

## COMPARATIVE STUDY ON ELECTROCHEMICAL CORROSION OF BORONIZED X52 STEEL IN 1 M HCl AND H<sub>2</sub>SO<sub>4</sub> SOLUTIONS

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### Abstract

This paper investigates the effect of boronizing treatment on the corrosion resistance of API X52 steel. Borides were grown on API X52 steel in a powder mixture containing 5% B<sub>4</sub>C as a boron source, 5% NaBF<sub>4</sub> as an activator, and 90% SiC as diluents for 4 hours at 950 °C. X-ray diffraction (XRD) analysis revealed that the sample's boride layer contains only Fe<sub>2</sub>B phases. The corrosion behavior of borided and unborided specimens was investigated using the Tafel extrapolation method in 1M HCl and H<sub>2</sub>SO<sub>4</sub> solutions. The results show that borided specimens have better corrosion resistance than unboronized specimens. The formation of layers of protective iron borides reduces the corrodability of the steel in the borided specimens. Boronizing increased the corrosion resistances of X52 steel in HCl and H<sub>2</sub>SO<sub>4</sub> by 23 and 77-fold, respectively.

**Keywords:** pipeline steel; boronizing; corrosion.

### Introduction

Algeria's natural resources (oil and natural gas) are geographically isolated from consumption centers in industrialized areas. As a result, they must be transported over long distances via pipelines. These infrastructures (pipelines) must be built over hundreds, if not thousands, of kilometers and must meet certain requirements such as adequate mechanical properties, weldability, and safety. As a result, API X52 steel is one of the most commonly used materials for pipelines by SONATRACH (The national oil company of Algeria). Because of their interconnected properties (high elastic limit, good ductility, excellent weldability, and chemical stability against a variety of aggressive media) [1-3], they are used in the petroleum industry. Corrosion is a natural phenomenon in petroleum installations, particularly oil and gas pipelines, that cannot be avoided but

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can be controlled and reduced. When exposed to offensive solutions such as chloride and acid, it is a major issue that usually limits the applications of pipeline steels in industry [4-7]. Corrosion of pipeline steels is a major issue due to the high cost and time required to replace, repair, and maintain corroded parts. Several researchers continue to be interested in corrosion degradation for this purpose [8-10]. Significant efforts have been made to improve pipeline steel corrosion resistance [11,12]. As a result, extensive research has been conducted in recent years on the development of surface treatment processes to improve the wear, corrosion, and oxidation resistance of steels for high-pressure applications [13,14,15].

Boronizing is a thermochemical diffusion process that involves enriching the surface of steel with boron in order to form boride layers. This boride layer allows for very high surface hardness and hardness retention at high temperatures, as well as good wear resistance, corrosion resistance, and oxidation resistance [16,17]. Boron atoms diffuse into steel, forming iron borides ( $\text{FeB}$  or/and  $\text{Fe}_2\text{B}$ ), and the thickness of the boride layer is determined by boronizing parameters and the boronized substrate [18, 19]. Corrosion Resistance of boronized AISI H11 Tool Steel was reported by *Gunen* [20]. He discovered an increase in corrosion resistance of up to 65 times after the boronizing process. *Wang et al.* [21] investigate the corrosion behavior of 65Mn steel after boronization in two acid mediums. The results show that boronizing significantly improves corrosion resistance. *Medvedovski et al.* [22] investigated the effect of boronizing on steel performance under Erosion-Abrasion-Corrosion conditions and discovered that boride layers performed significantly better in abrasion and erosion-abrasion-corrosion conditions. *Kayali et al.* [23] investigated the Corrosion Behaviors of Boronized AISI 316L Stainless Steel in Different Solutions. Corrosion experiments show that the boride layer increased the corrosion resistance of the AISI 316L in HCl solution significantly.

The corrosion resistance behaviors of borided and unborided API X52 steels in 1 M HCl and  $\text{H}_2\text{SO}_4$  acid solutions are investigated in this study. The study's goal is to determine whether the formation of borides layers improves the steel's resistance to aggressive corrosion environments.

