

## CHARACTERIZATION OF BORIDE LAYERS ON RYALLOY STEEL

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### Abstract

Boronizing is a thermochemical process in which the boron atoms are introduced into the steel surfaces. During this process, the boride layers with high hardness, wear- and corrosion-resistance are formed. In this study, the Royalloy (0.05 wt.% C; 12.6 wt.% Cr; 0.4 wt.% Si and 1.2 wt.% Mn) steel was powder-boronized at 900, 950, 975, 1000 or 1050 °C, and for 1, 3, 5, 7 or 10 h. The boronized samples were analyzed by X-ray diffraction analysis (XRD) to analyze their phase composition, and by scanning electron microscope to analyze their thickness and morphology at the interface with the substrate. To investigate the chemical elements redistribution during the boronizing process, the EDS mapping and EDS point analysis were used. The treatments produced boride layers with a thickness from 8 to 168 μm, depending on the boronizing parameters. During the boronizing process, the chromium was redistributed between the boride layers, where creates the chromium borides, and the transient region underneath the boride layers, where creates the particles with the biggest amount of chromium. The silicon was focused at the layer – substrate interfaces. The concentration of manganese was slightly higher in substrate compared to the boride layers.

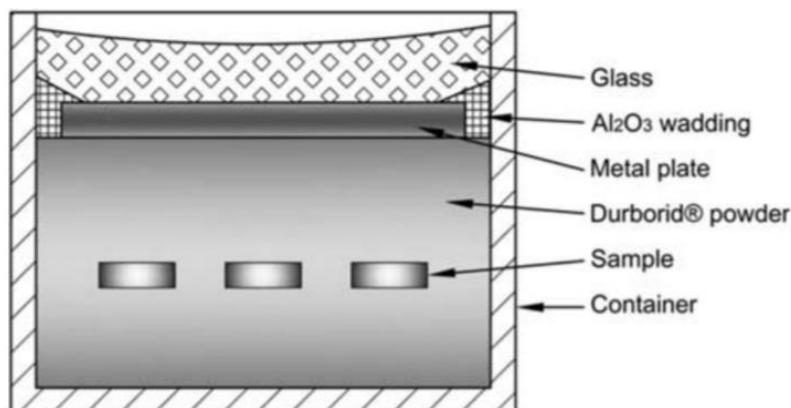
**Keywords:** Boride layers, boronizing, chromium, borides

### 1. INTRODUCTION

For ferrous alloys the boronizing process is realized in the temperature range of 800 – 1050 °C and for 0.5 – 10 h. By this process, it is possible to improve some properties of steels, such as surface hardness, corrosion resistance, wear resistance etc. [1,2]. Boronizing can be realized in gaseous medium [3], in solid medium (powder, paste) [2,4,5], in plasma [4,6] or by electrolysis [7]. In the case of carbon steels, the formation of boride layers on their surface takes place according to the iron - boron equilibrium diagram. During the formation of the boride layers, the Fe<sub>2</sub>B phase with a content of 8.83 wt.% B is formed first. The hardness of this phase is around 1700 HV [1]. The FeB phase is formed as the second one. It contains 16.23 wt.% B and has a hardness of around 2200 HV [1]. In case of high- alloy steels, borides of alloying elements, especially chromium borides (Cr<sub>x</sub>B<sub>y</sub>), may also occur in the boride layers [1,8]. The thickness of boride layers increases as both the boronizing temperature and time, however, increasing carbon and alloying elements content inhibits the growth of boride layers. The reason of this phenomenon is that the carbon and alloying elements, especially chromium, decrease active diffusion of boron. For this reason, in case of high-alloy steels, the morphology of boride layers at interface with the substrate becomes smooth and loses characteristic sawtooth morphology [1,2]. The current paper deals with the basic characteristics of boronized layers developed on low-carbon high-chromium steel substrate. The plastic mould steel Uddeholm Royalloy was used as a model material. The thickness of each individual boronized region, redistribution of main elements between borides and substrate is described and discussed.

