Characterization and corrosion resistance of boride layers on carbon steel

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Abstract. Boriding treatment was carried out at 850, 900, 950, 1000 and 1050 °C for 2, 4 and 8 h on carbon steel. The effect of some treatment parameters such as the chemical composition of the mixture, boriding temperature and time were investigated. X-ray diffraction (XRD), scanning electron microscopy (SEM) and microhardness tests were used to describe the formed boride layers. Some properties of boride layers have been studied such as corrosion and wear resistance. The obtained results confirm that the corrosion resistance of boride carbon steel was improved compared to no-boriding steel. The dry abrasive wear resistance of boride alloy samples is about 5 times greater than that of non-boride ones.

1. Introduction

Boriding or boronizing is well known as a thermochemical diffusion surface treatment in which boron atoms are diffused into the surface of samples to form borides on the surface of material. This treatment can be useful for several different types of steels as carbon steels, alloy steels, stainless steels and tool steels and some non-ferrous materials such as titanium alloy and niobium [1-5].

Temperatures process ranging between 850 and 1050 °C in either solid, liquid or gaseous, salt media [6]. Boriding treatment is a prominent optimal for a wide range of tribological applications. Boron atoms can enter smoothly into the samples forming a single or double phases FeB and Fe₂B. The boride layers on carbon steels and low alloy steels have an accentuated acicular form oriented perpendicular to the surface being treated. This serrated formed ensures a good snap of the boride layers to the base metal. In the case of highly alloyed steels, this perforation is muted or non-existent steels. Scaling is done during the quenching oil, where the substrate should be hardened.

To assess the nature and the quality of a given boride layer, simply a metallographic test that allows checking the presence of one or two phases and evaluating the depth of the layers and the nature of the interface between the substrate and the boride layer and making a classification.

Depending on time and temperature process, chemical composition of the substrate, boron potential of medium, a single phase Fe₂B or double phases (Fe₂B, FeB) achieved by diffusing boron atoms into the surface of the substrate [7-10].

In this study, boriding treatment based on the information gathered from the literature taking into consideration the availability of chemicals and their cost. Searching of treatment must be made to ensure a good quality of the layers of borides formed on the carbon steel and a powder whose constituent chemical products may be available on the local market, a reasonable cost of the mixture depending on the proportion and nature of constituents used. Once the boriding treatment is realised, nature and quality of the borides layers formed on the carbon steel substrate were identified, the
influence of parameters such as boriding temperature and time of on the nature, quality and microstructure of the obtained boride layers were examined. The microhardness of the layers of borides obtained on carbon steel and that obtained on the underlying layers and substrate were investigated. The corrosion resistance of the boride layers made by the technique of powders in various aggressive environments (acidic, basilicon carbide media and salt water) and the wear on abrasive and erosive of borides layers formed were studied.

Thus, the aim of present study is realised boriding treatment and then characterize the boride layers formed and measure the thickness and hardness of boride layer after different boriding treatments, and study some properties of boride layers such as wear and corrosion resistance.

2. Experimental procedure

2.1 Microstructure of the boride layer

The carbon steel essentially containing 0.36 wt. % C, 0.04 wt. % Cr, 0.28 wt. % Mn, and 0.13 wt. % Si was used as substrate. Substrate used had a rectangular shape and were 6×6×2.5 mm3. Boriding treatment was performed in a liquid medium based on borax at temperatures of 850 to 1050 °C include the time intervals for 2, 4 and 8 h.

The nature and the morphology of boride layers formed on the carbon steel substrate were established by optical microscopy using LEICA microscopy. The attendance of boride phases on the carbon steel substrate was determined by X-ray diffraction (XRD) analysis. X-ray diffraction patterns were taken immediately from the surface of samples using Cu Ka radiation with a wavelength of 1.7902 Å was used over a 2θ range of 20–90°. X-ray diffraction shapes were taken on each boride sample [11-13].

Microhardness measurements on metallographic cross-sections was carried out using SHIMATZU tester with the diamond pyramid (Vickers indenter). The microhardness of boride layers was measured six times for each point for the same distance between the surfaces and indentation points by means of Vickers indenter with applied load of 1 N (100 g/force).

Abrasive wear resistance tests were carried out on P180 Silicon carbide emery paper tape (main fraction grain size, 50 mm; maximum, 80 mm) using an AWRD device. The load is 50 N (5100 g/force). The wear resistance was determined by means of weighing the samples and measuring their height.

