

Evaluation of the corrosion resistance of iron boride coatings obtained by paste boriding process

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Abstract

An evaluation of corrosion resistance of boride coatings in AISI 304 steel was carried out. Formation of iron boride layers (FeB and Fe₂B) at the material surface was obtained by paste boriding process. Boron paste thicknesses of 4 and 5 mm were applied to the steel surface. A thermochemical treatment, for each boron potential, was carried out at temperatures of 1173, 1223 and 1273 K; with exposure times of 4 and 6 h. Corrosion resistance of the borided samples was evaluated by the electrochemical techniques of open circuit and polarization resistance with a 0.1 M solution of NaCl. Dependence between the polarization resistance and the experimental parameters is observed. The results show that the corrosion resistance is maximized with a treatment time of 4 h and a boron paste thickness of 4 mm.

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1. Introduction

Boron is widely used to protect materials from being oxidized at high temperatures as well as a lubricant and as a corrosion inhibitor during the manufacturing process of steel [1,2]. Thus, the boriding process enhances the corrosion and wear resistance of metallic and non-metallic surfaces covered with boride layers. Paste boriding is an alternative method of sample treatment when the manual work required in powder boriding needs to be decreased. In addition, its advantage lies in high volumes of work and in selective treatments [2,3]. Boron paste consists of B₄C (approximately 76% wt. boron) and cryolithe (Na₃AlF₆, flux additive). A maximum of 10–20% of water can be added without impairing the boriding effect. The layers obtained at the material surface, due to boron diffusion, can be a FeB/Fe₂B bilayer or a Fe₂B monolayer; depending upon the boron potential, the chemical composition of the substrate, the time process, and temperature of the treatment [3]. Furthermore, the morphology of iron borides is influenced by the alloying

elements present in the material. It has been shown that a high concentration of chromium and nickel generates a flat front growth of the layers,¹ besides the presence of both borided phases is influenced by the alloying elements in the steel [4,5].

In this study, the corrosion resistance of iron boride layers obtained by the paste boriding process in AISI 304 steel is evaluated. The corrosion data were obtained through the linear polarization and the open circuit electrochemical techniques. The corrosion resistance of boronized samples was compared with untreated samples of AISI 304 steel.

2. Experimental procedure

2.1. Thermochemical treatment

The paste boriding treatment was applied to cylindrical samples (diameter=19.05 mm, large=27 mm) of AISI 304 steel, whose chemical composition is shown in Table 1. The

¹ In pure iron and in low and medium carbon steels, the morphology of the boride layers is saw-toothed, showing anisotropic nature, where the presence of Fe₂B monolayer is recommended in industrial applications, due to its minor fragility in comparison with a FeB/Fe₂B bilayer.

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Table 1
Chemical composition (% wt.) of AISI 304 steel

C	Mn	P	S	Si	Ni	Cr
0.08 maximum	2.00 maximum	0.045 maximum	0.030 maximum	1.00 maximum	8–10.5	19–20

machined samples were initially annealed in argon at 923 K during 1 h in order to increase short paths for the diffusion of boron; once cooled to room temperature, the samples were placed into an acrylic mould. The empty space between the sample and the mould was filled with a Dur–Ferrit boron paste in such a way that the thickness of the paste was either 4 or 5 mm. The water/paste ratio used was 0.2, which is optimal to minimize the porosity of the mixture during its drying stage [7]. The covered samples were taken out of the mould and placed into a muffle furnace to sinter the paste, allowing the boron to diffuse into the steel substrate. Such processes were carried out at 1173, 1223 and 1273 K during 4 and 6 h, respectively, under an inert atmosphere (high-purity argon). After the boriding process, the excess paste was removed and the samples were cross-sectioned and prepared for metallographic examination and for corrosion testing. Thicknesses of boride layers were characterized with the aid of the MSQ Plus image analyzer.

2.2. Electrochemical assays

The electrochemical techniques of open circuit (OC) and linear polarization (LP) were done with the aid of the EG&G model 273 potentiometer. A schematic representation of the experimental setup is presented in Fig. 1. The electrochemical characterization techniques were established because they show, in a simple and effective way, the corrosion resistance of the different materials under evaluation. The borided samples were covered with an epoxy resin, in order to isolate them from the electrolyte, thus leaving only a testing area of only 1 cm². Once the encapsulation of the samples was done, a hole of 1/8 in. was made along the samples, in order to