## 2. MATERIAL AND EXPERIMENTAL TECHNIQUES

The analysed material was Royalloy steel with a chemical composition (in mass%) 0.05 % C; 0.4 % Si; 1.2 % Mn; 12.6 % Cr [9]. A total of 51 samples were made from this steel, each of which was numbered (R0 - R50). The samples were metallographically prepared by grinding on SiC sandpapers with a grain size 600 and 1200 and polished with a polishing wheels using a diamond paste with a particle size of 6, 3 and 1  $\mu\text{m}$ . After metallographic preparation, the samples were ultrasonically cleaned and degreased in acetone for 15 min. Subsequently, the samples were boronized in Durborid powder mixture, when the powder mixture and samples were added into the steel container and hermetically sealed (**Figure 1**) [10]. The container was placed into an electrical resistance furnace and heated to the pre-determined boronizing temperature. The boronizing process was carried out at 900, 950, 975, 1000 or 1050  $^{\circ}\text{C}$ , and for 1, 3, 5, 7 or 10 h at each temperature. After the boronizing process, the samples were cooled down slowly to the room temperature and removed from the containers. For microstructural examinations boronized specimens were prepared by grinding on SiC sandpapers with a grain size 80, 280, 600 and 1200 and polished with polishing wheels using a diamond paste with a particle size of 6, 3 and 1  $\mu\text{m}$ . After polishing, the samples were etched in COR etchant ( $\text{CH}_3\text{COOH}$ ;  $\text{HCL}$ ; picric acid,  $\text{CH}_3\text{OH}$ ) [11] for 5 – 7 s. The microstructures were analysed by a scanning electron microscope (SEM) Jeol JSM-7600F, using a secondary electrons by an acceleration voltage 15 kV. Thickness of individual boride layers were measured on at least five randomly acquired SEM images, at appropriate magnification. To obtain a sufficient reliability of the obtained results an approach by Kunst and Schaaber [12] has been used. For a more precise determination of chemical elements redistribution, the microscopic analysis was supplemented by an energy dispersive spectroscopy (EDS), where the point analysis (min. 8 measurements in each borides) and chemical elements mapping were realized.

