

A kinetic model for analyzing the growth kinetics of Fe₂B layers in AISI 4140 steel

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Abstract

A kinetic model based on the mass balance at the growing interface and the effect of the boride incubation time was used to evaluate the growth of Fe₂B layers. The parabolic growth constant obtained by the model was expressed as a function of boron content in the Fe₂B layer and the process temperature. The simulated values were compared with experimental data derived from the literature, basically, for the boriding of AISI 4140 steel in the temperature range of 1123–1273 K. In addition, an expression of the Fe₂B layer thickness was obtained that showed good agreement with the experimental results. Finally, the instantaneous velocity of the Fe₂B/substrate interface and the weight gain produced by the formation of the Fe₂B layer were evaluated.

Key words: boriding, kinetic model, diffusion, layers, simulation

1. Introduction

The term “boriding” means the enrichment of the surface of a work piece with boron by thermochemical treatment. By means of thermal energy, the boron atoms are transferred into the lattice of the parent material and, together with the atoms in that material, form the respective borides [1]. The boriding treatment applies in the temperature range 1073–1273 K between 1 and 10 h and it can be carried out in gaseous, liquid and solid medium. Iron borides are mainly formed on steel, and there are two kinds of iron borides: FeB, which is rich in boron, and Fe₂B, which is poor in boron. The thickness of the layer formed (known as the case depth), which affects the mechanical and chemical behavior of borided steels, depends on the boriding temperature, the treatment time and the boron potential that surrounds the surface sample [2].

A monolayer Fe₂B with a particular morphology is suitable for practical use due to the difference between the specific volume and coefficient of thermal expansion

of the Fe₂B layer and the substrate. Saw-tooth shaped morphology of the boride layer/substrate interface is observed in low-alloy steels whereas in high-alloy steels the interface tends to be flat [3].

During the last decades, the modeling of the growth kinetics of boride layers has attracted much attention to understand the effect of process parameters (boron potential, temperature and time) on the kinetic behavior of boride layers. For this reason, various diffusion models [4–11] were proposed in the literature. These models do not take into account the effect of the boride incubation time on the kinetics. Recently, a certain number of published works have considered this fact [12–17].

In this work, a kinetic model was applied to simulate the growth kinetics of Fe₂B layer considering the effect of boride incubation time. In addition, the parabolic growth constant (k) was evaluated at the Fe₂B/substrate interface as a function of boron content in the Fe₂B layer and process temperature. As a fitting parameter of the model, the upper boron content ($C_{up}^{Fe_2B}$) in the Fe₂B layer was estimated in

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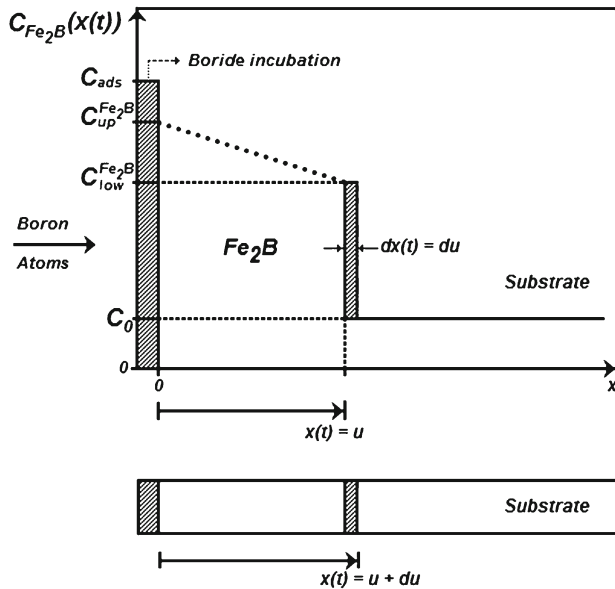


Fig. 1. Boron concentration profile for a diffusion controlled growth of Fe_2B into an initially homogeneous two-phase alloy. The hashed area indicates the amount of boron needed to advance the Fe_2B by du .

order to compare the simulated values with the experimental data obtained from the literature for AISI 4140 borided steels [17]. The model was extended to obtain simple but comprehensive expressions for the Fe_2B layer thickness, the instantaneous velocity of the Fe_2B /substrate interface, and the contribution of the Fe_2B layer in the weight gain of the sample.

