Boriding of High Chromium Steels

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Abstract: Two boride layers having different kinds of microstructure are formed on the surface of industrial high chromium steel (13 and 25% Cr) samples during their interaction with boron powder at 850–950°C and reaction times 3600–43200 s (1–12 h). In the case of 13% Cr steel, the outer layer bordering boron consists of the FeB phase, whereas the inner layer adjacent to the solid substrate consists of the Fe₂B phase. Each layer is a homogeneous phase. It is a microstructure of the first kind. With 25% Cr steel, each of boride layers is two-phase. The outer layer comprises the FeB and CrB phases, while the inner layer the Fe₂B and Cr₂B phases. It is a microstructure of the second kind. Both boride layers on both steels are characterized by a profound texture. Growth kinetics of boride layers obeys a parabolic relation. Boride layers with the microstructure of the second kind exhibit a much higher dry abrasive wear resistance than those with the microstructure of the first kind.

Keywords: 13 and 25% Cr steels, boride layers, microstructure, phase identity, chemical composition, growth kinetics, wear resistance.

1. INTRODUCTION

In many practical applications, specific physical, chemical or mechanical properties are only needed for a thin surface layer, a few tens of nanometers to a few tens of micrometers thick, while the main body of a part may be made from a low-cost ordinary alloy or steel. Thermochemical boriding (or boronizing) is one of the surface treatments aimed at improving the service characteristics of products and parts from metals, alloys and steels [1, 2]. It provides a high increase in their hardness and resistance to abrasion, wear, corrosion in air and aggressive media, and oxidation at elevated temperatures.

A variety of borided steel parts are now routinely manufactured. Examples include agricultural machinery and aerospace components, pipe fittings, high wear pumps, tools and dies, burner nozzles, steam turbine blades and many others. Such parts usually serve two to five times longer than those treated with conventional techniques such as hardening, carburizing, nitriding or nitrocarburizing. If necessary, all these may readily be combined to obtain a surface coating of desirable properties. Boriding can also be employed to repair any steel components that wear quickly in service and therefore require frequent replacement.

To choose an optimum regime of the boriding procedure for each particular metal, alloy or steel, it is essential to find out experimentally the main physico-chemical processes that are likely to take place in its course. This work is aimed at establishing the microstructure, phase identity, chemical composition, growth kinetics and dry abrasive wear resistance of boride layers formed at the interface of industrial 13% (4X13) and 25% (15X25T) chromium steels having relatively small amounts of other elements with amorphous boron powder in the temperature range 850–950°C. These high chromium steels were chosen for the investigation because the studies of previous researchers were carried out largely either with low alloyed chromium steels (4% Cr or less) or with highly alloyed (more than 25% Cr) ones containing in addition considerable amounts of other elements, notably nickel, manganese, tungsten, molybdenum and silicon (see, for example, [3–14]).

As the effect of various elements on physical and chemical properties of boride layers is often opposite, a few significant features typical of the layers formed on the surface of steel samples with
Cr contents around 25% and large amounts of other elements proved masked and therefore unrevealed earlier (see Section 3.1 of the paper). Of those, the layer microstructure, phase identity and chemical composition are most essential from academic and technological viewpoints, even though the work was not directed towards finding any immediate practical application of borided steels investigated.

2. EXPERIMENTAL PROCEDURE

2.1. Materials and Samples

Rods of industrial steels were used in the as-received condition (without any additional heat treatment). The content of main components of 13% Cr steel was 85.2% Fe, 13.6% Cr, 0.38% C, 0.30% Mn, 0.30% Si and 0.20% Ni. 25% Cr steel contained 72.8% Fe, 25.2% Cr, 0.13% C, 0.50% Mn, 0.46% Si, 0.45% Ni and 0.28% Ti. The microstructure of the steels consisted of the body centered cubic α-phase (ferrite) with fine inclusions of iron and chromium carbides. Reagents were amorphous boron powder (98.3% B) and analytical-grade KBF$_4$.

Samples in the form of tablets, 11.28 mm in diameter (1.0 cm$^2$ area) and 5.5 mm high, were machined from steel rods. Flat sides of the tablets were ground and polished mechanically.

2.2. Investigation Methods

The vacuum device VPBD-2S employed for boriding steel samples, details of the boriding procedure and investigational techniques used to characterize initial steel samples and boride layers formed on their surface have been described elsewhere [15, 16]. The experimental cell is shown schematically in Fig. (1).