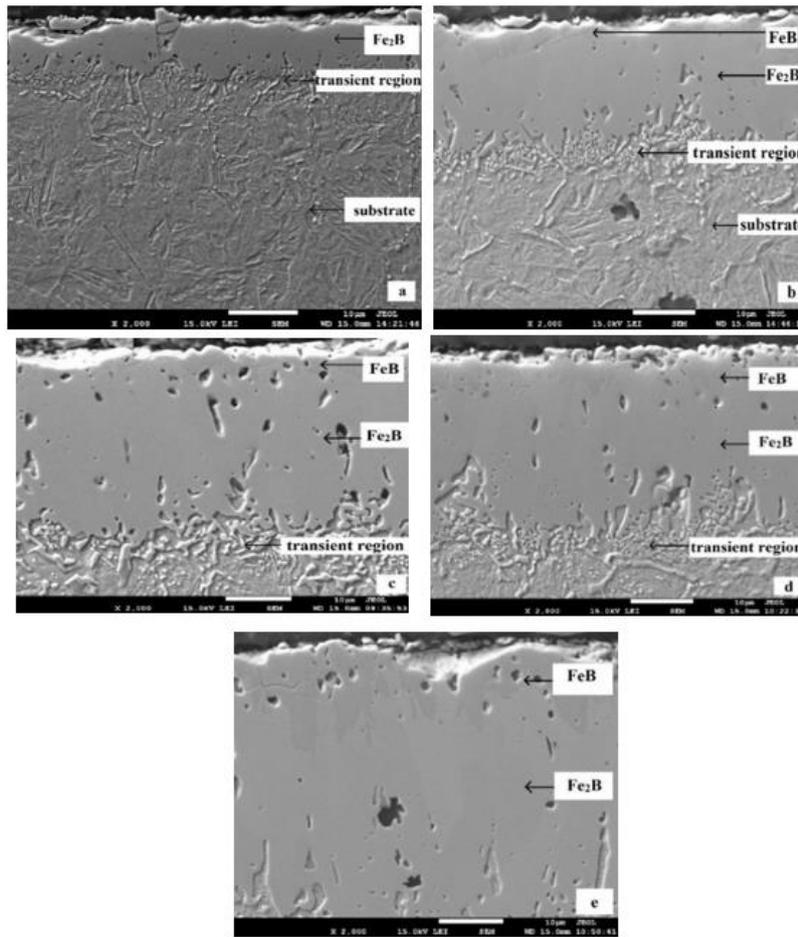


**Figure 1** The scheme of Durborid powder mixture boronizing [5]

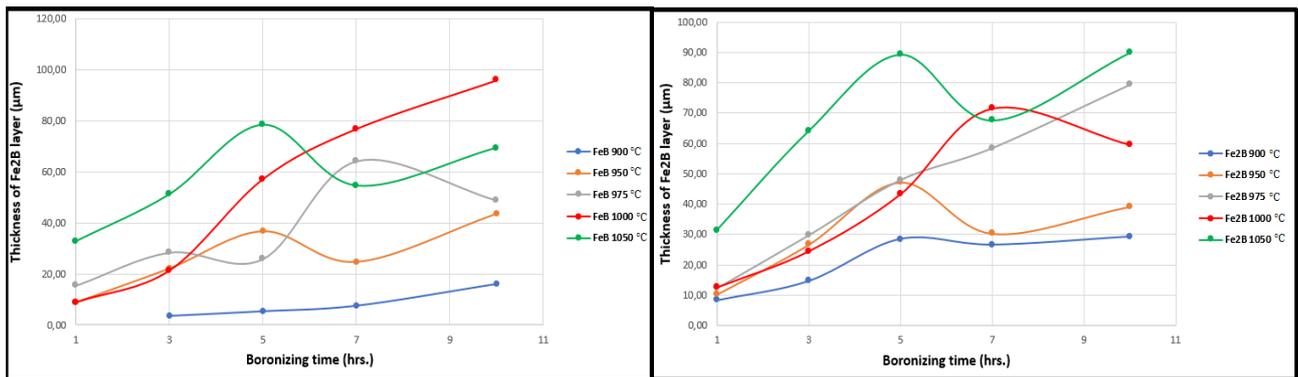
## 3. EXPERIMENTAL RESULTS AND DISCUSSION

Cross sectional SEM images of boronized samples at 900  $^{\circ}\text{C}$  for 1, 3, 5, 7 and 10 h are shown in (**Figure 2**). The boride layers were two-phase, composed of  $\text{FeB}$  and  $\text{Fe}_2\text{B}$  phase, except the sample boronized at 900  $^{\circ}\text{C}$  for 1 h. In this case, the boride layer was composed of  $\text{Fe}_2\text{B}$  only. Underneath the boride layers, there is an area called transient region. As can be seen a lot of small particles are present there. However, they nature is not clarified yet, and this issue needs further investigation.

As shown in (**Figure 3**) the thickness of boride layers increases with increasing the boronizing temperature and/or duration. However, the thickness increase does not obey a parabolic thickness-duration relationship, which is typical for most thermo-chemical treatments. Specifically, the most of deviations from the parabolic law of the layer growth can be found for processes that were carried out for either 5 or 7 h. A redistribution of alloying elements between the matrix and borides, see (**Figure 4**), can be considered as a possible source of mentioned deviations.