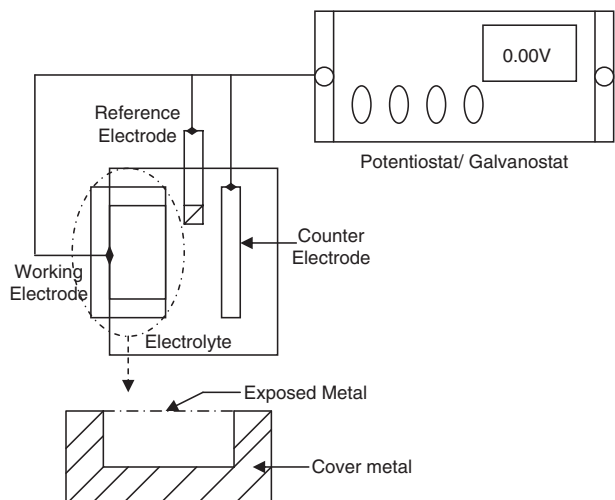


Fig. 1. A schematic representation of the experimental setup.

Table 2
Experimental parameters of electrochemical techniques, OC and LP

Parameters	Value
<i>Open circuit technique</i>	
Assay time	1000 s
Number of points	24
<i>Linear polarization technique</i>	
Potential	$-20.0E-3 V_{oc}$ to $20.0E-3 V_{oc}$
Current range	Automatic
Scanning	Range $166.0E-3$ mV/s (increments of 100 mV and 401 points)

obtain contact between the potentiometer and the work electrode, and to close the circuit in the electrolytic environment. The electrolyte consisted of a 0.1 M NaCl solution; while the auxiliary electrode was graphite and the

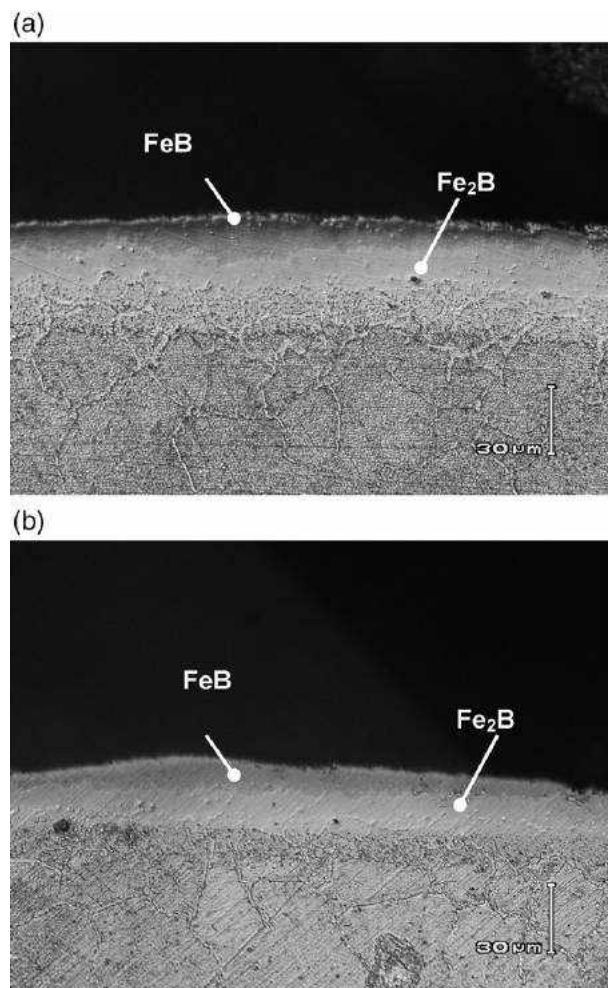


Fig. 2. Cross-sectional views of borided AISI 304 steels at 1223 K during 6 h of treatment and boron potentials: (a) 4 mm and (b) 5 mm.

reference electrode was made of Ag/AgCl (+0.25 V with respect to the normal hydrogen electrode). Table 2 shows the experimental parameters selected for the corrosion measurements.

3. Results and discussion

Growth fronts of borided layers, as well as FeB and Fe₂B on the surface of AISI 304 steel samples at 1223 K, with a treatment time of 6 h and boron potentials of 4 and 5 mm are presented in Fig. 2. The morphology of the layers is flat due to high surface tension resulting from alloying elements at the substrate. Likewise, dependence of the process on time and temperature results in an increase of layer growth kinetics, thus obtaining layer thicknesses between 7.47±0.65 μm and

15.18±3.47 μm for FeB, and between 13.00±1.02 μm and 33.98±2.73 μm for Fe₂B phase, in the boriding temperatures of 1173 K and 1273 K and time process of 4 and 6 h, respectively.

