

# Role of RE Element Nd on Boronizing Kinetics of Steels

Z.G. Su, X.X. Lv, J. An, Y.L. Yang, and S.J. Sun

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**Boronizing of AISI 1045 and ASTM W1-111/2 steels was carried out by pack boriding using  $\text{Nd}_2\text{O}_3$ -containing agent in the temperature range of 1053 to 1213 K. The effect of RE element Nd on boronizing kinetics was analyzed in terms of possible chemical reactions in boriding agent, surface elemental distribution and morphology evolution of the steels boronized at different temperatures. The results showed that the RE element Nd has two opposite effects on boronizing process, i.e., promoting effect at high temperatures and hindering effect at low temperatures. Boronizing using  $\text{Nd}_2\text{O}_3$ -containing agent can remarkably reduce the diffusion activation energy at higher temperatures. Empirical equations relating the boride layer thickness with processing time and temperature are established. Based on these equations, the contour diagrams of boride layer thickness for the studied steels boronized with addition of 5%  $\text{Nd}_2\text{O}_3$  are presented.**

**Keywords** activation energy, boronizing, diffusion, kinetics

## 1. Introduction

Boronizing is a widely used thermochemical surface-hardening process to improve the friction and wear properties of metal materials. It could increase the steel surface hardness to as high as 1200-2000 HV, thus it is more advantageous than the carburizing and nitriding treatments (Ref 1). The boronizing of ferrous-based materials is generally carried out at a temperature ranging from 1073 to 1273 K for periods varying between 2 to 10 h (Ref 2). Among currently available boronizing techniques, pack boronizing is applied and studied the most because of its many advantages including ease of treatment, ability to achieve a smooth surface, and simplicity of the required equipment (Ref 3-6). The pack contains a source of boron (usually boron carbide ( $\text{B}_4\text{C}$ )), an activator (usually  $\text{KBF}_4$ ) to deposit atomic boron at the workpiece, and a diluent ( $\text{SiC}$  or  $\text{Al}_2\text{O}_3$ ). A typical pack boronizing process involves placing a component in the powder mixture, sealing it in a container and heating the container up to the required temperature for the required period of time, and cooling in the furnace or by air. Boron atoms, owing to their relatively small size and high mobility, can diffuse into ferrous alloys, forming  $\text{FeB}$  and  $\text{Fe}_2\text{B}$  intermetallic compounds. The diffusion rate and the thickness of the boride layer depend on the processing temperature and time. Due to slow boronizing rate and thin boride layer associated with pack boronizing with conventional boriding agent, the treatment is usually carried out at high temperatures ranging from 1173 to 1273 K to accelerate the diffusion process, and for a period of 4 to 6 h to obtain a desired thickness of the boride layer. The conventional pack

boronizing treatment is, therefore, very costly that its application is limited mainly to tool materials such as D2 and H13 tool steels (Ref 4, 7).

The catalysis of rare earth (RE) element added into the boriding agent may improve the production efficiency to a great extent. In recent years, investigations have shown that addition of RE element into boriding agent could significantly accelerate the boronizing rate, increase the thickness of the boride layer, and simultaneously promote formation of the desired  $\text{Fe}_2\text{B}$  phase in the boride layer. The differences in the specific volume and coefficient of thermal expansion between the  $\text{Fe}_2\text{B}$  phase and steel substrate is much less than those between the  $\text{FeB}$  phase and the steel substrate (Ref 8-11). Thus, the addition of RE element to boriding agent could reduce brittleness of the steel, and consequently improve wear and corrosion resistance as well as oxidation resistance.

So far two catalysis mechanisms of RE elements have been proposed: the active cores and surface activating mechanism (Ref 12), and the gas group and channel mechanism (Ref 13). In the active cores and surface effect mechanism, the RE elements contribute to the formation of boride layer in two ways: firstly, due to their low electronegative values and high negative values of the Gibbs free energy increment after reaction with non-metallic elements, the RE elements display strong affinity for the non-metallic elements. In the RE elements and B diffusion system, the RE elements can break the bonds of  $\text{BF}_3$ , capture the O atoms from  $\text{B}_2\text{O}_3$ , therefore, freeing the B atoms from the boriding agent and activating them. Secondly, the RE elements as surface active elements are prone to be absorbed by the surface of the component; a portion of them diffuse into the metal, the others capture O atoms by reacting with the oxide film formed on the metal surface, eliminating the surface contamination, and facilitating absorption of B atoms by the metal surface. In the gas group and channel mechanism, the active RE atoms absorbed by metal surface diffuse into surface lattice defects such as grain boundaries and dislocations. The large-sized RE atoms can create substantial lattice distortion, causing B atoms congregating around them hence forming a gas group. As the gas group is saturated under boronizing condition, the B atoms will leave the RE atoms diffusing inwards to the metal substrate.

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However, up to now, the role of RE elements in boronizing process has not been fully understood, and the details of the operating mechanism and effect on the boronizing kinetics have not been experimentally validated. The primary objective of this paper is to investigate the effects of RE element Nd on the pack boronizing process and the diffusion activation energy of boron atoms for two typical steels: a medium carbon structural steel (AISI 1045) and a high carbon tool steel (ASTM W1-111/2). The Nd operating mechanism is mainly discussed based on the analysis of the chemical reactions probably occurred in the boriding agent, surface element distribution and morphology evolution on the steels boronized at different temperatures.

## 2. Experimental Procedures

The AISI 1045 and ASTM W1-111/2 steels were used in the experimental study. The chemical compositions of the steels are given in Table 1. The specimen dimensions are 6 mm in diameter and 10 mm in length. These samples were cleaned ultrasonically in acetone and dried prior to treatment. Boronizing was carried out at temperatures ranging from 1053 to 1213 K for 2-5 h. The boriding agents were prepared by thoroughly mixing powders of  $B_4C$ ,  $KBF_4$ , Mn-Fe, SiC, and/or  $Nd_2O_3$ . The chemical compositions of the boriding agents are listed in Table 2.