2. The kinetic model

The model considers a substrate saturated with boron atoms. By adjusting the boron potential of the reaction medium, it is possible to obtain a configuration consisting of the Fe_2B layer [18, 19]. The boron concentration profile is assumed to be linear through the Fe_2B layer as shown in Fig. 1.

In the development of the diffusion model, the following assumptions were taken into account:

1. The growth of the boride layer is a consequence of the boron diffusion perpendicular to the sample surface.

2. Local thermodynamic equilibrium occurs at the Fe_2B /substrate interface.

3. The differences in the molar volumes between the Fe_2B layer and the substrate were taken into account.

4. The influence of the chemical composition of the substrate on the growth kinetics of the boride layer was not considered.

The initial condition was established as:

$$C_{\text{Fe}_2\text{B}} [x(t > 0) = 0] = 0.$$

The boundary conditions were set as:

$$C_{\text{Fe}_2\text{B}} [x(t = t_0) = 0] = C_{\text{up}}^{\text{Fe}_2\text{B}} \text{ for } C_{\text{ads}}^{\text{B}} > 8.83 \text{ wt.\% B,}$$

$$C_{\text{Fe}_2\text{B}} [x(t = t_0) = u] = C_{\text{low}}^{\text{Fe}_2\text{B}} \text{ for } C_{\text{ads}}^{\text{B}} < 8.83 \text{ wt.\% B,}$$

where $C_{\text{up}}^{\text{Fe}_2\text{B}}$ represents the upper limit of boron content in the Fe_2B layer (9 wt.% B), $C_{\text{low}}^{\text{Fe}_2\text{B}}$ is the lower limit of boron content in the Fe_2B layer (35×10^{-4} wt.% B), and $t_0(T)$ is the boride incubation time. The term $C_{\text{ads}}^{\text{B}}$ denotes the absorbed boron concentration in the boride layer [10]. The two values of boron concentration lie between two limit values (upper and lower) resulting in the formation of Fe_2B over the material substrate [20–22]. In this context, Massalski [23] reported that the Fe_2B layer had a narrow range composition of about 1 at.%.

The mass balance equation through the Fe_2B /substrate is described by Eq. (1):

$$(C_{\text{low}}^{\text{Fe}_2\text{B}} - \beta C_0) \frac{du}{dt} = - D_{\text{Fe}_2\text{B}} \frac{dC_{\text{Fe}_2\text{B}} [x(t)]}{dx(t)} \Big|_{x(t)=u}. \quad (1)$$

C_0 is the boron solubility in the austenite phase (35×10^{-4} wt.% B) [8]. The β constant represents the ratio of specific volume per solvent atom, and it is expressed by $\beta = V_0^{\text{m}} / 2V_{\text{Fe}_2\text{B}}^{\text{m}}$, where V_0^{m} is the molar volume ($\text{m}^3 \text{mol}^{-1}$) of the substrate and $V_{\text{Fe}_2\text{B}}^{\text{m}}$ is the molar volume ($\text{m}^3 \text{mol}^{-1}$) of the Fe_2B layer.

From Fig. 1, the boron concentration profile in the Fe_2B layer is expressed by:

$$C_{\text{Fe}_2\text{B}} [x(t)] = C_{\text{up}}^{\text{Fe}_2\text{B}} + \frac{C_{\text{low}}^{\text{Fe}_2\text{B}} - C_{\text{up}}^{\text{Fe}_2\text{B}}}{u} x(t). \quad (2)$$

Substituting Eq. (2) into Eq. (1) yields:

$$\left(\frac{C_{\text{low}}^{\text{Fe}_2\text{B}} - \beta C_0}{C_{\text{up}}^{\text{Fe}_2\text{B}} - C_{\text{low}}^{\text{Fe}_2\text{B}}} \right) \int_0^u u du = D_{\text{Fe}_2\text{B}} \int_{t_0(T)}^t dt. \quad (3)$$

Hence, Eq. (3) can be expressed as:

$$\left(\frac{C_{\text{low}}^{\text{Fe}_2\text{B}} - \beta C_0}{C_{\text{up}}^{\text{Fe}_2\text{B}} - C_{\text{low}}^{\text{Fe}_2\text{B}}} \right) u^2 = 2D_{\text{Fe}_2\text{B}} [t - t_0(T)]. \quad (4)$$

For a diffusion-controlled growth it results in:

$$u = k [t^{1/2} - t_0^{1/2}(T)] \quad (\mu\text{m}), \quad (5)$$

where u represents the Fe_2B layer thickness, k denotes the parabolic growth constant, and $t_0(T)$ is the boride incubation time as a function of the temperature.