A digital measurement instrument devoted to the optical microscope and via a second method by ImageJ Launcher software to calculate the thickness of the boride layer. The thickness average of six different measurements.

3. Results and discussion

Figures 1 and 2 shown the cross-sectional micrographs of boride layers formed on carbon steel substrate at 900 °C for 2 h and 950 °C for 4 h, respectively. Boriding treatment of carbon steel mains to the formation of two borides, FeB and Fe2B. FeB near to the surface and Fe2B approximately close to the carbon steel substrate (Figure 1).

The boride layers were obtained on the entire surface of the treated samples, even in curved areas showing samples of hexagonal shape edges, it uniforms clear that the obtained boride layer covers the entire surface of the sample with an equivalent thickness across the entire surface. Depending on boriding temperature and time, the boride layers obtained on carbon steel are single-phase or double-phase in silicon carbide as shown in Figure 2.
When higher temperature and hold-time is prolonged, the proportion of boride FeB is more important. Therefore, we can say that the choice between a layer single-phase boride consisting of the unique boride Fe$_2$B or another or double-phase in silicon carbide consisting of two FeB borides and Fe$_2$B can occur depending on the operating conditions. It should be mentioned that the boride layer FeB at the top, close to the surface was darkly etched in comparison to the luminously etched inner Fe$_2$B and the highly etched substrate, as shown in Figure 3.

At present study, the attendance of borides was identified and confirmed using XRD analysis. Optical microscopy examination of borides formed on the surface of carbon steel substrate shown a columnar and saw-tooth morphology at the interface of the substrate without any evidence of break. Depending on boriding temperature and time there is a semi parabolic relationship between boride layers thickness and boriding parameters (time and temperature). Increasing the boriding temperature not only reinforced to increase the boride layers thickness but also affected to roughening the microstructure in the substrate.
As estimated before, higher boron contents were detected at the boride layers than the substrate. The saw-tooth morphology of boride layers was clearly detected between Fe$_2$B and FeB layers during high magnification SEM examinations. The cross-sectional SEM micrographs of the samples boride are presented in Figure 4 along with the EDX line scan profile of boron as shown in Figure 5. There is no peaks of boron due to the low porcentage of this element.

![Figure 4. SEM image of microstructure boride carbon steel at 900 °C for 4 h](image1)

![Figure 5. SEM image of microstructure of FeB and Fe$_2$B borided carbon steel at 900 °C for 2 h](image2)
The is no remarkable difference was registered with regard to the form of the boride layers obtained on carbon steel substrate, the borides layers obtained have a wild form with needles that are perpendicular to the treated surface orientation. The wild form of the boride layers formed on steel presented a good way of hanging for these layers on the substrate. Decohesion at the coating/substrate interface problems often encountered in surface treatments are virtually absent in this case. FeB Boride appears darker than boride Fe$_2$B. The proportion of Fe$_2$B boride is greater than FeB boride. It is clear to observe the difference between the boride and the rest of the material that appears with a color slightly lighter than FeB boride as confirmed previously. It should be noted also that FeB boride which is located towards the outside of the formed layer is characterized by its wild form.

Microstructural and properties of boride layers depended on the boriding temperature and the treatment time. Longer boriding time and higher boriding temperature resulted in a thicker boride layer and the boride layer thickness was ranged between 20 and 387 µm [14].

On the XRD patterns of the samples borided based on borax-Al or borax- $B_4$C, the peaks of the Fe$_2$B phase were detected as shown in Figure 6.a and 6.b. However, on the XRD patterns of the samples boride based on borax- Silicon carbide only FeB peaks were present (Figure 6.c). The XRD results exhibited that the dominant phases formed on the surface of carbon steel are FeB and Fe$_2$B phases, depending on the temperature, time of process and mixture of compounds. The average thickness of boride layers along with the thicknesses of Fe$_2$B and FeB phases is grouped in Table 1.

**Table1.** The average thickness of boride layers at 900 °C for different times

| Boriding time (h) | Fe$_2$B Thickness (µm) | FeB Thickness (µm) | Total thickness (µm) |
|------------------|------------------------|---------------------|----------------------|
| 2                | 128                    | -                   | 128                  |
| 4                | 137                    | 12                  | 149                  |
| 8                | 146                    | 19                  | 265                  |
The higher boriding temperatures at 1000 °C encouraged the growth of boride layers. It is perceptible that in the case of double boride layers phases, the thickness of the Fe$_2$B was about approximately more than the double of FeB thickness.