The phases formed in the surface coatings were identified by x-ray diffraction (XRD) measurements using a  $Cu K_\alpha$  radiation source of wavelength 1.541 Å. The thickness of the boride layer and microstructures of coatings were examined using a LEXT-OLS3000 laser scanning confocal microscope. The boride layer thickness is defined as the average value of the long boride teeth. At least ten measurements were taken at different points of the layer for each sample. The morphology and element contents of polarization spherical clusters formed on the surfaces of the boronized steels were analyzed by using a scanning electron microscopy (SEM) attached with energy dispersive x-ray spectroscopy (EDS).

## 3. Results and Discussion

### 3.1 Coating Characterization

The comparison of the boride layer thickness between AISI 1045 steel and ASTM W1-111/2 steel boronized with and

**Table 1 Chemical composition of the studied materials (wt.%)**

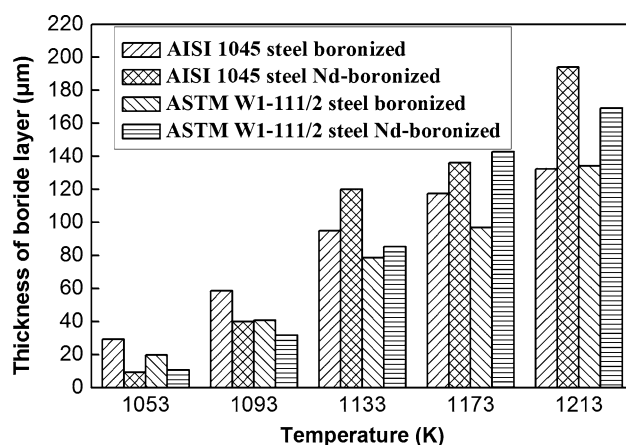
Material	C	Si	Mn	P	S	Cr	Cu	Ni
AISI 1045	0.46	0.31	0.61	0.023	0.020	0.13	0.18	0.22
W1-111/2	1.17	0.31	0.32	0.021	0.019	0.13	0.11	0.15

**Table 2 Chemical composition of the boriding agents (wt.%)**

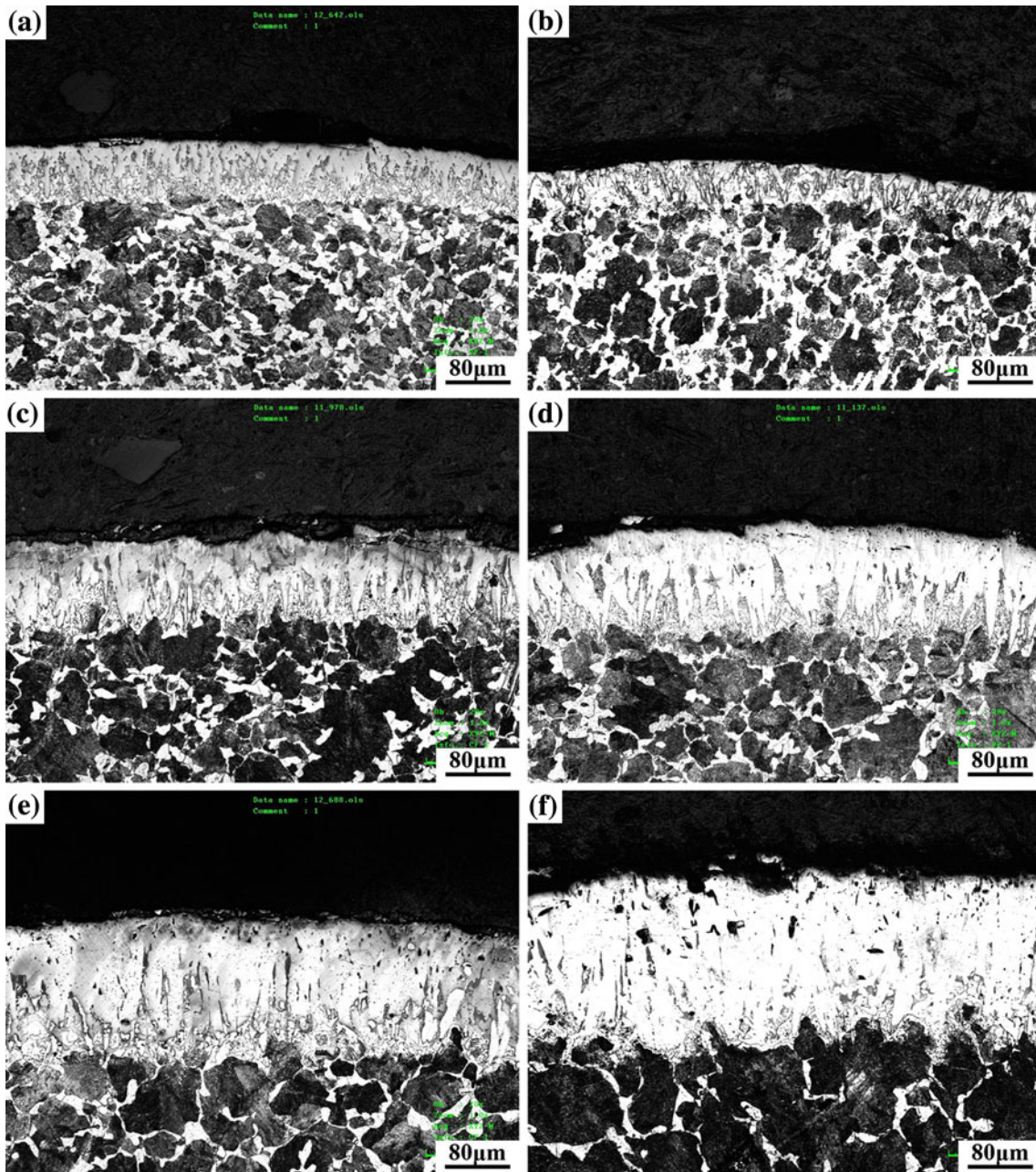
Boriding agent	$B_4C$	$KBF_4$	Mn-Fe	$Nd_2O_3$	SiC
Without RE	5	5	10	...	Balance
With RE	5	5	10	5	Balance

without Nd element addition at different temperatures for 5 h is shown in Fig. 1. The results show that increasing boronizing temperature increases the thickness of the boride layer on both steels. It is also noted that under the same boronizing temperature the boride layer on the AISI 1045 steel is thicker than that on ASTM W1-111/2 steel. This is associated with poor solubility of C in FeB and  $Fe_2B$  phases, therefore, a C-rich zone is formed beneath the boride layer in the boronizing process, which requires more C atoms expelled by B atoms into the C-rich zone in ASTM W1-111/2 steel than in AISI 1045 steel. The addition of Nd into boriding agent has opposite effects on the thickness of boride layer in different temperature ranges: it decreases the thickness in lower temperature range of 1053-1093 K, whereas it increases the thickness in higher temperature range of 1133-1213 K. This indicates that the Nd element hinders the diffusion of B atoms into steel substrate in lower temperature range for some reason, and consequently resulting in a thinner boride layer than that boronized without Nd element addition. On the contrary, in the higher temperature range the Nd element can significantly promote growth of the boride layer, for example, at 1213 K the thickness of boride layer for AISI 1045 steel is about 195  $\mu m$ , an increase of 26.6% compared with that boronized without Nd element addition.