The steel tablet was embedded into a mixture of boron powder with 5% KBF$_4$ as an activator. This amount of the activator is known to be optimum [1, 17]. KBF$_4$ is considered to be one of most effective activators due to the formation of volatile compounds, mainly BF$_3$, at elevated temperatures. Compared to other boriding agents such as Na$_2$B$_4$O$_7$, a mixture of 70% Na$_2$B$_4$O$_7$ with 30% SiC or a mixture of 65-70% Na$_2$B$_4$O$_7$ with 35-30% B$_4$C, its application allows much thicker and regular boride layers to be obtained under similar temperature-pressure conditions.

Experiments were carried out at a temperature of 850, 900 and 950°C (99.999 vol.% Ar) at a reduced pressure of 2.5 × 10$^4$ Pa. Their duration was 3600–43200 s (1–12 h).

3. RESULTS AND DISCUSSION

3.1. Microstructure, Phase Identity and Chemical Composition of Boride Layers

With both steels, two continuous boride layers were found to form at the interface between the reactants at a temperature of 850, 900 and 950°C (Fig. (2)), in agreement with findings of other researchers [1-14]. Layer-by-layer X-ray analysis showed that in the case of 13% Cr steel samples (Fig. (2a)) the outer layer bordering the boriding agent is a solid solution based on the FeB compound, while the inner layer adjacent to the steel base is a solid solution based on the Fe$_2$B compound. The average chromium content is 8% in the FeB layer and 9 % in the Fe$_2$B one [18]. Each layer is one-phase. It is a microstructure of kind I which has been observed by most researchers [1-14].

In contrast, both boride layers formed on the surface of 25% Cr steel samples was found to be two-phase. This is a microstructure of kind II. The outer layer comprises the FeB and CrB compounds, while the inner the Fe$_2$B and Cr$_2$B compounds [19]. It should be mentioned that the microstructure of kind II has been overlooked by previous researchers, probably for two following reasons.

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Figure 1: Experimental cell of VPBD-2S vacuum device employed for boriding steel samples.
(1) Though readily visible metallographically on plan-view sections of Fe–25% Cr alloy samples obtained at all the temperatures investigated (Fig. 3), it is seen in Fig. (2b’ and c’) to be much less profound with 25% Cr steel samples. Note that even with this alloy containing no additives or impurities it is not so

Two kinds of microstructure of boride layers

Kind I – one-phase

X-rays

Kind II – two-phase

X-rays

Fig. (2). Scheme of X-ray diffraction investigations of borided (a) 13% and (a’) 25% chromium steel samples, and (b–d’) microstructure of their appropriate plan-view sections. Section I is shown at different magnifications. Boriding conditions: 950°C, 21600 c (6 h).
easy to notice the two-phase microstructure on longitudinal cross-sections. Therefore, if not suspected, this kind of microstructure can hardly be revealed in the case of steels or alloys of complicated chemical composition.

(2) If formed under non-equilibrium conditions, the FeB and CrB phases as well as the Fe$_2$B and Cr$_2$B ones are indistinguishable by X-ray diffraction or other methods of structural analysis, and not only because of the similarity of crystal structures of those pairs of the phases [20-25]. Any structural method will show the presence only of FeB in the outer boride layer and Fe$_2$B in the inner. The main reason appears to be difficulties of solid state phase transformations. Merely, lattice rearrangements FeB → CrB and Fe$_2$B → Cr$_2$B are not completed in view of time limitations. Therefore, part of iron sites of the FeB lattice, very similar to that of CrB, is replaced by chromium atoms, without any structural changes. In other words, the non-equilibrium CrB phase crystallizes in the FeB lattice. Hence, being far from equilibrium, the outer boride layer appears to be single-phase structurally (crystallographically) and two-phase compositionally (chemically).

Similar considerations are also applicable to another pair Fe$_2$B and Cr$_2$B which are the constituents of the inner boride layer. As seen in Table 1, however, both pairs of the phases are readily distinguishable, besides metallographical examination, by electron probe microanalysis because of the large difference in their iron and chromium content.

Both boride layers possess a pronounced \{002\} texture and therefore consist of columnar crystals oriented preferentially in the direction of diffusion.

