Catalysis of Rare Earth Element Nd on Boriding of AISI 1045 Steel

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(Received on November 5, 2010; accepted on March 1, 2011)

The present study evaluate the catalysis of Nd$_2$O$_3$ on the boriding of AISI 1045 steel using a 5% Nd$_2$O$_3$- containing boriding agent in a temperature range of 1 213 K to 1 350 K for 2 h–5 h. The morphology and types of borides formed on the steel surface were confirmed by optical microstructure, scanning electron microscopy and X-ray diffraction. The results show that the Nd$_2$O$_3$ has contrary effects on boriding process, i.e. promotion at high temperatures or hindrance at low temperatures. Nd$_2$O$_3$ addition can significantly reduce the activation energy of boride growth at high temperatures, decreased it from 198 kJ/mol to 137 kJ/mol, reduced by 31% in the high temperature range of 1 133 K–1 213 K as compared with that without Nd$_2$O$_3$ addition. The catalysis mechanism of RE element Nd during boriding process was discussed through the analysis of chemical reactions probably occurred in boriding agent, changes in surface morphology and chemical composition.

KEY WORDS: boriding; rare earth element; activation energy; kinetics.

1. Introduction

Boriding is a thermochemical surface treatment for metals, in which boron is diffused into, and combine with, the substrate forming metal boride layer on the surface, that can substantially improve surface characteristics including hardness, wear and corrosion resistance.1,2) Boriding is divided into pack boriding, liquid boriding, and gas boriding. Among these, the pack boriding, a process similar to pack carburizing, is mostly applied and studied at the present time because of its technical advantages, including ease of treatment, ability to achieve a smooth surface, and simplicity of required equipment.3) The pack contains a source of boron (usually boron carbide (B$_4$C)), an activator (usually KBF$_4$) to deposit atomic boron at the workpiece and a diluent (SiC or Al$_2$O$_3$). The boriding temperature generally ranges from 973 K to 1 273 K, and the boriding time is usually fixed from 2 h to 12 h.4) Boron atoms, owing to their relatively small size and high mobility at process temperature, can diffuse into ferrous alloys and according to Fe–B binary phase diagram, result in formation of both single Fe$_2$B and Fe$_5$B and FeB-based polyphases coatings.

It is of great importance to establish the process parameters that affect the boriding kinetics in order to control automated procedures and obtain the optimal properties. A number of diffusion models have been proposed for studying the boride layer growth kinetics,5–7) and growth kinetics of boride layers on a variety of metallic materials have been analyzed by measuring the thickness of the layer as a function of the boriding time and temperature, including AISI 5140, 4340, D2, H13, W1, M2, 316 stainless steels, etc.8–12) Due to the slow boriding rate and thin boride layer associated with the conventional pack boriding, in industry application, boriding is usually carried out at the high temperature ranging from 1 173 K to 1 273 K to accelerate the diffusion process, and for a period of 4 h to 6 h to attain a desired boride layer thickness. These problems give rise to the low production efficiency and high production cost for the pack boriding process. Therefore, it is of great interest to address the involved problems by taking some simple and effective methods.

The catalysis effect of adding rare earth (RE) element into the powder boriding agent may improve the production efficiency of the boriding to some extent. In recent years, investigations have shown that the addition of RE element into boriding agent can significantly accelerate the boriding rate, and increase the thickness of the boride layer, and at the same time promote formation of the desired Fe$_2$B phase in the boride layer, which could reduce the brittleness, improve the wear and corrosion resistance and the oxidation resistance of boride layer.13–16)

So far two catalysis mechanisms of RE elements have been proposed: the active cores-surface effect mechanism, and the gas group-channel mechanism.17,18) The role of RE elements can be reduced to three aspects: (a) the rare earth elements can react both with BF$_3$ produced by the thermal decomposition of KBF$_4$, in this way giving rise to RE fluoride and contributing to liberate B atoms for boriding, and (b) react with metal oxides eventually formed on the metal surface and acting as a barrier to B diffusion, and (c) diffuse into the steel and, being largely sized atoms, they can produce lattice distortions promoting the boron penetration. However, at present, the operating mechanism of RE elements in boriding process has not been fully understood, and their effects on the boronizing kinetics have not been experimentally validated. The present paper aims to investigate the effects of RE element Nd addition into boriding agent on the pack boriding and the diffusion activation energy of...
boron atoms of the AISI 1045 structural steel. The Nd operating mechanism is also discussed via the analysis of chemical reactions probably occurred in the boriding agent, and chemical composition and morphology of polarization spherical clusters formed on the steel surface.