## Materials and experimental procedures

The material used in this study is X52 API low carbon steels, which is supplied by Alpha pipe steel Company – Ghardaia – Algeria which manufactures pipelines for “SONATRACH”. The chemical composition of the steel is shown in Table 1. Before boronizing, all the samples were successively grounded on finer silicon carbide papers up to 600 grains, then, carefully rinsed with distilled water and acetone.

Table 1. Chemical composition of X52 steel (wt.%).

Elements	C	Mn	Si	S	P	Nb	V	Ti	Al
X 52	0.12	1.22	0.23	0.001	0.011	0.03	0.03	0.002	0.034

Boronizing was carried out in a powder mixture containing 5% B<sub>4</sub>C as the boron source, 5% NaBF<sub>4</sub> as the activator, and 90% SiC as the diluent. Boronizing was conducted for 4 hours at 950 °C. The boride thickness was measured using a SEM microscope and an integrated digital instrument. The electrochemical techniques were carried out using an ASTM G102-89 compliant potentiostat (Type EGG model 273A voltalab instrument). The API X52 pipeline steel coupon specimens were connected with copper wire as a working electrode in a three-electrode glass cell with two graphite counter electrodes and a saturated calomel electrode (SCE) as a reference electrode. The area of the X52 samples exposed to corrosion is 72 mm<sup>2</sup>. The reference electrode used was a saturated calomel electrode, characterized by the electrochemical sequence Hg / Hg<sub>2</sub>Cl<sub>2</sub> / KCl<sub>sat</sub>. The polarization curves were carried out with a scan rate of 1 mVs<sup>-1</sup>. Subsequently, microstructural observations and the nature of the corrosion products obtained for each solution were carried out using Tescan Vega 3 scanning electron microscopy (SEM).

### Results and discussion

#### Microstructure

Figure 1 shows SEM optical micrograph of unborided specimens microstructure (ferrite+pearlite). It demonstrates that the as-received specimens are primarily composed of a ferrite matrix phase (dark area) and pearlite (light area) at the grain boundaries. Near the ferrite matrix, the pearlite lamellas are easily visible. The reverse segment method revealed a 12.8% pearlite content in X52 steel.

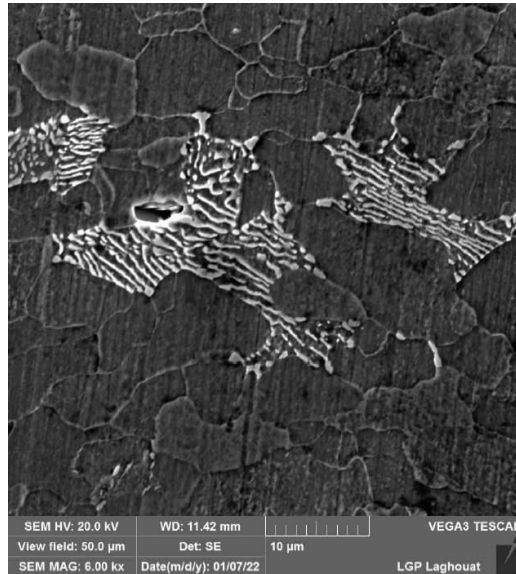
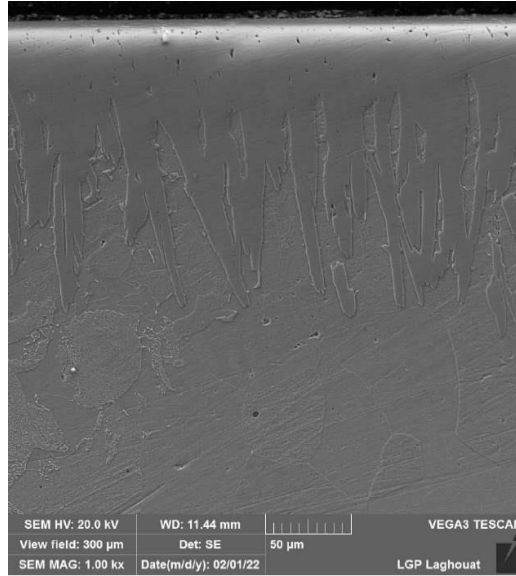