The boride layers on AISI 1045 steel boronized using different boriding agents are shown in Fig. 2(a-f). It shows a dual-phase boride layer formed on the steel substrate (see (c) and (d)); the outmost is FeB phase zone, which is incompact with some pores, beneath is a rather thick  $Fe_2B$  phase zone with a saw-tooth morphology followed by AISI 1045 steel substrate comprised of pearlite and netlike ferrite. At temperatures of 1133 K or higher, boride layer formed with the addition of Nd element is thicker than that treated without Nd element, and the opposite is true for those treated at lower temperatures. In addition, as shown in the micrographs (Fig. 2(d), (f)), the boride layer formed with Nd element addition mainly consists of  $Fe_2B$  phase, whereas the layer formed without Nd element addition consists of a rather large FeB phase zone. This suggests that the addition of Nd element into boriding agent promotes the formation of  $Fe_2B$  phase. Generally, for industrial applications a mono-phase layer of  $Fe_2B$  with sawtooth morphology is more desirable than a dual-phase layer of FeB and  $Fe_2B$ , because the orthorhombic FeB phase is more brittle than the tetragonal  $Fe_2B$  phase (Ref 14, 15). Furthermore, crack initiation is often observed at the FeB/ $Fe_2B$  interface due to



**Fig. 1** Variation in the thickness of boride layer with boronizing temperature for 5 h on AISI 1045 steel and ASTM W111-1/2 steel



**Fig. 2** Microstructures of boride layers grown on AISI 1045 steel at various boronizing temperatures for 5 h: (a) 1093 K, (b) 1093 K with  $\text{Nd}_2\text{O}_3$  addition, (c) 1133 K, (d) 1133 K with  $\text{Nd}_2\text{O}_3$  addition, (e) 1213 K, (f) 1213 K with  $\text{Nd}_2\text{O}_3$  addition

substantial difference in the thermal expansion coefficients between the two phases (Ref 16).

X-ray diffraction analysis, as illustrated in Fig. 3, reveals that the boride layers formed on the AISI 1045 steel substrate at 1213 K contain FeB and  $\text{Fe}_2\text{B}$  phases regardless of the boriding agent used. However, the intensity ratio of  $\text{Fe}_2\text{B}$  to FeB in boride layer with Nd element addition is much higher than that without Nd element, in agreement with micro-structural observation shown in Fig. 3. Hence, the same conclusion can be drawn as before that the boride layer formed using Nd-boriding agent consists of more  $\text{Fe}_2\text{B}$  phase than that formed using non-Nd-boriding agent.

According to the Fe-B binary alloy phase diagram, in the regular boronizing temperature range, active boron atoms diffuse into  $\gamma\text{-Fe}$  first, forming the solid solution of B in  $\gamma\text{-Fe}$

until the boron content reaches 8.83 wt.%, which is the B content of  $\text{Fe}_2\text{B}$ , then the  $\text{Fe}_2\text{B}$  phase nucleates and grows on the steel surface. If the boron atoms diffuse fast and deep into the  $\gamma\text{-Fe}$ , the preferential growth of  $\text{Fe}_2\text{B}$  phase is favored; if the diffusion of boron atoms is not fast enough, the B content in the surface zone will accumulate, and when accumulation is up to 16.23 wt.%, which is the B content of FeB, FeB phase is formed on the outmost surface. The boride layer grown using Nd-boriding agent has a smaller FeB phase, indicating that RE element Nd accelerates the diffusion of the boron atoms into the  $\gamma\text{-Fe}$ . With Nd being 40% larger than Fe in atomic radius, the diffusion of Nd atoms into the steel leads to lattice distortion. The distortion of lattice is conducive to the growth of  $\text{Fe}_2\text{B}$  phase (Ref 17), as it promotes the interstitial diffusion of B atoms and hence reduces the activation energy of B atoms.

### 3.2 Boronizing Kinetics Study

The growth kinetics of boride layer is controlled by the diffusion of boron into Fe<sub>2</sub>B. The formation of the boride layer is the consequence of the boron diffusion perpendicularly to the specimen surface. The growth of Fe<sub>2</sub>B layer obeys the parabolic law (Ref 4, 7, 18):

$$d^2 = Kt \quad (\text{Eq 1})$$

where  $d$  is the depth of boride layer,  $K$  is the growth rate constant depending on boronizing temperature,  $t$  is the boronizing time. The values of  $K$  at different temperatures were calculated in terms of the layer thickness and boronizing time and listed in Table 3.