2. Experimental Details

The AISI 1045 steel was used in this study, and was sized to 6 mm in diameter and 10 mm length for boriding. These samples were cleaned ultrasonically in acetone, dried, and placed in the boriding agent, then sealed in a container. The boriding was achieved at different temperatures from 1 053 K to 1 213 K for 2 to 5 h. The boriding agents were prepared by thoroughly mixing the powders of B₄C, KBF₄, Mn–Fe, SiC and/or Nd₂O₃. The chemical compositions of these boriding agents are listed in Table 1. The phases formed in the bride layer were identified by X-ray diffraction (XRD) measurements that were performed using a CuKα radiation sauce of a wavelength of 1.541Å. The thickness of coatings and their morphology were examined using a LEXT-OLS3000 laser scanning confocal microscope. The morphology and contents of the elements on the surfaces of the borided samples were analyzed by means of scanning electron microscopy (SEM) attached with energy dispersive X-ray spectroscopy (EDS).

3. Results and Discussion

3.1. Microstructure and Characterization

X-ray diffraction analysis, as illustrated in Figs. 1(a) and 1(b), reveals that boride layers on the surfaces of AISI 1045 steel substrate at 1 213 K for 5 h consist of FeB and Fe₂B phases regardless of boriding agent. However, the boride layer obtained from Nd₂O₃-boriding agent was mainly Fe₂B phase because the intensity ratio of Fe₂B peaks to FeB becomes stronger as compare with those treated without Nd₂O₃-boriding agent, and the layer without Nd₂O₃ addition had a large amount of FeB phase.

The boride layers formed on AISI 1045 steel treated by boriding agents with RE or non-RE element addition at different temperatures for 5 h are shown in Fig. 2. It can be seen that a dual-phase boride layer forms on the steel substrate, the outmost zone of FeB phase is incompact with some pores formed, next to which is a rather thick Fe₂B phase zone with the saw-tooth morphology followed by substrate. It is apparent that at high temperature, boride layer formed with Nd₂O₃-boriding agent is stronger as compare with those treated without Nd₂O₃-boriding agent, and the layer without Nd₂O₃ addition had a large amount of FeB phase, suggesting that the boronizing agent with RE element addition is conducive to the formation of Fe₂B Phase. Generally, the formation of a monophase (Fe₂B) with saw-tooth morphology is more desirable than a double phase layer of FeB and Fe₂B for industrial applications, because orthorhombic FeB phase is more brittle than tetragonal Fe₂B phase.[19,20] Furthermore, crack formation is often observed at the FeB/Fe₂B interface due to substantial difference in coefficient of thermal expansion between them.[21]

3.2. Kinetics Study

The graphical representation in Fig. 3 shows that the boride layer thickness increases with boriding time for each process temperature. However, the addition of Nd₂O₃ exerts different influences on the thickness of boride layer in different temperature ranges, decreasing the thickness of boride layer in low temperature range of 1 053–1 093 K, whereas increasing the thickness of boride layer in high temperature range of 1 133–1 213 K. This indicates that the RE element Nd delays the diffusion of B atoms into steel substrate in low temperature range of 1 133–1 213 K, and conversely in high-er temperature range of 1 133–1 213 K, the RE element Nd...
can significantly promote the growth of the boride layer, for example, at 1213 K the boride layer thickness is 195 μm, increase by 26.6% compared with that borided without Nd2O3 addition.

The growth kinetics of bride layer is controlled by the boron diffusion into the Fe2B and the growth of boride layer occurs as a consequence of the boron diffusion perpendicular to the specimen surface. The fact that the growth of Fe2B layer obeys the parabolic law has been proved experimentally by other previous studies,8–10) therefore it is also assumed acting this way as follows:

\[ d^2 = Kt \] (1)

where \( d \) is depth of boride layer, \( K \) is the growth rate constant depending on the boriding temperature, \( t \) is process time. The values of \( K \) at different given temperatures have been calculated in terms of the layer thickness and boriding time as listed in Table 2.