![Fig. (3). Microstructure of plan-view sections of borided Fe–25% Cr alloy samples crossing the outer boride layer. The layer is two-phase. Its brighter regions are the (Fe,Cr)B phase, while the darker regions (thin long crystals) are the (Cr,Fe)B phase. Reaction time 21600 c (6 h).](image)

Table 1. Average iron, chromium and boron contents of reacting phases, found by EPMA measurements on borided 25% Cr steel samples after their X-ray diffraction investigations [19]

<table>
<thead>
<tr>
<th>Section in Fig. (2a')</th>
<th>Region</th>
<th>Content (mass %/at.%)</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Fe</td>
<td>Cr</td>
</tr>
<tr>
<td>I</td>
<td>Brighter of the outer boride layer</td>
<td>71.4/42.2</td>
<td>12.2/7.7</td>
</tr>
<tr>
<td></td>
<td>Darker of the outer boride layer</td>
<td>53.8/31.8</td>
<td>30.2/19.1</td>
</tr>
<tr>
<td>II</td>
<td>Brighter of the outer boride layer</td>
<td>54.3/31.6</td>
<td>28.9/18.1</td>
</tr>
<tr>
<td></td>
<td>Darker of the outer boride layer</td>
<td>21.9/12.6</td>
<td>61.6/38.2</td>
</tr>
<tr>
<td>III</td>
<td>Brighter of the inner boride layer</td>
<td>68.1/48.6</td>
<td>22.6/17.3</td>
</tr>
<tr>
<td></td>
<td>Darker of the inner boride layer</td>
<td>24.6/17.4</td>
<td>66.8/51.0</td>
</tr>
<tr>
<td>IV</td>
<td>Brighter</td>
<td>84.1/83.2</td>
<td>15.9/16.8</td>
</tr>
<tr>
<td></td>
<td>Darker</td>
<td>27.0/18.8</td>
<td>63.8/48.0</td>
</tr>
<tr>
<td>V</td>
<td>Brighter</td>
<td>81.3/80.2</td>
<td>18.7/19.8</td>
</tr>
<tr>
<td></td>
<td>Darker</td>
<td>24.6/17.4</td>
<td>66.8/51.0</td>
</tr>
<tr>
<td>VI</td>
<td>Homogeneous matrix</td>
<td>80.7/79.6</td>
<td>19.3/20.4</td>
</tr>
</tbody>
</table>
This is considered to be a consequence of the existence of paths of enhanced diffusion in the FeB and Fe₂B crystal lattices [1, 7].

It should be noted that the larger orientation order (higher peak intensity) is characteristic of the inner portions of both boride layers compared to their near-interface ones. It is easily explainable because near-interface portions of any boride layer are less equilibrated in comparison with its inner ones. Therefore, near-interface crystals have less time to align themselves in the preferred direction of growth.

3.2. Layer-Growth Kinetics

Growth kinetics of compound layers are conventionally treated from a diffusional viewpoint giving parabolic equations of the type \( x^2 = 2k_1t \), where \( x \) is the layer thickness, \( k_1 \) is the layer growth-rate constant and \( t \) is the time [1, 15, 16]. For rather thick boride layers, such equations produce a quite satisfactory fit to the experimental data. In the case of 13% Cr steel, temperature dependence of the growth-rate constant \( k_1 \) is described by relations of the Arrhenius type

\[
k_1 = 1.37 \times 10^{-8} \exp(-132.9 \text{ kJ mol}^{-1}/RT) \text{ m}^2 \text{ s}^{-1}
\]

for total thickness of both boride layers,

\[
k_1 = 1.49 \times 10^{-7} \exp(-149.5 \text{ kJ mol}^{-1}/RT) \text{ m}^2 \text{ s}^{-1}
\]

for the FeB layer,

\[
k_1 = 7.90 \times 10^{-9} \exp(-116.4 \text{ kJ mol}^{-1}/RT) \text{ m}^2 \text{ s}^{-1}
\]

for the Fe₂B layer,

where \( R \) is the gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)) and \( T \) is the absolute temperature, K.