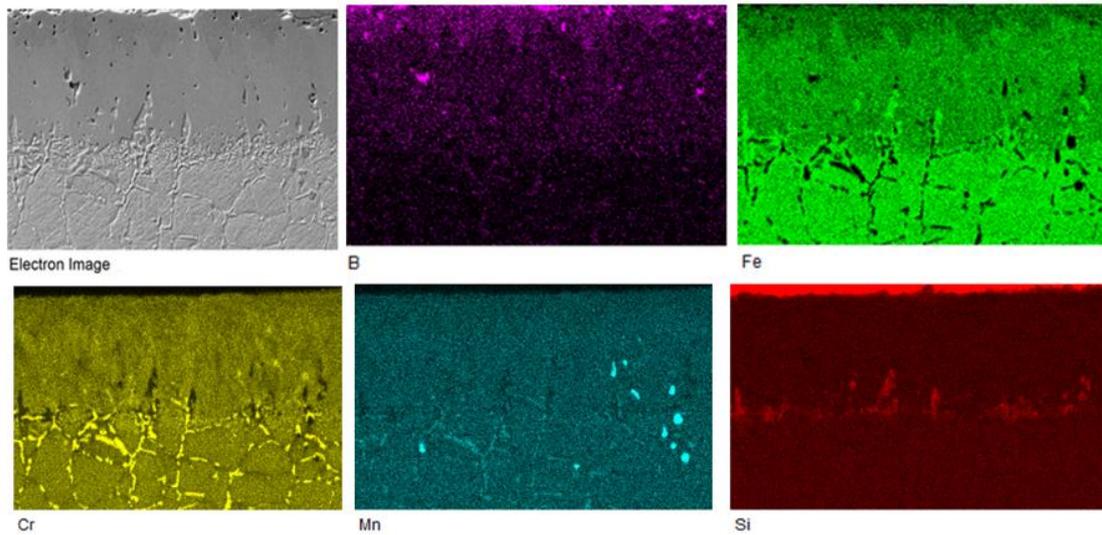


**Figure 2** Cross sectional SEM images of samples boronized at 900 °C for 1(a), 3(b), 5(c), 7(d) and 10(e) h.

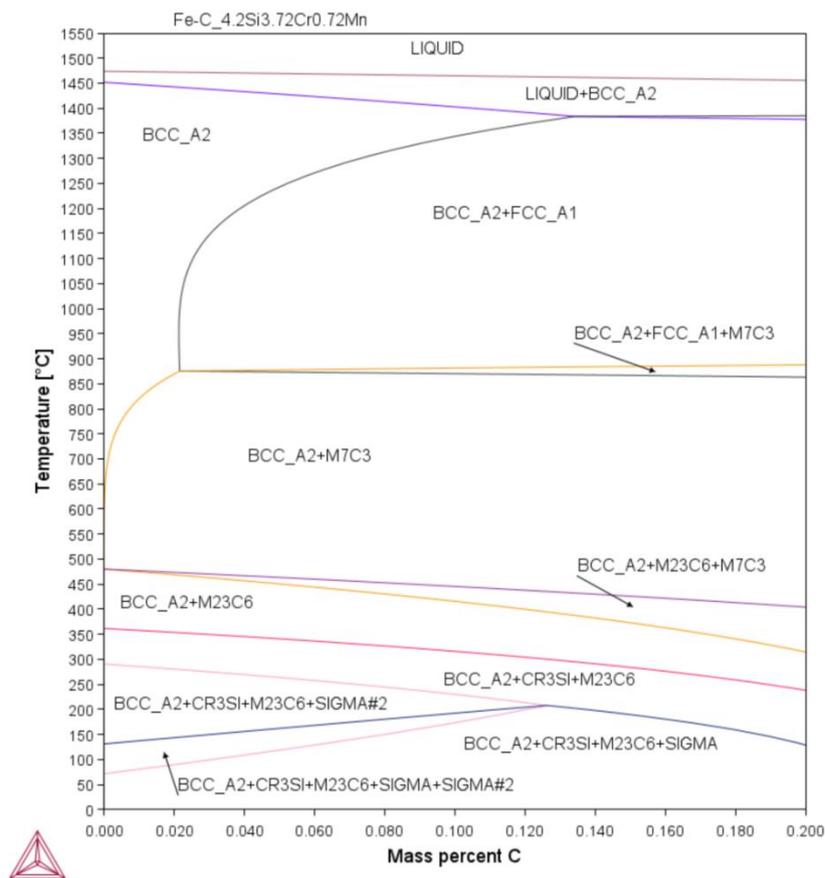


**Figure 3** The growth of boride layers depending on boronizing parameters: FeB layer (left), Fe<sub>2</sub>B layer (right)

**Figure 4** shows an example of EDS maps acquired from the sample boronized at 900 °C for 10 h. It is seen that chromium undergoes considerable redistribution during the boronizing process; the Fe<sub>2</sub>B contains slightly higher Cr content than the FeB. Moreover, significantly enhanced Cr content is visible in the transient region, in different particles present here. Mn is pushed out from borides, and the most part of this element is contained in particles in the transient region. Silicon does not assist in particles formation; the most part of Si is in solid solution close to the Fe<sub>2</sub>B/matrix interface, with maximum concentrations above 4 mass%. It is also worth noting that the analyses of other boronized specimens gave very similar results, and they differ only in the extent of elemental redistribution.