The relationship between growth rate constant, \( K \) (m²s⁻¹), and the process temperature in Kelvin, \( T \), can be expressed by an Arrhenius equation as follows:

\[ K = K_0 e^{-\frac{Q}{RT}} \] (2)

where \( K_0 \) is constant, called the collision factor and is a measure of the effectiveness of collision between reacting species, \( Q \) is the activation energy (J mol⁻¹), \( R \) is the gas constant (J mol⁻¹K⁻¹). Taking the natural logarithm of Eq. (2), Eq. (3) can be derived as follows:

\[ \ln K = \ln K_0 - \frac{Q}{RT} \] (3)

Consequently, the activation energy for boron diffusion in the boride layer is determined by the slope obtained by the
of Nd$_2$O$_3$ addition, two separate lines with different slopes given boriding temperature range, whereas in the presence of Nd$_2$O$_3$ addition, two contrary effects i.e. promotion or retardance depending on temperature ranges. The calculated activation energy of borided AISI 1045 steel decreases by 31%, whereas at low temperature, the value of activation energy increases by 216%, respectively, compared with those without Nd$_2$O$_3$ addition. The calculated growth rate constants and values of activation energy for borided AISI 1045 steel at different temperatures are listed in Table 2. It notes that at high temperatures, the value of activation energy for AISI 1045 steel decreases by 31%, whereas at low temperature, the value of activation energy increases by 216%, respectively, compared with those without Nd$_2$O$_3$ addition. The great difference in activation energy between high temperatures and low temperature indicates that Nd$_2$O$_3$ addition has two contrary effects i.e. promotion or retardance depending on temperature ranges.

### 3.3. Role of Nd$_2$O$_3$ in Different Boriding Temperature Ranges

The participation of Nd$_2$O$_3$ in chemical reactions between constituents of boriding agent was analyzed by XRD analysis of boriding agent used at different temperatures, as shown in Fig. 5. After all treatments at different temperatures, SiC and Fe are the only constituents remained, other main constituents were not detected surviving by XRD measurements, indicating their general participation in the chemical reactions. At 803 K, KBF$_4$ begins to decompose:

\[
\text{KBF}_4 = \text{KF} + \text{BF}_3 \uparrow
\]

Based on the newly formed compounds such as NdF$_3$, C, KO$_2$, K$_2$O at 1 053 K, FeF$_2$ and SiO$_2$ at 1 133 K and 1 213 K, the other chemical reactions probably occurred are deduced as follows:

\[
2\text{BF}_3 + \text{B}_4\text{C} = 3\text{BF}_2 \uparrow + 3[n] + \text{C} \quad \Delta G_5 \quad \cdots \quad (5)
\]

\[
3\text{KF} + 3\text{BF}_3 + 2\text{Nd}_2\text{O}_3 = 4\text{NdF}_3 + 3\text{KO}_2 + 3[n] \quad \Delta G_6 \quad \cdots \quad (6)
\]

\[
2\text{KO}_2 = \text{K}_2\text{O}_2 + \text{O}_2 \uparrow \quad \Delta G_7 \quad \cdots \quad (7)
\]

\[
2\text{BF}_3 + 3\text{B}_4\text{C} + \text{Nd}_2\text{O}_3 + 6\text{O}_2 = 2\text{NdF}_3 + 2\text{B}_2\text{O}_3 + [n] + 3\text{CO} \uparrow \quad \Delta G_8 \quad \cdots \quad (8)
\]

\[
2\text{BF}_3 + \text{B}_4\text{C} + 3\text{Fe} + 2\text{O}_2 = 3\text{FeF}_2 + \text{B}_2\text{O}_3 + 6[n] + \text{CO} \uparrow \quad \Delta G_9 \quad \cdots \quad (9)
\]

\[
\text{B}_4\text{C} + 2\text{KF} + \text{Fe} + 3\text{O}_2 = 2[n] + \text{FeF}_2 + 2\text{K}_2\text{O} + \text{CO} \uparrow \quad \Delta G_{10} \quad \cdots \quad (10)
\]

\[
2\text{BF}_3 + \text{SiC} + 3\text{Fe} + 3\text{O}_2 = 2\text{FeF}_2 + \text{SiO}_2 + \text{B}_2\text{O}_3 + \text{CO} \uparrow \quad \Delta G_{11} \quad \cdots \quad (11)
\]

\[
\text{B}_4\text{C} + 2\text{KF} + 3\text{O}_2 = [n] + \text{BF}_2 + \text{B}_2\text{O}_3 + \text{K}_2\text{O} + \text{CO} \uparrow \quad \Delta G_{12} \quad \cdots \quad (12)
\]

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

\[
\Delta G_T^0 = \Delta H_T^0 - T \Delta S_T^0 \quad \cdots \quad (13)
\]

The changes in the Gibbs function of reactions are computed using the raw data in Ref.22, and illustrated in Fig. 6. The results indicate that the reactions (6) and (8) involving the element Nd are more likely to occur at the boriding temperatures and favor the formation of active B atoms.