With 25% Cr steel, kinetic data were treated using only the values of the total thickness of both layers because the thickness of each of them could hardly be measured separately with a sufficient accuracy due to its extreme irregularity. In this case, the value of the diffusional constant \( k_1 \) was found to be 0.72 \times 10^{-14} \text{ m}^2 \text{ s}^{-1} \) at 850°C, 1.36 \times 10^{-14} \text{ m}^2 \text{ s}^{-1} \) at 900°C, and 2.40 \times 10^{-14} \text{ m}^2 \text{ s}^{-1} \) at 950°C. These constants can be employed to estimate boride layer thicknesses at intermediate values of time.

For the total thickness of both boride layers formed on the surface of 25% Cr steel samples, the Arrhenius-type equation is

\[
k_1 = 1.72 \times 10^{-8} \exp(-137.1 \text{ kJ mol}^{-1}/RT) \text{ m}^2 \text{ s}^{-1}
\]

Values of the pre-exponential factor \( K_0 \) and the activation energy \( E \) obtained are typical of diffusion-controlled processes [1, 15, 26, 27] and can be used in practice to evaluate the growth-rate constants of boride layers at intermediate temperatures.

It is worth noting that from a physicochemical viewpoint a more adequate description of growth kinetics of compound layers is generally provided by a system of two differential equations [15]. It covers the whole time range of layer formation from the beginning of interaction of initial reactants to the establishment of equilibrium at which, according to the Gibbs phase rule, at most two phases must remain in any binary system under constant temperature-pressure conditions. In contrast, diffusional (parabolic) equations are only applicable at long reaction times when the rate of diffusion across layer bulks becomes much less than the rate of subsequent chemical transformations at phase interfaces.

Two essential inconsistencies of purely diffusional considerations must be mentioned.

1. Both boride layers are usually assumed to grow at the expense of diffusion of boron atoms. It is possible only under conditions of reaction (chemical) control characteristic of thin layers. Under conditions of diffusion control, much more frequently satisfied in practice, FeB layer bordering the boron-containing agent grows at the expense of diffusion of boron atoms across its bulk and their subsequent interaction with the surface portions of the Fe₂B layer. Similarly, the Fe₂B layer adjacent to the steel base grows at the expense of diffusion of iron atoms across its bulk and their subsequent interaction with the surface portions of the FeB layer. Thus, both layers thicken at their common interface, with only one component diffusing across each of them. Clearly, two components can diffuse, if a single boride layer is formed, whatever its growth regime (reaction or diffusion controlled).

2. Existing kinetic descriptions of diffusional growth of boride layers (see, for example, [28, 29]) are tacitly or explicitly based on an assumption of the existence of a rather wide homogeneity range HR of appropriate boride phases. However, iron borides FeB and Fe₂B have no noticeable homogeneity range. Also, the concentration profiles of the elements within the growing layers are assumed to be close to linear. In such a case, the parabolic growth-rate constant \( k_1 \) proves to be proportional to the diffusion coefficient \( D \) of a given component and the difference \( \Delta c \) in its concentration (content) at the interfaces of a growing compound layer: \( k_1 \sim D \Delta c \). The latter is
conventionally considered to be equal to the width of the homogeneity range HR of an appropriate compound: \( \Delta c = HR \). If it were so, however, then the layers of compounds without any range of homogeneity, like FeB and Fe\(_2\)B, would not grow at all that contradicts available experimental data.

Even for compounds with a narrow range of homogeneity these descriptions are misleading and yield the unrealistically high values of diffusion coefficients because in the limit it means dividing by zero. Hence \( D \to \infty \), as \( \Delta c \to 0 \). From a physical viewpoint, such values are hardly possible.

In fact, however, the layer of any compound grows at the expense of stoichiometry of that compound and not at the expense of its range of homogeneity. The value of \( \Delta c \) is the difference in concentration of vacancies at layer interfaces [15]. It is necessary to distinguish between the newly-formed and native (equilibrium) vacancies. The newly-formed vacancies arise in the course of partial chemical reactions proceeding at layer interfaces. These are thus reaction-induced vacancies which do not exist in a given equilibrated compound. The native (inherent), mainly thermal, vacancies are present in the compound initially (in the equilibrium state). Their amount is quite negligible by comparison.

The concentration of newly-formed vacancies of a given component in a growing compound layer at its interface where a product-forming partial chemical reaction takes place is numerically equal (with the opposite sign) to the content of this component in the compound, while that at another (non-reacting) interface is zero (ideal case in which no native vacancies are available in the compound).