The relationship between growth rate constant,  $K$  (m<sup>2</sup> s<sup>-1</sup>), and the processing temperature,  $T$ , in Kelvin,

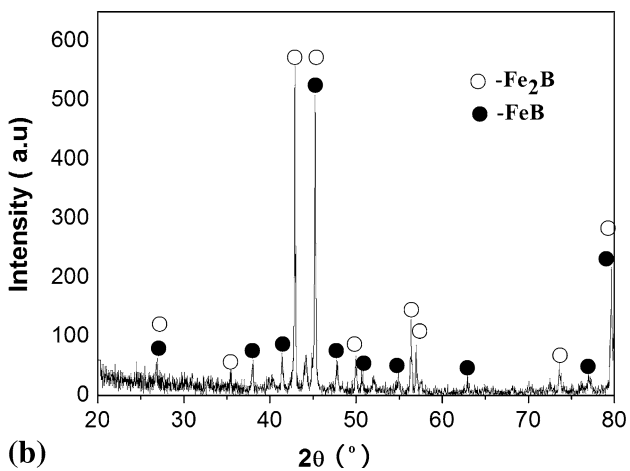
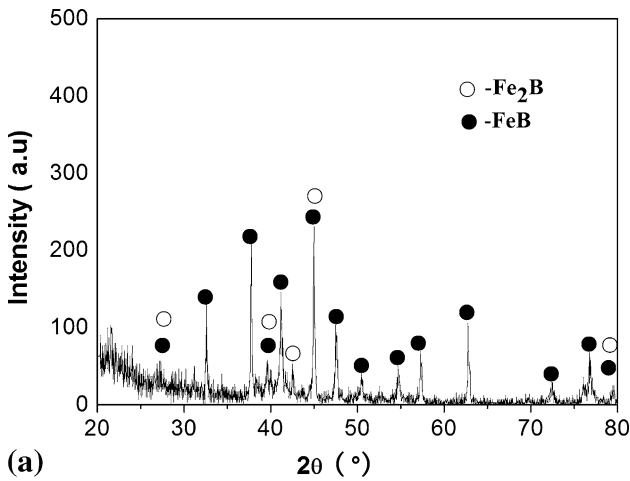
can be expressed by an Arrhenius-type equation as follows (Ref 18):

$$K = K_0 \exp(-Q/RT) \quad (\text{Eq 2})$$

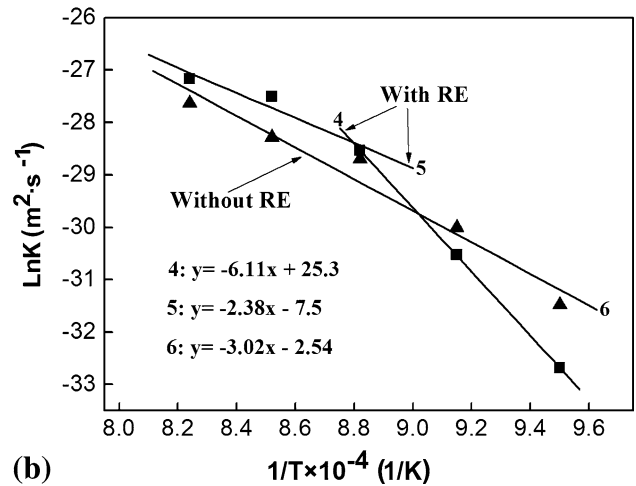
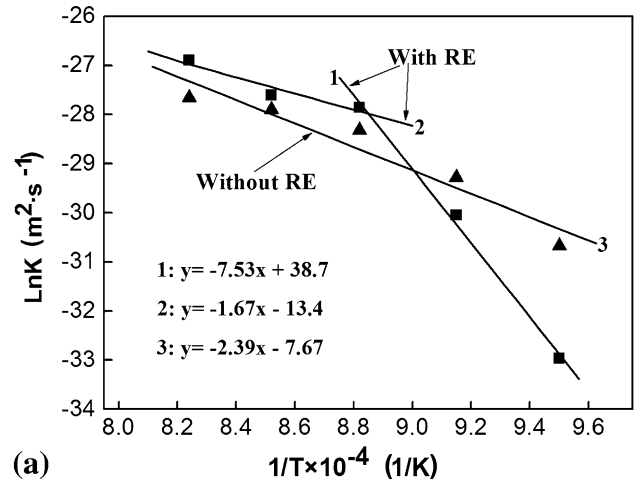
where  $K_0$  is a constant called the collision factor which is a measure of the effectiveness of collision between reacting species,  $Q$  is the activation energy which indicates the amount of energy (J mol<sup>-1</sup>) required for the reaction to occur, and  $R$  is the gas constant (J mol<sup>-1</sup> K<sup>-1</sup>). Taking the natural logarithm of Eq. 2 results in the following equation:

$$\ln K = \ln K_0 - Q/RT \quad (\text{Eq 3})$$

Using Eq. 3 the activation energy,  $Q$ , for boron diffusion in the boride layer, is determined from the slope of the plot  $\ln K$  versus  $1/T$ , as shown in Fig. 4.



**Fig. 3** XRD patterns of AISI 1045 steel treated with different boriding agents at 1213 K: (a) without Nd addition, (b) with Nd addition



**Fig. 4** Logarithmic growth rate constant versus reciprocal of boronizing temperature: (a) AISI 1045 steel, (b) ASTM W111-1/2 steel

**Table 3** Values of growth rate constant and activation energy

Steel	Condition	Growth rate constant, m <sup>2</sup> /s			$Q$ , kJ/mol
AISI 1045	Without RE	$K_{1133} = 5.02 \times 10^{-13}$	$K_{1173} = 7.64 \times 10^{-13}$	$K_{1213} = 9.74 \times 10^{-13}$	198
	With RE	$K_{1133} = 8.00 \times 10^{-13}$	$K_{1173} = 1.03 \times 10^{-12}$	$K_{1213} = 2.09 \times 10^{-12}$	137
W111/2	Without RE	$K_{1133} = 3.44 \times 10^{-13}$	$K_{1173} = 5.22 \times 10^{-13}$	$K_{1213} = 1.00 \times 10^{-12}$	251
	With RE	$K_{1133} = 4.04 \times 10^{-13}$	$K_{1173} = 1.13 \times 10^{-12}$	$K_{1213} = 1.59 \times 10^{-12}$	198