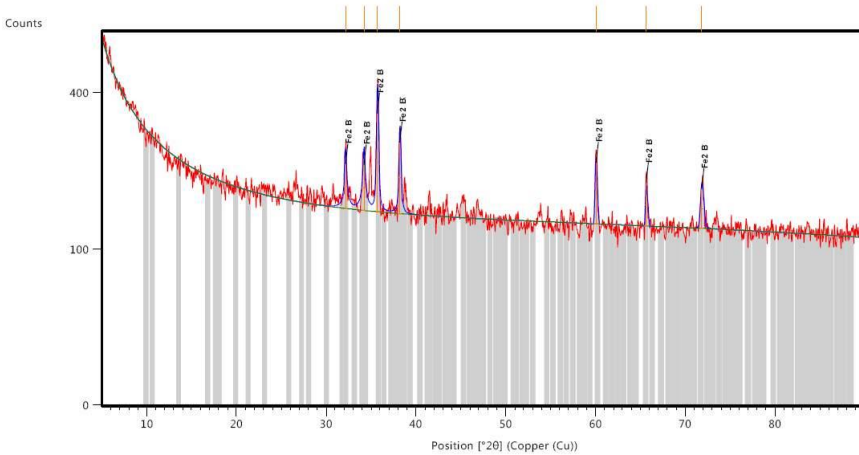
Fig. 1. Microstructure of ferrite -pearlite structure X52 steel.

*Microstructure of Boride layer*

Uncloaked borided X52 steel SEM cross-sectional examinations reveal that the boride layer formed on the surface of the substrate has a saw tooth shape, as shown in Figure 2.



*Fig. 2. Micrograph of boride layer on X52 steel.*



*Fig.3. X-ray diffraction patterns of boronized X52 steel.*

According to the results, the boride layers formed on the surface of the X52 steel may be single phase, consisting only of bi-iron boride (Fe<sub>2</sub>B) with an average thickness of 140 μm. X-ray diffraction confirmed the presence of only Fe<sub>2</sub>B borides, as shown in figure 3. According to the literature [25,26], the Fe<sub>2</sub>B phase can be formed by controlling the boronizing process parameters, such as boronizing powder composition, temperature

and time, and the chemical composition of the base materials. In our case, the powder containing only 5% boron source and 5% activator prevents the formation of the boride FeB. It should be noted, however, that this thickness is an average of several needle lengths of the boride layer. This property of the boride layer in steels is strongly related to the boronizing source used, the temperature and duration of boronizing, and the properties of the steel to be boronized. [27- 29].

The temperature and duration of the boronizing process govern the diffusion and subsequent absorption of boron atoms through the matrix.

Another important parameter influencing boron diffusion is the chemical composition of the steel [30, 31].

### Corrosion properties

The polarization curves of API X52 steel with and without boronizing are determined in 1 M HCl and H<sub>2</sub>SO<sub>4</sub> solutions (Figure 4). Table 2 summarizes the corrosion polarization results of the X52 steel. According to the results, before boronizing, the H<sub>2</sub>SO<sub>4</sub> solution produced the highest corrosion rate of 5.855 mm/yr, followed by the HCl solution, which produced 5.319 mm/yr. For the borided samples, the H<sub>2</sub>SO<sub>4</sub> solution had the lowest corrosion rate of 0.0682 mm/yr, followed by the HCl solution at 0.2514 mm/yr. The corrosion resistance of boronized samples is higher than that of non-boronized samples, regardless of the type of acid solution used.

Table 2. Summary of the results obtained from corrosion tests of X52 steel performed in HCl and H<sub>2</sub>SO<sub>4</sub> solutions.