Then, \( k_1 = D \), if \( \Delta c = HR = 0 \).

Hence, the parabolic growth-rate constant \( k_1 \) is identified with the reaction-diffusion coefficient \( D \) of a given component in the lattice of a chemical compound. If \( HR \neq 0 \), then \( k_1 \approx D \). The difference between \( k_1 \) and \( D \) decreases, as \( HR \) tends to zero. It means that the closer the compound to its stoichiometric composition, the more nearly \( k_1 \) approaches \( D \). The self-consistent approach excluding dividing by zero and yielding physically reasonable values of the diffusion coefficient \( D \) are thus obtained.

It must also be emphasized that, contrary to wide-spread and nonetheless misleading views, the role of native point defects, such as vacancies of a given component, in the reaction-diffusion process of formation of any chemical compound, like boriding, carburizing, nitriding, metallization and others, is opposite to their role in the process of self-diffusion of that component in the compound taken as a separate phase. In the absence of complicating factors, the higher the amount of native vacancies, the higher is the rate of self-diffusion of the component in the separate phase. Contrary to this, the higher the amount of native vacancies, the less is the rate of growth of the compound layer in any reaction couple at the expense of diffusion of that component, i.e. the less is a value of the constant \( k_1 \). This effect may roughly be estimated quantitatively as \( HR = c_{\text{total}} \), \( c_{\text{total}} \) being the content (concentration) of a given component in a chemical compound. If \( HR = 0 \), it is also zero. If, for example, \( HR = 1\% \) and \( c_{\text{total}} = 50\% \), its numerical (negative) value is 2%. Surely, in more exact calculations the values of \( HR \) and \( c_{\text{total}} \) must be expressed in mol m\(^{-3}\) and not in mass or atomic percent.

From a chemical viewpoint, the conclusion made appears to be quite obvious and substantiated because unoccupied (empty) sites (vacancies) present initially can hardly take part in chemical reactions yielding product phases. It is just available atoms, ions, molecules or radicals, and not native vacancies, which are responsible for the progress of any interfacial chemical reaction.

3.3. Microhardness of Reacting Phases

With 13% Cr steel, microhardness HV\(_{100}\) of the outer layer was found to be 17.9 GPa, while that of the inner 16.1 GPa. Appropriate values for the layers on 25% Cr steel samples are 17.8 and 15.9 GPa.

Microhardness was found to vary considerably (±1.5 GPa) within both boride layers, especially those with the second type of microstructure in view of their non-homogeneity. The difference in microhardness of near-boride and far-away regions of the steels is insignificant (around 0.2 GPa). The microhardness values obtained are close to those reported in the literature [1].

3.4. Dry Abrasive Wear Resistance of Boride Layers

Boriding of steel tablets for abrasive wear resistance tests was carried out at 950 °C for 6 h. The initial results of wear resistance tests are presented in Table 2 for 13% Cr steel as an
example, while the final comparative data for both steels in Table 3.

The wear resistance of the outer FeB layer, found from mass loss measurements, is 10–25 times greater than that of the steel base. Its deeper portions display a higher wear resistance compared to near-surface ones due to a more profound texture and a much less amount of cracks. The wear resistance of the inner Fe₃B layer is around 15 times greater than that of the steel base. Boride layers with the microstructure of kind II are seen to be much more wear resistant than those with the microstructure of kind I. Most probably, it is due to structural and morphological rather than compositional reasons because the difference in their wear resistance exceeds 25 times, whereas that in chromium content is only around 2.

CONCLUSIONS

Two boride layers possessing two different kinds of microstructure occur at the interface of high chromium (13 and 25% Cr) steel samples with boron in the course of their boriding at 850–950 °C and reaction times up to 43200 s (12 h). In the case of 13% Cr steel, both boride layers are one-phase. It is a microstructure of kind I. Each of the two boride layers formed on the surface of 25% Cr steel samples is two-phase. It is a microstructure of kind II which was not observed by previous researchers. Both layers possess a pronounced texture. Their growth kinetics on both steels are close to parabolic. Boride layers with the microstructure of the second kind exhibit a much higher wear resistance than those with the microstructure of the first kind. The difference exceeds an order of magnitude.

CONFLICT OF INTEREST

The author confirms that this paper content has no conflict of interest.

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