The influence of alloying elements on boride layer thicknesses can be explained considering that while chromium easily dissolves into iron borides depleting the underlying base alloy, nickel displays a much lower tendency to dissolve in iron borides and, therefore, concentrates beneath the boride coatings [5,6]. If the alloying elements of the substrate steel are increased (for example, chromium and nickel), the development of a jagged boride/substrate interface is suppressed, and a smooth interface is formed. In fact, the atomic radii of Cr and Ni are about the same and larger than that of Fe, and it can then be expected that Cr and Ni dissolved on the Fe sublattice of the

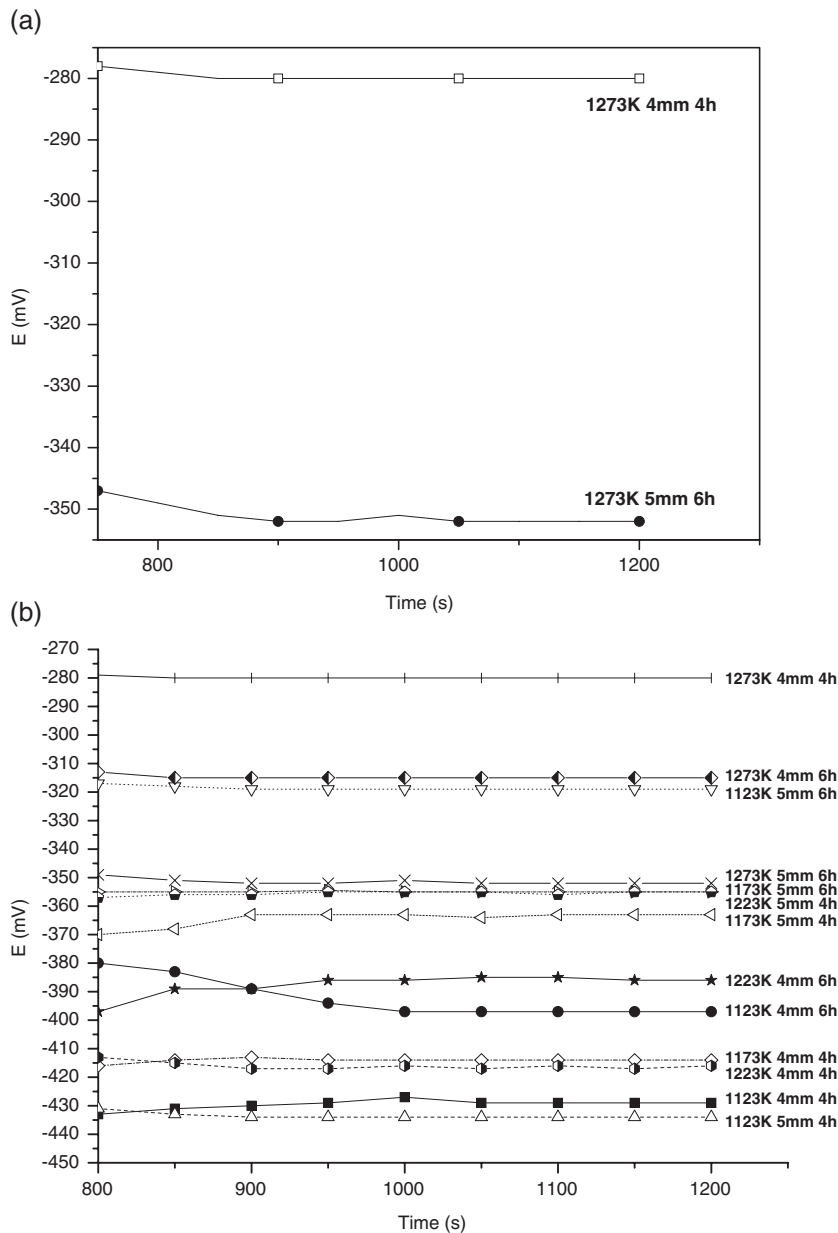


Fig. 3. (a) Open circuit plots obtained from borided samples at 1273 K. (b) Values of equilibrium potential (mV) obtained by the OC electrochemical technique.