**Figure 4** SEM image + EDS maps of chemical elements in the sample boronized at 900 °C for 10 h.

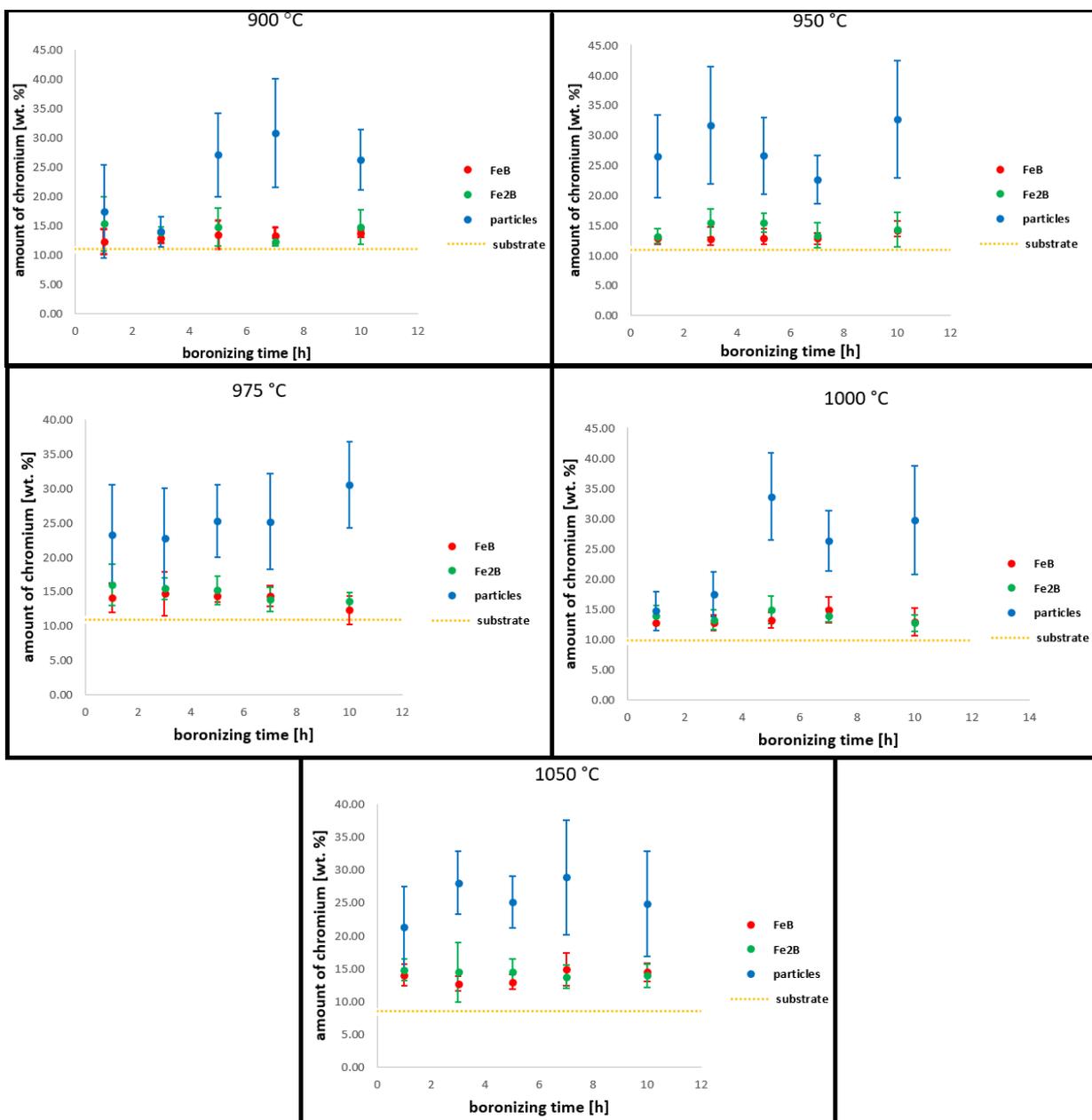


**Figure 5** Result of Thermo-calc simulation of phase equilibria for 4.2%Si – 3.72Cr – 0.72 Mn (maximum determined Si content below the borides. BCC – ferrite, FCC – austenite, other phase are carbides or sigma phase.

**Figure 5** shows a result of Thermo-calc simulation of phase equilibria for maximum Si content below the borides. It is shown that silicon stabilizes the ferrite; at very low carbon content the steel microstructure is ferritic up to the solidus temperature. Since the boron solubility in ferrite is very low [13] the presence of the

BCC solid solution may provide serious obstacles in the growth of boronized layers. The ferrite stabilization through enhanced Si content may also provide a possible explanation of deviations in growth kinetics of boronized layers from parabolic law (**Figure 3**).

For exact quantification of chromium partitioning between borides and substrate the EDS point analysis was used. The graphical interpretation of the obtained results is shown in (**Figure 6**). It is seen that borides contain more Cr than is the content of this element in the substrate. This indicates that Cr is transported to borides leaving the adjacent close-to-borides region depleted by this element (**Figure 4**). Another important aspect is that Fe<sub>2</sub>B contains slightly higher Cr content than FeB. This may be a result of gradual Cr-diffusion from the substrate to the free surface, but also a consequence of the fact that Cr can more easily be incorporated into Fe<sub>2</sub>B than into FeB. This phenomenon, however, needs further careful investigation. Also it is clearly visible that the newly formed particles in transient region contains enhanced (20 – 30 mass% in most cases) Cr content.



**Figure 6** The chromium contents in FeB, Fe<sub>2</sub>B, particles underneath the boride layers and substrate

#### 4. CONCLUSION

In this article, the Royalloy steel was subjected to a boronizing process for different time and temperature. The following conclusion can be derived from the obtained results:

- All the boride layers are two-phase, except the sample boronized at 900 °C for 1h;
- The total thickness of boride layers increases with both the temperature and time, with the maximum thickness of 168 µm obtained for 10 h treatments at either 1000 or 1050 °C;
- Strong deviations from generally valid “parabolic law” of layer growth was determined; an enhanced Si content underneath the borides can cause ferrite stabilization and thereby retardation of growth of borides, for longer treatments in particular;
- A great number of „extra“ particles is formed underneath the boride layers. These particles contain very high amount of chromium;
- Also, borides are enriched with Cr as compared with the nominal substrate Cr content; the Fe<sub>2</sub>B contains slightly higher Cr content than the FeB.

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