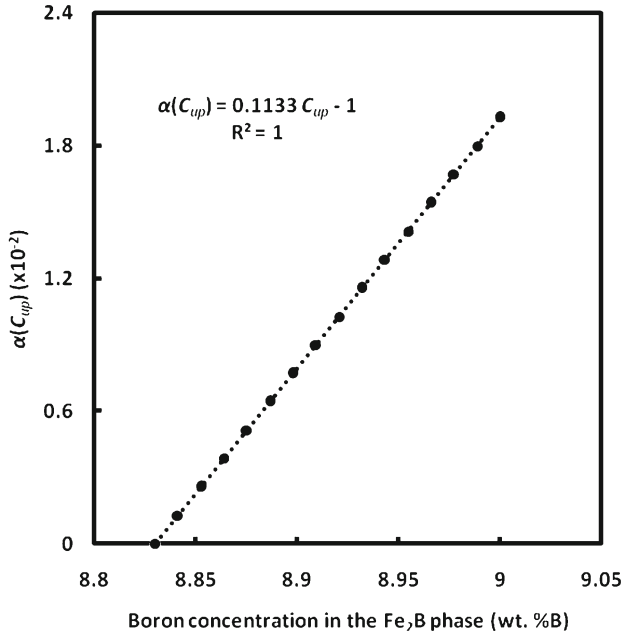


Fig. 2. The behavior of $\alpha(C_{up}^{Fe_2B})$ parameter as a function of boron concentration in the Fe_2B layer.

Thus, Eq. (4) is then modified in the following manner:

$$\left(\frac{C_{low}^{Fe_2B} - \beta C_0}{C_{up}^{Fe_2B} - C_{low}^{Fe_2B}} \right) k^2 = 2D_{Fe_2B} \left\{ \frac{1 - t_0(T)/t}{[1 - [t_0(T)/t]^{1/2}]^2} \right\} \quad (6)$$

or

$$k^2 = 2\alpha(C_{up}^{Fe_2B}) \varepsilon(T) D_{Fe_2B} \quad (\mu m s^{-1/2}), \quad (7)$$

where

$$\alpha(C_{up}^{Fe_2B}) = \frac{C_{up}^{Fe_2B} - C_{low}^{Fe_2B}}{C_{low}^{Fe_2B} - \beta C_0}$$

and

$$\varepsilon(T) = \frac{1 - t_0(T)/t}{\{1 - [t_0(T)/t]^{1/2}\}^2}.$$

The $\alpha(C_{up}^{Fe_2B})$ parameter is a linear function of the boron concentration in the Fe_2B layer, and from the results of Fig. 2, it is expressed by:

$$\alpha(C_{up}^{Fe_2B}) = 0.1133 C_{up}^{Fe_2B} - 1. \quad (8)$$

As pointed out by Brakman et al. [4], the boride incubation time decreases when the temperature increases. It is seen that the $\varepsilon(T)$ parameter has no physical dimension. It depends only on the process

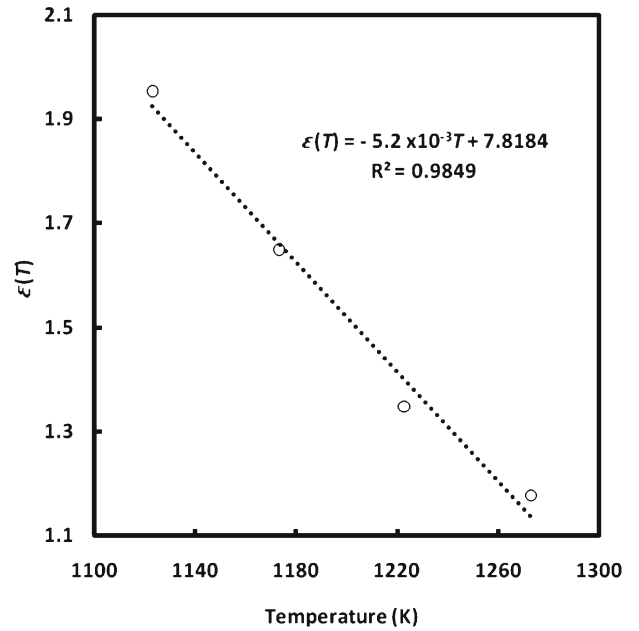


Fig. 3. The $\varepsilon(T)$ parameter as a function of boriding temperature.