The results of micro hardness measurements exhibited on the boride surfaces are design in Figure 7 with respect to the indentation load. Depending on the phase structure of the boride layer, hardness of the boride surfaces followed two different pathways; boride layers which the hardest zone, transition zone and matrix.

![Figure 7. Hardness profiles of carbon steel](image)

Higher boriding temperatures creating a double phase boride layer provided higher hardness than lower boriding temperatures inducing a single-phase boride layer [15-17]. At the minimum indentation load applied in the present study (100 g), hardness values obtained from the single (1600 HV) and double phase boride layer (1850 HV) coated surfaces were in the range reported in the literature for the Fe$_2$B and FeB phases, respectively. While the hardness of the double phase boride layer coated surface reduced about 1000 HV. Vickers indenter estimated the values of fracture toughness of boride layers of carbon steel. It depends on the boriding parameters (time and temperature), indentation loads applied and the distance from the surface. Their values were located between 3.42 and 4.57 MPa m$^{1/2}$ depending on time and temperature of treatment [14].

The effect of the chemical composition on boriding mixture was studied and confirmed that the mixture boriding provide boride layers where boron carbide is replaced by borax as a boron source. Increasing the content of activator in the boriding mixture where the boron source is boron carbide growths, the thickness of the boride layer formed. While it does not change the non-effectiveness of the powder where the boron source is borax. Addition of NaBF$_4$ and/ or NH$_4$Cl as an additional activator to the boriding mixture does not change the effectiveness of this mixture. The boron activation energy on carbon steel surface was found about 227.51 kJ mol$^{-1}$ and the kinetic studies of boride layers showed a semi parabolic relationship between the boride layer thickness and the process time [18].

The boriding treatment of carbon steel greatly improves its corrosion resistance in acidic environments in general and particularly in sulfuric acid. This treatment clearly ameliorates the corrosion resistance of carbon steel in the aqueous solution of NaCl (30 g/l). The boriding has not the same effect on the corrosion resistance in basilicon carbide solutions used, it improves in the case of normal aqueous NaOH solution and slightly in the case of normal aqueous KOH solution. The
The corrosion rate of boride steel in acidic solutions is much higher than basic aqueous solutions. The boride steel has a good resistance to corrosion in the aqueous solution of NaCl (30g/l).

Figure 8 represents the effect of corrosive environment on the surface of boride layers, it can be seen that the areas where the boride layer is relatively weak are completely corroded, while the areas where the borured layer is quite large remain intact. Boride layers of carbon steel for dry abrasive wear resistance tests was carried out at 950 °C for 4 h. An optical microscope observation of different samples after the wear tests revealed that the deterioration of boride surface by abrasive silicon carbide particles (SiC) is of the purely abrasive type as revealed in Figure 9. Figure 9 shows clearly the damage caused by the silicon carbide abrasive particles leaving visible scratches on the test surface. There is no evidence of adhesion was observed on the tested samples to consider that the wear tests performed are abrasive wear tests. A comparison of the wear resistance of boride carbon steel samples with that non boride samples investigated around 5 times greater than non-boride samples.

![Figure 8. Optical microscopy of a boride surface attacked by corrosive environment](image1)

![Figure 9. Wear traces by the abrasive particles of silicon carbide on the boride surface](image2)

4. Conclusion
The following conclusions can be derived as:
In the present study, carbon steel was borided at five different temperatures between 850, 900, 950, 1000 and 1050 °C for 2, 4 and 8 h.

The progress of boride layer thickness can be increased as a function of boriding time, depending on the temperature.

Boriding treatments compounds based on borax and Silicon carbide formed a single-phase of boride layer (Fe₂B), while the compound based on boron carbide (B₄C) formed double phase (Fe₂B and FeB). Single and double phase boride layers shown almost similar tribological performance and superior wear resistance.

The micro hardness values of the boride layers formed on carbon steel were ranging from 1600–1850 HV, depending on parameters boriding treatment (time and temperature) and the compounds of process, while the non-boride steel substrate is 250 HV. Micro hardness measurements conducted on the borided surfaces revealed higher micro hardness.

The wear resistance shown a tendency to decrease with increasing temperature. The double phase boride layer yielded better wear resistance than the single-phase boride layer at high temperatures and the wear resistance of boride carbon steel samples is greater than non-boride sample about 5 times.

Acknowledgement
The authors would like to acknowledge the financial support of Ecole Normale Supérieure de Laghouat- Algeria.

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