Figure 4(a) and (b) reveals a linear relationship between the logarithmic growth rate constant and the reciprocal of boronizing temperature for both AISI 1045 and ASTM W1-111/2 steels without Nd element addition throughout the boronizing temperature range; whereas with Nd element addition, the original linear relationship is replaced by two lines with different slopes depending on temperature range. In the low temperature range (1053 and 1093 K), the slope is greater than that without Nd element addition, and in the high temperature range (1133, 1173, and 1213 K) the slope is smaller than that without Nd element addition. The calculated values of growth rate constant and activation energy for AISI 1045 steel and ASTM W1-111/2 steel at high temperature are listed in Table 3. It is expected that the activation energy vary with the boron potential of the medium and the chemical composition of the substrate material. The kinetics results of present study are effectively comparable with (Ref 4, 7, 19, 20) as seen in Table 4. The activation energies of borided AISI 5140 and AISI 4340 low alloy steels are close to each other. Difference between values of the calculated activation energy of AISI 1045 and those of the low alloy steels could attribute to the high chromium and molybdenum contents that tend to reduce boride layer thickness (Ref 21). The large difference between values of the activation energy of ASTM W1-111/2 and that of AISI W1 high carbon steel could result from the high carbon content that has a tendency to reduce boride layer thickness due to poor solubility of C in FeB and Fe<sub>2</sub>B phases. It should be noted that at high temperature, compared with those without RE addition the activation energy values for AISI 1045 steel and that for ASTM W1-111/2 steel are decreased by 31 and 21%, respectively, whereas at low temperature, they are increased by 216 and 102%, respectively. The large difference in activation energy between high temperature and low temperature treatments indicates that the RE element Nd has two different effects, namely promoting effect or hindering effect in different temperature ranges, and these effects are more prominent on AISI 1045 steel than on ASTM W1-111/2 steel.

To facilitate the selection of process parameters in industrial applications, substituting Eq. 2 and 3 into Eq. 1, the thickness of bride layer  $d$  is established as follows:

$$d_1 = 2.22 \times 10^4 \sqrt{t \cdot \exp\left(\frac{-23815}{T}\right)} \quad (\text{Eq 4})$$

$$d_2 = 1.23 \times 10^3 \sqrt{t \cdot \exp\left(\frac{-16478}{T}\right)} \quad (\text{Eq 5})$$

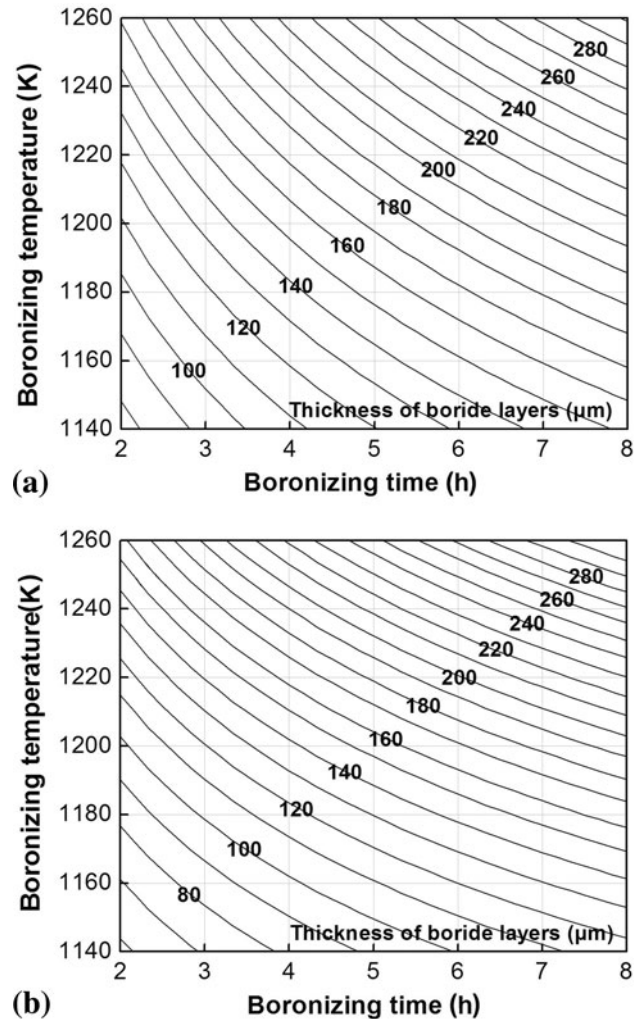
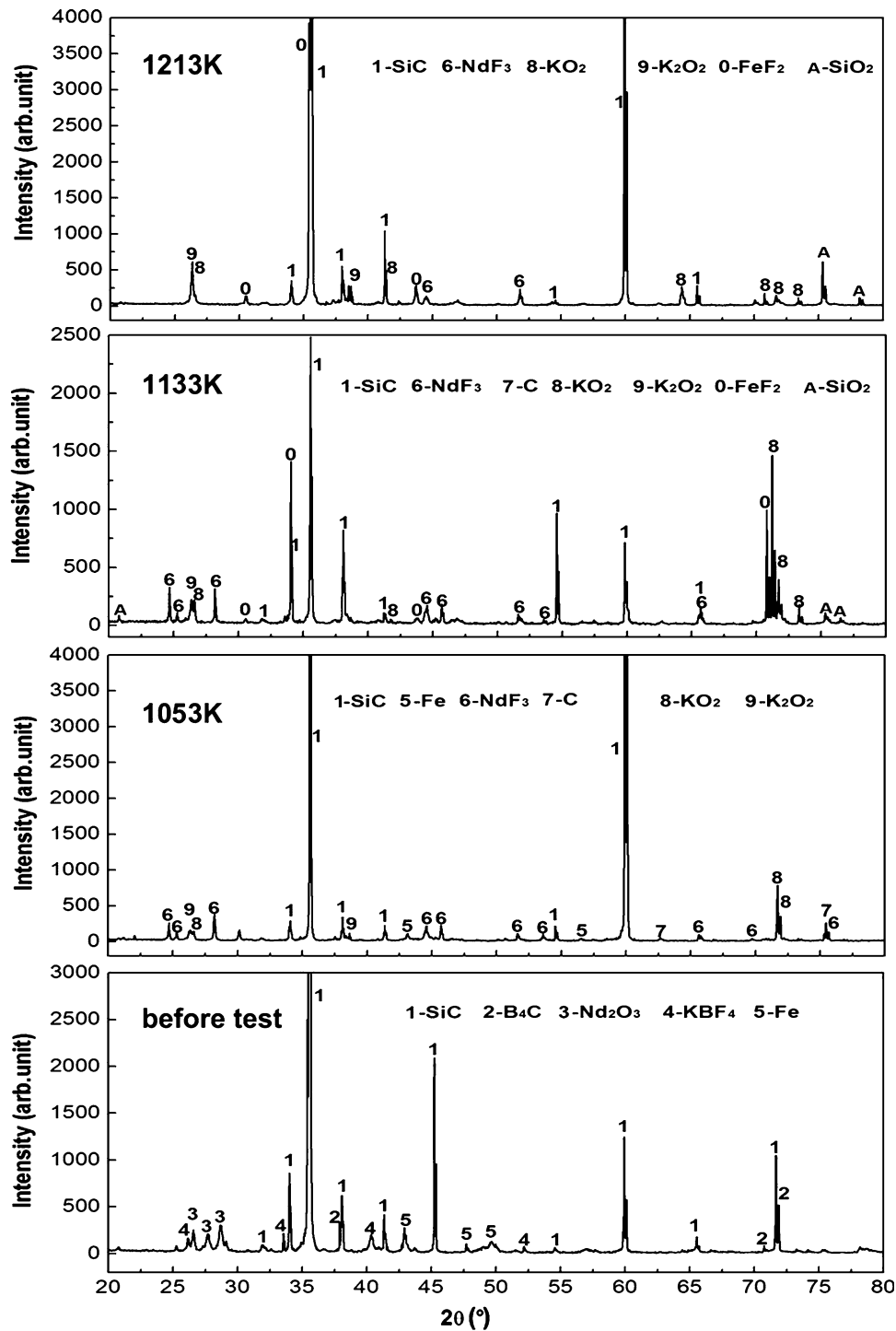