temperature and can be approximated by a linear relationship as shown in Fig. 3:

$$\varepsilon(T) = \frac{1 - t_0(T)/t}{\{1 - [t_0(T)/t]^{1/2}\}^2} = -5.2 \times 10^{-3} T + 7.8184. \quad (9)$$

Using Eqs. (8) and (9), the parabolic growth constant (k) can be expressed as:

$$k^2 = [2D_{Fe_2B}(0.1133 C_{up}^{Fe_2B} - 1) \cdot (-5.2 \times 10^{-3} T + 7.8184)]^{1/2} \quad (\mu m s^{-1/2}). \quad (10)$$

In addition, the boron diffusion coefficient in the Fe_2B layer (D_{Fe_2B}) was taken from [17] and it is given by:

$$D_{Fe_2B} = 5 \times 10^{-4} \exp\left(\frac{-173 \text{ kJ mol}^{-1}}{RT}\right) \quad (m^2 s^{-1}). \quad (11)$$

3. Results and discussion

To check the validity of the kinetic model, the experimental results of the parabolic growth constants for the Fe_2B layer in AISI 4140 borided steel were used (for more details see [17]). The experimental values of k were obtained by the slopes of the least-squares fitted lines from the plots of u versus \sqrt{t} . In addition,

Table 1. Comparison between the simulated values of the parabolic growth constant with those achieved in [17]

Temperature (K)	Experimental parabolic growth constant ($\mu\text{m s}^{-1/2}$)	Predicted parabolic growth constant ($\mu\text{m s}^{-1/2}$)
1123	0.416	0.367
1173	0.516	0.507
1223	0.663	0.671
1273	0.840	0.850

the boride incubation time was considered in the simulation work [17].

In Eq. (8), the fitting parameter ($C_{\text{up}}^{\text{Fe}_2\text{B}} = 8.89 \text{ wt.}\% \text{ B}$) was then chosen to reproduce the experimental parabolic growth constants in the temperature range of 1123–1273 K. It is visible from the results depicted in Table 1 that a good agreement was obtained when comparing the simulation results with the experimental data.

The growth of Fe_2B layer is governed by the parabolic growth law $x(t) = u = k [t^{1/2} - t_0^{1/2}(T)]$ and it reads:

$$u = [2\alpha(C_{\text{up}}^{\text{Fe}_2\text{B}})\varepsilon(T)D_{\text{Fe}_2\text{B}}]^{1/2} [t^{1/2} - t_0^{1/2}(T)] \quad (\mu\text{m}). \quad (12)$$

The boride incubation time and treatment time can be expressed as a function of boriding temperature defined as follows:

$$\eta(T) = 1 - [t_0(T)/t]^{1/2} = 1.6 \times 10^{-3}T - 1.0801. \quad (13)$$

The $\eta(T)$ parameter has no physical dimension, and it is approximated by a linear relationship as shown in Fig. 4.

Combining Eqs. (9) and (13), the $\varepsilon(T)$ parameter yields:

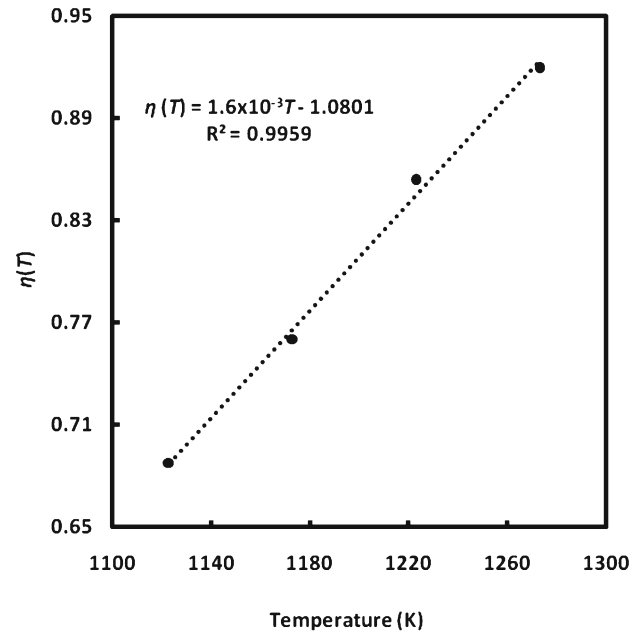


Fig. 4. Influence of the temperature on the $\eta(T)$ parameter.

