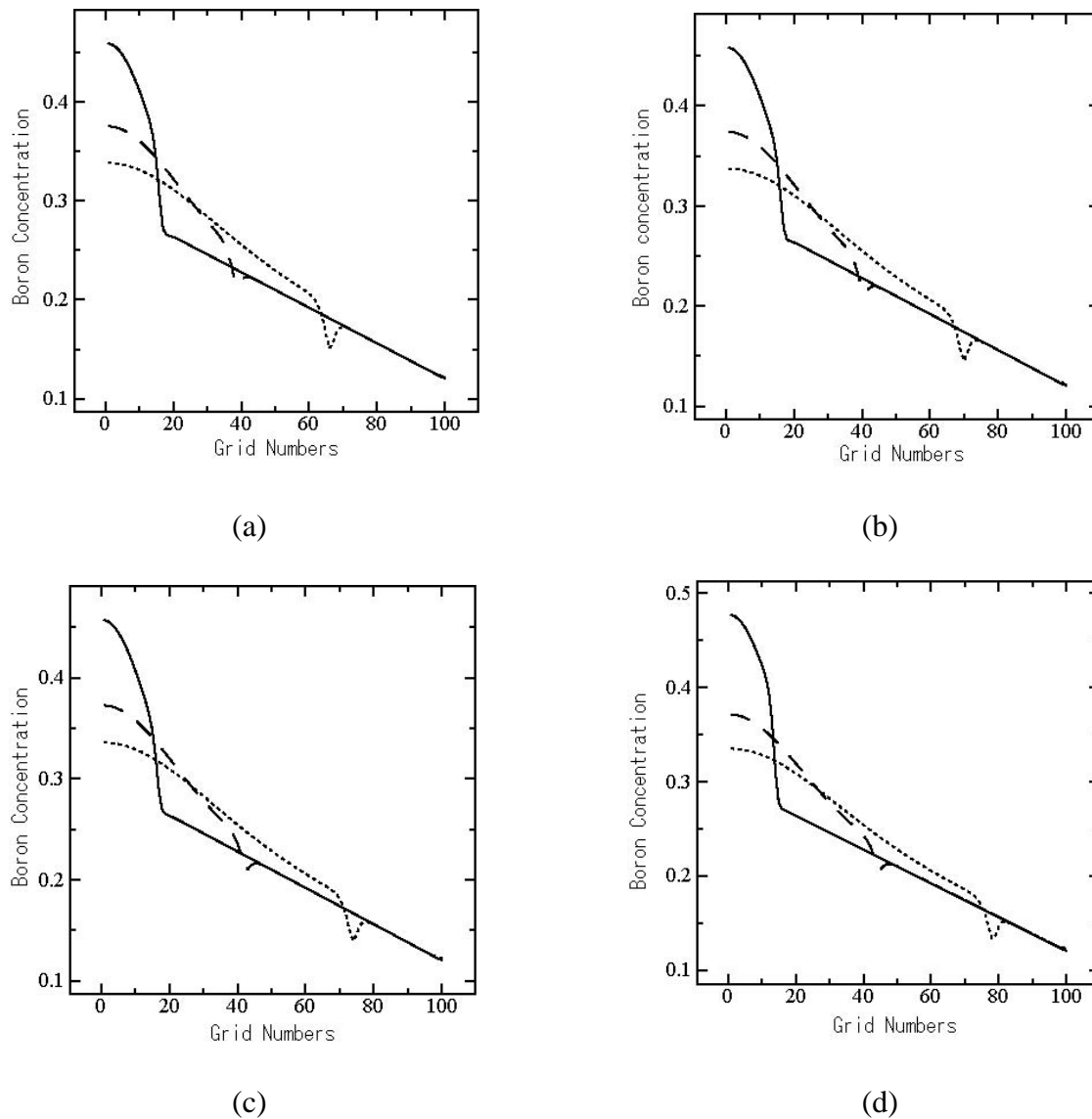


Fig. 6 The effect of Temperature of process on the boron concentration profile, (a) $T = 1000K$, (b) $T = 1100K$ (c) $T = 1200K$ and (d) $T = 1300K$

CONCLUSIONS

Phase-field model for the growth of Fe₂B phase from austenite phase was developed. For this purpose, several important parameters were taken from several literatures while the pre-exponential factor for interface mobility (M_0) and temperature of process (K) were chosen as the variable parameters. It was observed that the present variations of M_0 parameter does not influence the kinetics of phase transformation, which might indicate that a higher order magnitude of this parameter may be required to change the kinetics of phase transformation or the effect of this parameters might be suppressed by the setting of other parameter in the present simulation works. However since a slight difference in the boron concentration profiles were found with the present variations of M_0 value, it indicates that determination the optimum value of this parameter is required in order to get a good understanding between the kinetics of phase transformation and boron concentration profile. From the study on the effect of temperature of process on the kinetics of phase transformation and boron concentration profile, it was observed that there is a good agreement between the present simulation works and the previous study that higher temperature is required in order to allow higher phase transformation from austenite to Fe₂B. After all, it can be concluded that one dimensional phase-field method can be a good option for the easier and quicker study of the kinetics of phase transformation and boron concentration profile which might bring difficulty when study this subject experimentally.

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