Fig. 5 Thickness contour diagrams of boride layer formed with Nd additions: (a) AISI 1045 steel, (b) ASTM W111-1/2 steel

Table 4 Comparison of chemical compositions and activation energy of steels

Steel	Chemical composition, wt.%								$Q$ , kJ mol <sup>-1</sup>	Reference
	C	Cr	Mn	Ni	Si	Mo	W	V		
AISI 5140	0.43	0.74	0.78	0.06	0.22	0.1	...	...	223	4
AISI 4340	0.35	0.96	0.55	1.56	0.27	0.22	...	...	234	4
AISI D2	1.69	12.2	0.13	0.13	0.17	0.07	0.02	...	170	4
AISI H13	0.37	5.20	0.32	...	0.82	1.20	...	1.01	186.2	7
AISI W1	0.85	0.18	0.36	...	0.24	...	...	...	171.2 ± 16.6	19
AISI M2	1.0	4.0	...	...	...	5.0	6.0	2.0	239.4 ± 19.77	20
AISI 1045	0.46	0.25	0.61	0.30	0.31	...	...	...	198 without RE 137 with RE	Present study
ASTM W1-111/2	1.17	0.13	0.32	0.15	0.31	...	...	...	251 without RE 198	Present study



**Fig. 6** XRD patterns of the  $\text{Nd}_2\text{O}_3$ -containing boriding agents before and after treatment at different temperatures

$$d_3 = 2.88 \times 10^5 \sqrt{t \cdot \exp\left(\frac{-30190}{T}\right)} \quad (\text{Eq 6})$$

$$d_4 = 2.40 \times 10^4 \sqrt{t \cdot \exp\left(\frac{-23851}{T}\right)} \quad (\text{Eq 7})$$

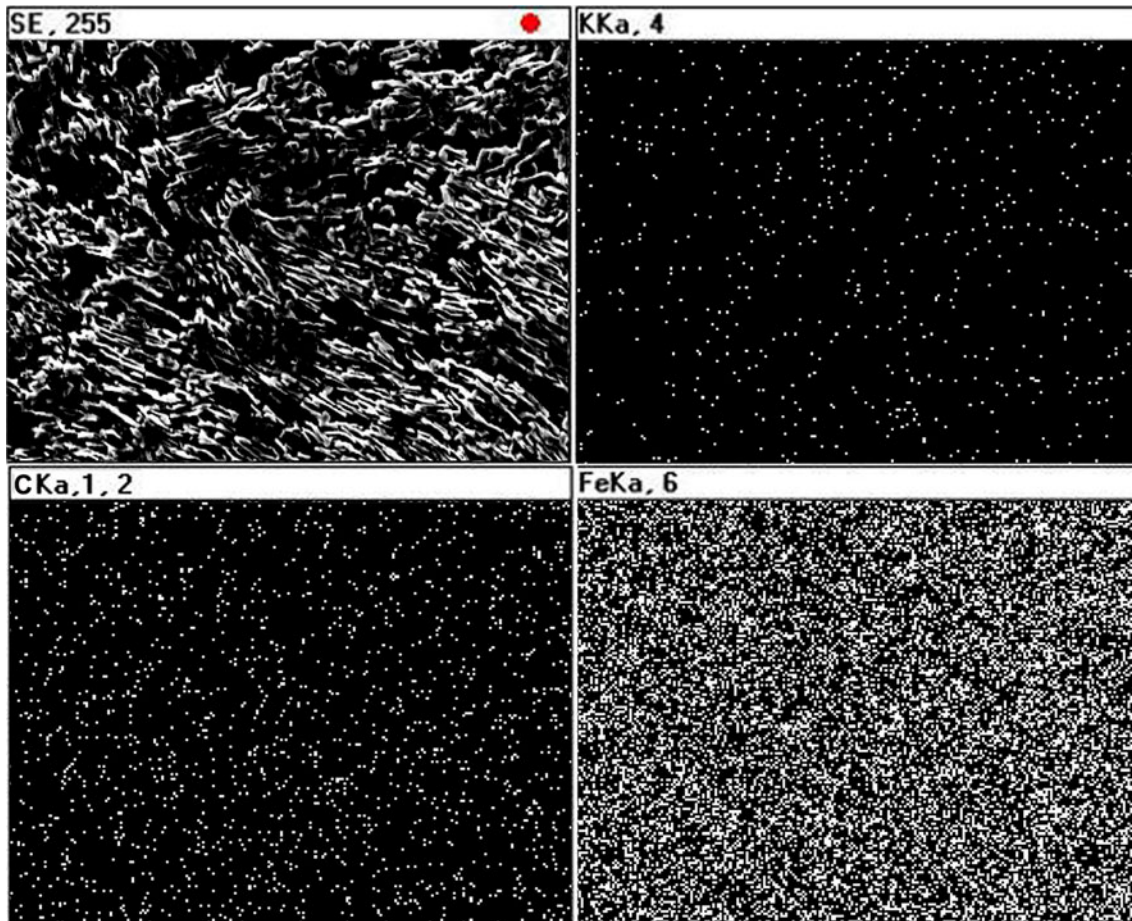
where  $d_1$  and  $d_2$  ( $\mu\text{m}$ ) are the thicknesses of boride layers of AISI 1045 steel treated with non-Nd-containing and Nd-containing boriding agents, respectively;  $d_3$  and  $d_4$  ( $\mu\text{m}$ ) are the

thicknesses of boride layers of ASTM W1-111/2 steel treated with non-Nd-containing and Nd-containing boriding agents, respectively;  $t$  (s) is the boronizing time and  $T$  (K) is the boronizing temperature.