$$\varepsilon(T) = \frac{2 - \eta(T)}{\eta(T)}. \quad (14)$$

So, the predicted Fe_2B layer thickness presented in Eq. (12) becomes:

$$u = \{2\alpha(C_{\text{up}}^{\text{Fe}_2\text{B}}) [2 - \eta(T)] \eta(T) D_{\text{Fe}_2\text{B}} t\}^{1/2}. \quad (15)$$

The results obtained in Eq. (15) are compared with experimental values obtained from [17] as shown in Table 2. Equation (15) can be used as a simple tool to predict the Fe_2B boride layers thicknesses of ferrous alloys according to their practical applications. The proposed approach, reflected by the exploitation of the model, can also serve to select the optimized parameters for the boriding process.

Table 2. Experimental and predicted values of the Fe_2B layer thickness for a set of experimental parameters obtained in [17]

Time (h)	Temperature 1123 (K)		Temperature 1173 (K)		Temperature 1223 (K)		Temperature 1273 (K)	
	Experimental Fe_2B layer thickness (μm)	Predicted Fe_2B layer thickness (μm)	Experimental Fe_2B layer thickness (μm)	Predicted Fe_2B layer thickness (μm)	Experimental Fe_2B layer thickness (μm)	Predicted Fe_2B layer thickness (μm)	Experimental Fe_2B layer thickness (μm)	Predicted Fe_2B layer thickness (μm)
2	22.255	21.241	30.111	32.168	43.299	46.831	59.940	65.822
4	29.325	30.037	52.073	45.493	67.765	66.229	88.979	93.086
5	38.008	33.583	58.005	50.862	78.357	74.047	114.942	104.074
6	43.823	36.788	68.001	55.717	86.017	81.114	117.997	114.008
8	54.676	42.479	77.695	64.336	99.099	93.663	127.906	131.645

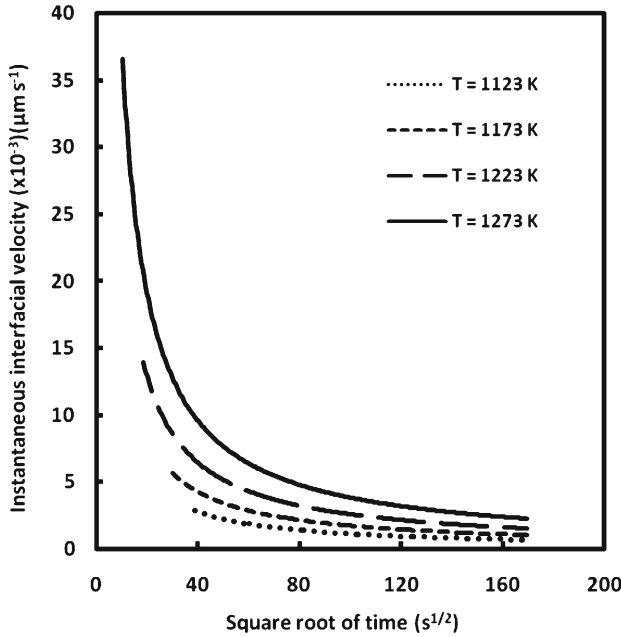


Fig. 5. Calculated instantaneous velocity of the Fe_2B /substrate interface as a function of the square root of time.