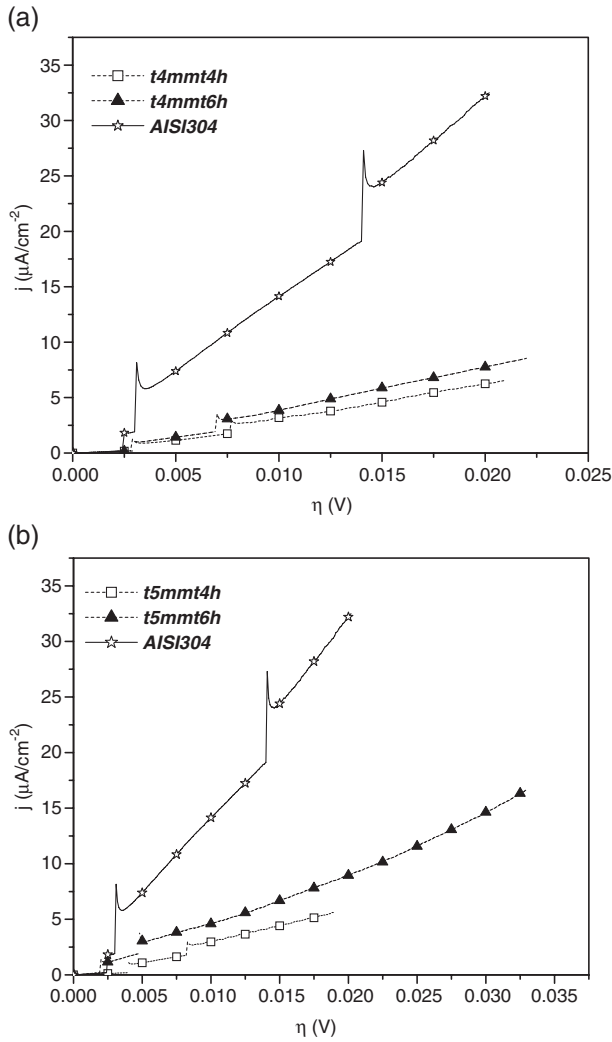


Fig. 4. Polarization resistance tests in borided samples at 1173 K: (a) 4 and 6 h with a boron paste thickness of 4 mm, (b) 4 and 6 h with a boron paste thickness of 5 mm. The samples are compared with the untreated AISI 304 steel.

borides and probably form solid solutions like $(\text{Fe,Cr})\text{B}$, $(\text{Fe,Cr})_2\text{B}$, $(\text{Fe,Ni})\text{B}$ and $(\text{Fe,Ni})_2\text{B}$ [11,13]. Finally, it can be seen in Fig. 2 that some microporosity was developed during the sintering of the boron paste.

Equally, an increase in the thickness of boron paste, under constant temperature and time, results in more compact and continuous layers of borided phases on the material base [7]. On the other hand, it is feasible that the presence of both chromium and nickel favors the growth of the FeB phase as both time and temperature increase. However, due to significant differences between expansion coefficients at both phases,² cracks induced by internal stress in the FeB/Fe₂B interphase are feasible [2,8].

The electrochemical tests used provide a convenient evaluation of corrosion resistance in samples of diverse

² The expansion coefficient of FeB phase is approximately three times higher than the coefficient of the Fe₂B phase ($23 \times 10^{-6}/^\circ\text{C}$ vs. $7.85 \times 10^{-6}/^\circ\text{C}$).

geometry. OC makes it possible to fix a voltage range which can also be used in polarization resistance to obtain a potential V_{oc} without the need of applying any external potential excitation. Fig. 3(a) shows the plot of data obtained with the OC technique on borided samples at 1273 K during 4 and 6 h varying the boron potential in 4 and 5 mm, respectively. This plot allows the identification of stabilization points within the system, hence, for 4 h and a boron paste thickness of 4 mm, the equilibrium value is -285 mV, and for 6 h and 5 mm, the value is -352 mV. Fig. 3(b) shows the values of the different equilibrium voltages found in every sample tested. These results are used in the LP technique, where a scan of ± 20 mV was carried out using the equilibrium potential values for each sample according to the following expression:

$$\eta = V_a - V_{oc} \quad (1)$$

where η is the overpotential of normalized results for each sample and V_a is equal to ± 20 mV. The values between each sample vary in different ranks of potential, which is the reason why a direct comparison between the samples does not exist. Therefore, the potential where the current density is equal to zero in each sample is identified. This potential serves as reference, in order to compare the samples exposed by corrosion. Consequently, the values that compose the graph must be subtracted by the potential, where the density of current is zero, so that the anodic and cathodic zones of the experiment are clearly identified.