		HCl	H <sub>2</sub> SO <sub>4</sub>
Before boronizing	I <sub>corr</sub> (mA/cm <sup>2</sup> )	0.5032	0.4548
	corrosion rate (mm/Y)	5.885	5.319
	E (I=0) (mV)	-502.8	-541.4
After boronizing	I <sub>corr</sub> (mA/cm <sup>2</sup> )	0.0215	0.00583
	corrosion rate (mm/Y)	0.2514	0.0682
	E (I=0) (mV)	-492.1	-452.0

When compared to unboronized steel, boronized steel has better corrosion resistance, a lower value (I<sub>corr</sub>), and thus a lower corrosion rate. According to the findings, the boronizing improves the corrosion resistance of API X52 steel. The primary goal of a boronizing treatment is to improve steel corrosion resistance. The treatment used determines the degree of improvement. In our experiments, we discovered that boronizing X52 steel increased corrosion resistance by 23-fold and 78-fold in HCl and H<sub>2</sub>SO<sub>4</sub> solutions, respectively.

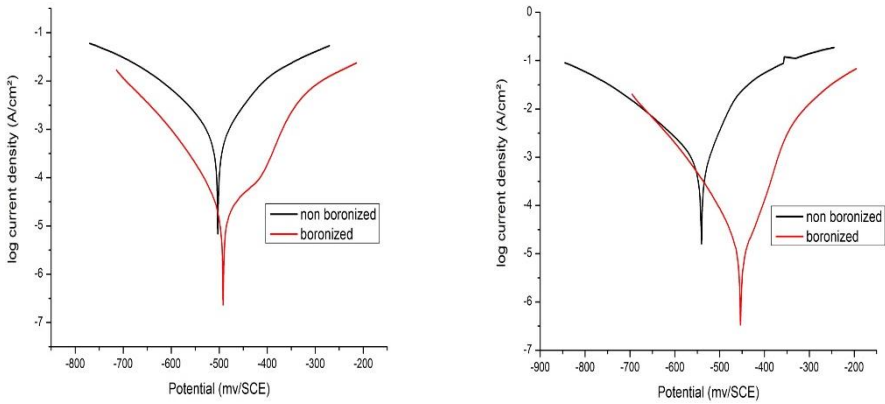


Fig. 4. Tafel curves of API X52 steel before and after boronizing in (a) HCl solution (b) H<sub>2</sub>SO<sub>4</sub> solution.

### Surface morphology

Figures 5 and 6 show the morphological aspects of the surface of X52 API steel corroded by 1M HCL and H<sub>2</sub>SO<sub>4</sub> acid solutions with and without boronizing.

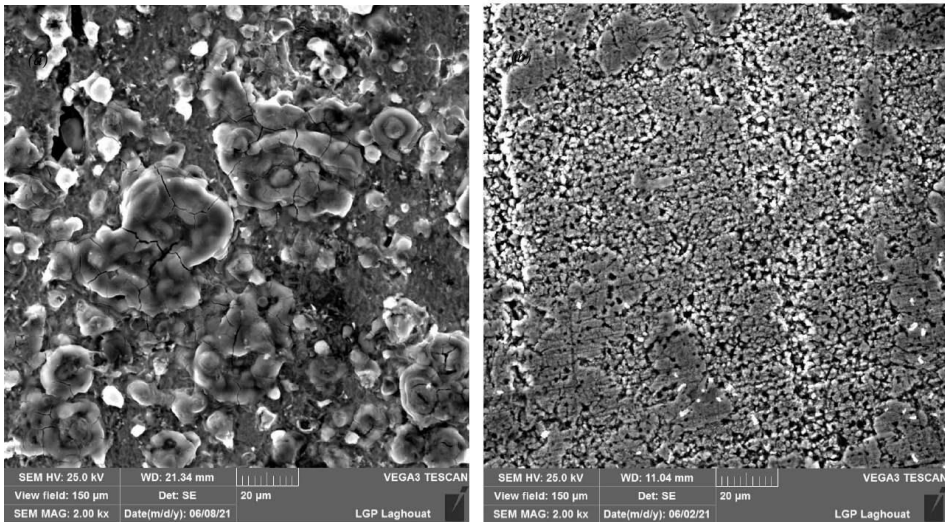


Fig. 5. SEM micrograph of corroded X52 steel after potentiodynamic polarization in 1M HCl solution a) Without boronizing b) With boronizing