Figure 5(a) and (b) is the contour diagrams of boride layers using Nd-containing boriding agent for AISI 1045 steel and ASTM W1-111/2 steel, respectively. These diagrams could provide a useful reference for industrial applications, as they can be used to estimate the expected thickness of boride layer given the temperature and time of a boronization process.

**Table 5** Possible chemical reactions occurring in the powder boriding agents

Reaction equation	$\Delta_r G_{m,T}^{\theta}$ , KJ		
	1053 K	1133 K	1213 K
$2BF_3 + B_4C = 3BF_2 \uparrow + 3[B] + C$ (9)	-97.9	-100.8	-103.7
$3KF + 3BF_3 + 2Nd_2O_3 = 4NdF_3 + 3KO_2 + 3[B]$ (10)	-337.4	-405.2	-432.9
$2KO_2 = K_2O_2 + O_2 \uparrow$ (11)	-179.3	-179.7	-180.1
$2BF_3 + 3B_4C + Nd_2O_3 + 6O_2 = 2NdF_3 + 2B_2O_3 + [B] + 3CO \uparrow$ (12)	-369.9	-363.8	-357.6
$2BF_3 + B_4C + 3Fe + 2O_2 = 3FeF_2 + B_2O_3 + 6[B] + CO \uparrow$ (13)	-161.5	-153.2	-144.8
$B_4C + 2KF + Fe + 3O_2 = 2[B] + FeF_2 + 2K_2O + B_2O_3 + CO_2 \uparrow$ (14)	-270.8	-264.4	-258.0
$2BF_3 + SiC + 3Fe + 3O_2 = 3FeF_2 + SiO_2 + B_2O_3 + CO \uparrow$ (15)	-306.8	-294.4	-282.0
$B_4C + 2KF + 3O_2 = [B] + BF_2 + B_2O_3 + K_2O + CO \uparrow$ (16)	-378.5	-377.8	-377.1



**Fig. 7** Element XRD maps on the surface of the AISI 1045 steel boronized at 1053 K using  $Nd_2O_3$ -containing boriding agent

### 3.3 Roles of Nd in Different Temperature Ranges

To understand the two contrary effects of Nd element on boronizing kinetics in low and high temperature ranges, it is necessary to understand the roles of RE element in chemical reaction stage and surface diffusion stage for B atoms. First, the effect of Nd element on the chemical reactions between the constituents of boriding agent needs to be discussed. The boriding agent with Nd element consists of  $B_4C$ ,  $KBF_4$ , Mn-Fe, SiC, and  $Nd_2O_3$ .  $KBF_4$  begins to decompose at 803 K:



The XRD analysis of the boriding agents used at different temperatures is shown in Fig. 6. It is seen that SiC and Fe are

the only constituents left after boronizing. The disappearance of other main constituents indicates their participation in the chemical reactions during the boronizing process. Based on the newly formed compounds such as  $NdF_3$ , C,  $KO_2$ ,  $K_2O_2$  at 1053 K,  $FeF_2$  and  $SiO_2$  at 1133 and 1213 K, it can be deduced that some chemical reactions probably occurred during boronizing, which are listed in Table 5.

The reactions during boronizing can be considered as an isothermal process so changes in the Gibbs function of reactions could be calculated by the Gibbs-Helmholtz equation:

$$\Delta_r G_{m,T}^{\theta} = \Delta_r H_{m,T}^{\theta} - T \Delta_r S_{m,T}^{\theta} \quad (\text{Eq 17})$$