Fig. 4 shows the results from the linear polarization tests on boronized samples at 1173 K under different conditions; such values are also compared with those obtained for the unprotected AISI 304 stainless steel. On one hand, polarization resistance is higher on borided steel than in AISI 304 untreated steel. This indicates that FeB as well as Fe₂B effectively protect the surface of the pieces from the effect of HCl, showing high stability and low current density.

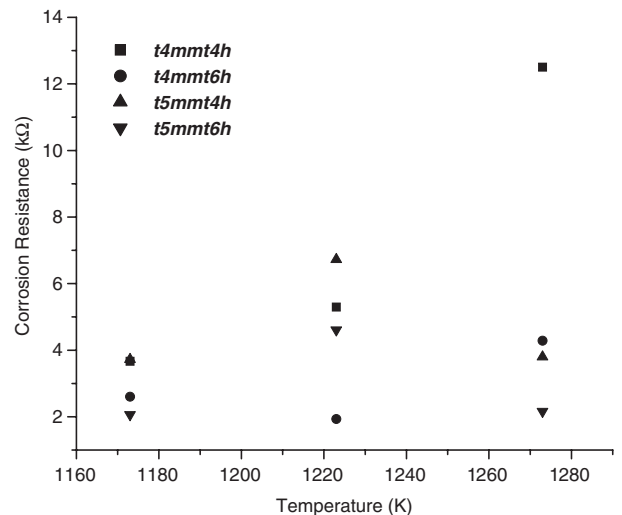


Fig. 5. Dependence between the corrosion resistance and the temperature of the boriding process.

Assuming a linear behavior in the anodic region with small perturbations³ of these tests [10], it is possible to estimate the corrosion resistance of the different test specimens. The corrosion resistance is defined as $1/m$, where m is the slope of the plots obtained by the LP technique.

Fig. 5 shows the corrosion resistance dependence on boriding temperatures. Although in most cases, corrosion resistance on material surface is increased by generated layers during the treatment, some differences appear in comparison to treatment times and boron potential used. Further, corrosion resistance for a boron potential of 4 mm shows a tendency to grow as the process temperature increases, having its highest value at a temperature of 1273 K and with a treatment time of 4 h. This indicates the formation of compact and continuous layers on the surface of the sample and presents in a qualitative way a minor microporosity at the generated bilayer.

Hence, considering treatment time and temperature of the process in a boron paste thickness of 5 mm, there is a drastic drop of corrosion resistance on the surface of the samples when a temperature of 1273 K is reached. This phenomenon is assumed due to microcracks formed in the FeB/Fe₂B interphase, which are generated by thermal stresses caused by the difference between the value of expansion coefficients of borided phases and the porosities along the surface of the layer. Thus, small contact spots are produced between the work piece and the acid solution, increasing the corrosion rate [9].

Also, for the boron paste thickness of 5 mm, it is feasible (at least, thermodynamically) for the protective chromium oxide film formed on the surface of steel,⁴ to be reduced during the growth of borided layers; this is due to the formation of B₂O₃, decreasing its corrosion resistance. Therefore, the chemical reaction results in



Yakhnina et al. [12], mainly on the basis of thermochemical calculations, reported that high-temperature oxidation of boron carbide in a B₄C-base boriding medium yields B₂O₃ in addition to CO; B₂O₃ should be able to react with a part of the remaining B₄C, producing gaseous B₂O₂ which, in turn, should boride the steel substrate, restoring B₂O₃ and allowing the boriding process to proceed.

4. Conclusions

The following conclusions can be assumed:

- (a) The influence of alloying elements such as chromium and nickel generates a flat growth front of the phases on the

surface of steel. Therefore, these elements mainly retard the boride layer thickness caused by restricted diffusion of boron into the steel because of the formation of a diffusion barrier.

- (b) The electrochemical techniques used determine, in a practical way, the corrosion resistance on the borided samples. LP demonstrates that the formed layers on the material surface show high stability and low current density, compared to non-boronized AISI 304 steel samples.
- (c) It is evident that the boron paste thickness does influence the corrosion rate of the boronized samples. Samples treated with a boron potential of 5 mm decrease its corrosion resistance, as temperature and time of the process increase. In fact, for these samples, the presence of microporosities through the boride layer becomes more evident.
- (d) By contrast, corrosion resistance is increased using a boron potential of 4 mm, having its highest value of 12 kΩ at a temperature of 1273 K with a treatment time of 4 h, making it possible to obtain minimum levels of microporosity and letting compact and continuous layers be formed.

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³ Recently, these perturbations have not been explained by other authors.

⁴ AISI 304 steel characterizes the behavior of a corrosion resistant material that develops surface passivation.