In the absence of boronizing (Figures 5a and 6a), the X52 steel surface is severely damaged in the aggressive acidic mediums. The entire surface is severely corroded and shows obvious deterioration by corrosive media, with large and dense corrosion holes. This is consistent with the findings of Deyab et al. [32], who discovered that chloride and sulphate ions accelerate aqueous corrosion of pipeline steel. The presence of this type of attack is suggested when steel is incapable of forming fully protective layers. As a result, the electrolyte's corrosive attack is limited by the steel's inability to form a

protective layer of corrosion product. The boronizing treatment, however, caused changes in the surface appearance of the X52 steel due to the formation of boride layers (Figure 5b and Figure 6b). The formation of 140  $\mu\text{m}$  thick boride layers on the sample surfaces, as shown in (Figure 2), is attributed to the results, forming a protective layer between the steel and the corrosive medium. This indicates that the X52 steel's surface was effectively protected by boride layers, which is consistent with the electrochemical experiment results.

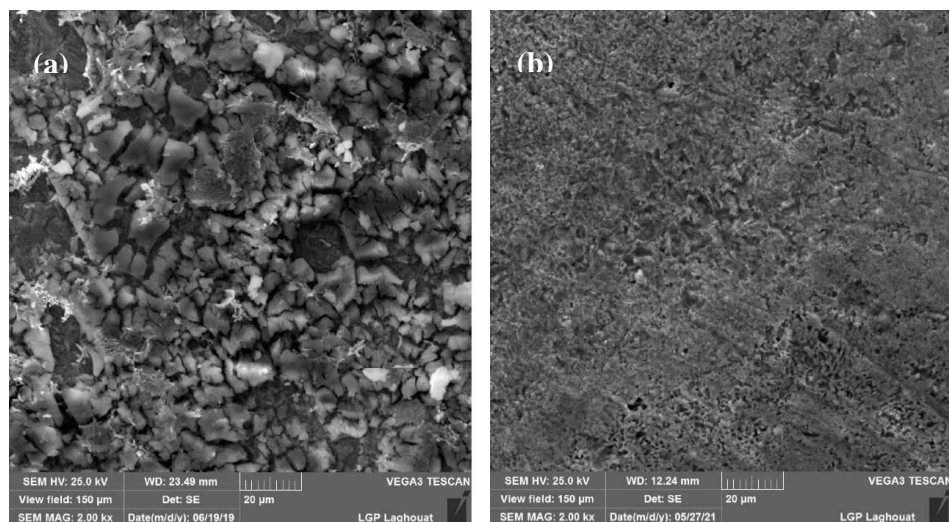


Fig. 6. SEM micrograph of corroded X52 steel after potentiodynamic polarization in 1M  $\text{H}_2\text{SO}_4$  solution: a) without boronizing, b) with boronizing.

## Conclusions

In this study, microstructure and corrosion properties of X52 steel with and without Boronizing were investigated in a 1M HCl and  $\text{H}_2\text{SO}_4$  solutions. The following conclusions can be drawn from the obtained results.

- 1- Boronizing powder technique used at a temperature of 950  $^{\circ}\text{C}$  for 4 hours produced a single layer of  $\text{Fe}_2\text{B}$  type with sawtooth morphology.
- 2- The boronizing process used produced a 23-fold and 78-fold improvement of the corrosion resistance of X52 steel in HCL and  $\text{H}_2\text{SO}_4$  respectively, compared with the unborided.
- 3- The entire surface of unborided steel shows obvious deterioration by corrosive media and the corrosion holes are large and dense. But, the formation of boride layers develops a protective layer that limit the corrosive attack with the same corrosive media.

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