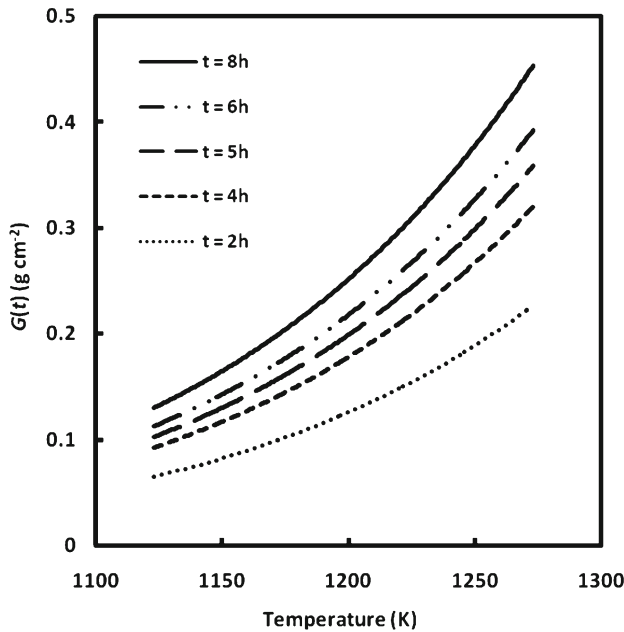


Fig. 6. The contribution of the Fe_2B layer in the weight gain of borided steel for different exposure times.

In addition, the instantaneous velocity of the Fe_2B /substrate interface [24] is established from Eqs. (1) and (15), combining the parameter $\alpha(C_{\text{up}}^{\text{Fe}_2\text{B}})$ as:

$$v = \frac{du}{dt} = -\frac{D_{\text{Fe}_2\text{B}}}{C_{\text{low}}^{\text{Fe}_2\text{B}} - \beta C_0} \left. \frac{dC_{\text{Fe}_2\text{B}}[x(t)]}{dx(t)} \right|_{x(t)=u} \quad (16)$$

Thus, Eq. (16) can be written in the following form:

$$v = \frac{du}{dt} = \left\{ \frac{D_{\text{Fe}_2\text{B}} \alpha(C_{\text{up}}^{\text{Fe}_2\text{B}})}{2[2 - \eta(T)] \eta(T)t} \right\}^{1/2} \quad (\text{ms}^{-1}). \quad (17)$$

By assuming local equilibrium at the interface it has also been assumed that atoms can be transferred across the interface as easily as they can diffuse to the substrate. It is clear from Fig. 5, that the instantaneous velocity of the interface showed an asymptotic behavior with respect to exposure time. When the treatment time is lengthened, the concentration of activated boron is lowered and the velocity of boron atom diffusion into the substrate is decreased.

Also, the weight gain produced by the formation of the Fe_2B layer at the material surface can be obtained from a simple relation as:

$$G(t) = W\rho \frac{du}{dt} t = W\rho \left\{ \frac{D_{\text{Fe}_2\text{B}} \alpha(C_{\text{up}}^{\text{Fe}_2\text{B}}) t}{2[2 - \eta(T)] \eta(T)} \right\}^{1/2} \quad (18)$$

$G(t)$ is related to the evolution of the weight gain per surface unit (g cm^{-2}) from $t > t_0(T)$, ρ is the specific volume of iron (7.86 g cm^{-3}), and W is the amount of solute accumulated in the layer to maintain a concentration-depth profile $W = (C_{\text{low}}^{\text{Fe}_2\text{B}} - \beta C_0)$ [14]. Taking Eq. (18), the weight gain at the borided samples can be written in terms of the treatment time as:

$$G(t) = W\rho v t \quad (\text{g cm}^{-2}). \quad (19)$$

It can be concluded from Fig. 6 with an optimum boron concentration of 8.89 wt.%, that with prolonged boriding, a parabolic weight increases and a parabolic layer growth takes place.

4. Conclusions

The growth kinetics of Fe_2B layers was analyzed by means of a kinetic model that included the effect of the boride incubation time, and the mass balance equation at the growth interface. Through this model, it was possible to express the parabolic growth constant in terms of two parameters: the $\alpha(C_{\text{up}}^{\text{Fe}_2\text{B}})$ parameter which is a function of upper boron concentration in the Fe_2B layer and $\eta(T)$ which is a temperature-dependent parameter. In addition, the model was extended to estimate the boride layer thickness, the growth velocity of the corresponding interface and the contribution of the Fe_2B layer in the weight gain.

The kinetic model developed here can be used to predict the boride layer thicknesses of different borided steels for a given set of experimental conditions. This ability will facilitate the automation of the boriding process.

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