The effect of RE element Nd on surface diffusion of B is analyzed via element mapping on the borided surfaces, as shown in Figs. 7 and 8. At low temperature of 1 053 K, no trace of Nd element was found, whereas at high temperature of 1 133 K, large amount of tiny spheres with about 5 μm diameter were formed on the surface, and high contents of Nd and F elements were detected by electron probe as shown in Fig. 9. Even though the element Nd may promote the formation of active B atoms at 1 053 K on the basis of calculated result of Gibbs function, the absence of RE element Nd on borided surface could produce two disadvantages: (a) no catalysis of RE element Nd could promote the diffusion of B atoms into steel substrate, (b) low electronegative Nd atom can attract the nonmetal atoms like F and B, and stimulate formation of the polarization ball within boriding agent, preventing the B atoms from reaching the borided surface and hence decreasing the boriding rate. However, the tiny spheres containing Nd and F elements

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**Table 2.** Growth rate constant and activation energy as a function of Nd$_2$O$_3$ and processing temperature.

| Nd$_2$O$_3$ addition | Growth rate constant (m$^2$/s) | Q (kJ/mol) |
|----------------------|-------------------------------|------------|
|                      | 1 053 K                       | 1 093 K    | 1 133 K | 1 173 K | 1 213 K | Low temperature | High temperature |
| Without              | $4.77 \times 10^{-14}$        | $1.19 \times 10^{-13}$ | $5.02 \times 10^{-13}$ | $7.64 \times 10^{-13}$ | $9.74 \times 10^{-13}$ | 198 | 198 |
| With                 | $4.81 \times 10^{-15}$        | $8.89 \times 10^{-14}$ | $8.00 \times 10^{-13}$ | $1.03 \times 10^{-12}$ | $2.09 \times 10^{-12}$ | 626 | 137 |

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![Fig. 4.](image-url) Growth rate constant vs. temperature of borided AISI 1045 steel.
formed on the borided surface at high temperature suggests that large amount of B atoms could be absorbed by the borided surface together with RE element Nd migration to the borided surface, which favors the interfacial reaction between the B and Fe atoms. Furthermore, the diffusion of the active RE element Nd atoms, induced by interfacial reaction, into steel surface could accelerate the diffusion of B atoms remarkably, especially as the temperature was increased to 1213 K, the RE element atoms with higher diffusion ability could diffuse into the shallow steel surface easily and quickly, since the tiny spheres disappeared, and the mapping of element Nd confirmed a uniform distribution on the borided surface (see Fig. 10). The atomic radius of Nd being 40% larger than that of Fe atom, the diffusion of Nd atoms into the steel causes lattice distortion. The distortion of the lattice is conducive to the growth of Fe2B phase, as it promotes the interstitial diffusion of B atoms and reduces the activation energy of B. However, the diffusion of Nd into shallow steel surface is not be confirmed by cross-sectional
EDS element mapping in the present study, may be it is because of the relatively low content of Nd in surface boride layer, which is beyond the measurement precision. The diffusion of Nd into surface layer needs further investigation.

4. Conclusions

(1) The boride layers grown on both AISI 1045 steel consist of FeB and Fe₂B phases. The addition of Nd₂O₃ can retard the growth of boride layer in 1 053–1 093 K, whereas it can increase the boride layer thickness in 1 133–1 213 K.

(2) The diffusion activation of boride growth by addition of Nd₂O₃ is determined to be 137 kJ/mol, reduces by 31% in 1 053–1 093 K, but 626 kJ/mol, increases by 216% in 1 133–1 213 K.

(3) SEM and EDS studies reveal that migration of Nd atoms to the surface in the form of tiny spheres or uniform distribution favors the boriding process in 1 133–1 213 K.

Acknowledgements

The authors thank the Project 985-automotive engineering of Jilin University and Technology Development Program of Jilin Province (No. 20100329).

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