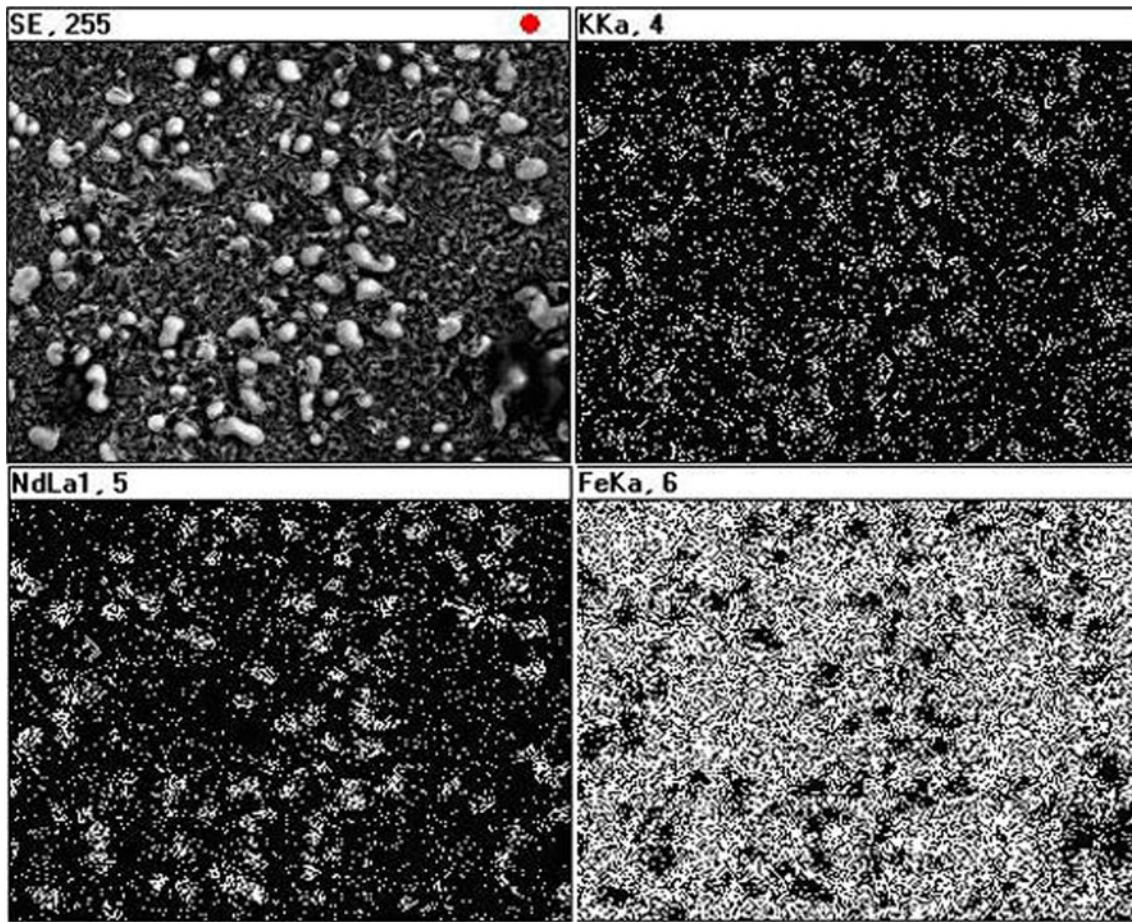


Fig. 8 Element XRD maps on the surfaces of the AISI 1045 steel boronized at 1133 K using  $\text{Nd}_2\text{O}_3$ -containing boriding agent

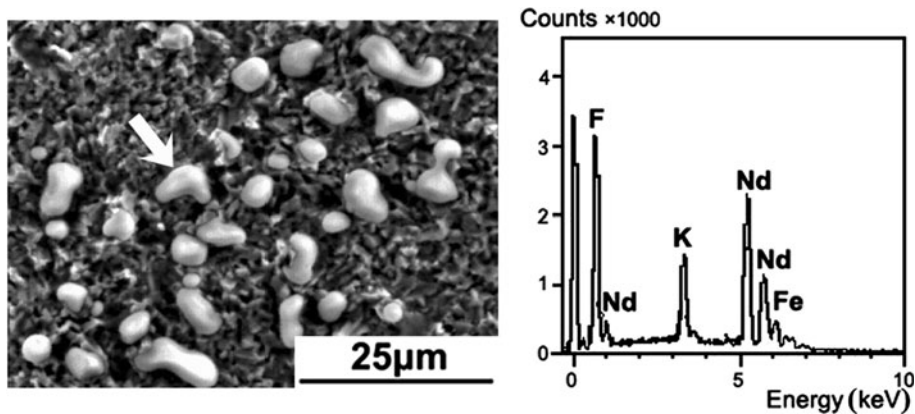


Fig. 9 EDS spectrum of tiny spherical particle shown in Fig. 8

The changes in the Gibbs function of reactions were computed using the raw data in (Ref 22), and listed in Table 5 as well. The results indicate that the reactions (10) and (12) involving the RE element Nd are more likely to occur at the boronizing temperatures. Therefore, the RE element has a positive effect on formation of active B atoms.

The effect of Nd element on surface diffusion of B atoms is analyzed via element mapping on the surfaces of the boronized

samples, as shown in Fig. 7 and 8. At 1053 K, no trace of Nd element was found. However, at 1133 K, a large number of tiny spheres of about 5  $\mu\text{m}$  in diameter were found on the surface. High contents of Nd and F elements were also detected from these spheres by electron probe as shown in Fig. 9. Even though the element Nd may promote the formation of active B atoms based on the calculated values of the Gibbs function at various treatment temperatures, at low temperature of 1053 K,



the absence of Nd element on boronized surface could hinder the diffusion of B atoms into the steel surface in two ways: firstly, there is no catalysis from Nd element promoting diffusion of B atoms into steel substrate; secondly, the low electronegative Nd atoms can attract the nonmetal light atoms like F and B, and stimulate formation of polarization spherical clusters inside boriding agent, which partially prevent B atoms from reaching the boronized surface, hence decrease the boronizing process. However, the tiny spheres containing Nd and F elements formed on the boronized surface at high temperature suggest that a large number of B atoms could be absorbed by the surface together with Nd element migration, which is of advantage to the interfacial reaction between the B and Fe atoms. In addition, the diffusion of the active Nd element atoms, induced by interfacial reaction, into steel surface could accelerate the diffusion of B atoms significantly. Particularly, as the temperature was increased to 1213 K, the Nd element atoms with higher diffusion ability could diffuse into the shallow surface region easily and quickly since the mapping of element Nd confirmed a uniform distribution on steel surface (not shown here), and consequently the catalysis effect was more significant on the internal diffusion of B atoms. Therefore, the higher the boronizing temperature, the greater increase in the boride layer thickness can be achieved using Nd-containing boride agent.

#### 4. Conclusions

The following conclusions can be drawn from the present study:

1. The boride layers grown on both AISI 1045 and ASTM W1-111/2 steel are comprised of both FeB and Fe<sub>2</sub>B phases. The addition of Nd<sub>2</sub>O<sub>3</sub> into boriding agent increases the thickness of boride layer in high temperature range of 1133-1213 K, but can hinder the growth of boride layer in low temperature range of 1053-1093 K.
2. The RE element Nd has two different effects on boronizing process, i.e., promoting effect at high temperature or hindering effect at low temperature. Boronizing using Nd-containing boriding agent can remarkably increase the diffusion rate of boron atom and reduce the diffusion activation energy at high temperatures. In the high temperature range of 1133-1213 K, the activation energy for AISI 1045 steel is decreased from 198 to 137 kJ/mol, a reduction of 31%; and the activation energy for ASTM W1-111/2 steel is reduced from 251 to 198 kJ/mol, a reduction of 21%.
3. Four empirical relations are proposed for estimating the boride layer thickness as a function of the processing time and temperature for AISI 1045 steel and ASTM W1-111/2 steel boronized using non-Nd-containing or Nd-containing boriding agents.
4. Two contour diagrams are established for predicting the depth of boride coating as a function of the process time and temperature on AISI 1045 steel and ASTM W1-111/2 steel using Nd-containing boriding agent. These diagrams might be useful for industrial applications.

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