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Research Article

Effect of Relative Humidity on the Tribological Properties of Self-Lubricating H_3BO_3 Films Formed on the Surface of Steel Suitable for Biomedical Applications

E. Hernández-Sanchez,[1] A. Chino-Ulloa,[1] J. C. Velazquez,[2] H. Herrera-Hernández,[3] R. Velázquez-Mancilla,[4] and R. Carrera-Espinoza[5]

[1] *Instituto Politécnico Nacional, UPIBI, Avenida Acueducto s/n, Barrio La Laguna Ticomán, 07340 México, DF, Mexico*
[2] *Gerencia de Proyectos Ambientales, Pemex Refinación, Piso 7 Torre Ejecutiva de Pemex, Marina Nacional 329, Colonia Petróleos Mexicanos, 11311 México, DF, Mexico*
[3] *Universidad Autónoma del Estado de México, Boulevard Universitario s/n, Predio San Javier, 54500 Atizapán de Zaragoza, MEX, Mexico*
[4] *Instituto Tecnológico de Tlalnepantla, Departamento de Postgrado, Avenida Instituto Tecnológico s/n, Colonia La Comunidad, Tlalnepantla de Baz, MEX, Mexico*
[5] *Instituto Tecnológico Superior de Poza Rica, Luis Donaldo Colosio Murrieta s/n, Arroyo del Maíz, 93230 Poza Rica, VER, Mexico*

Correspondence should be addressed to E. Hernández-Sanchez; enriquehs266@yahoo.com.mx

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The effect of environmental humidity on the self-lubricating properties of a thin film of boric acid (H_3BO_3) was evaluated. H_3BO_4 films were successfully formed on the surface of AISI 316L steel. The study was conducted on AISI 316L steel because of its use in biomedical applications. First, the samples were exposed to boriding to generate a continuous surface layer of iron borides. The samples were then exposed to a short annealing process (SAP) at 1023 K for 5 min and cooled to room temperature while controlling the relative humidity (RH). Five different RH conditions were tested. The purpose of SAP was to promote the formation of a surface film of boric acid from the boron atoms present in the iron boride layers. The presence of the boric acid at the surface of the borided layer was confirmed by Raman spectroscopy and X-ray diffraction (XRD). The self-lubricating capability of the films was demonstrated using the pin-on-disk technique. The influence of RH was reflected by the friction coefficient (FC), as the samples cooled with 20% of RH exhibited FC values of 0.16, whereas the samples cooled at 60% RH showed FC values of 0.02.

1. Introduction

Friction is the used term to describe the resistance to movement of individual bodies that are in contact with each other [1]. The study and understanding of this phenomenon are of a great importance because friction between mechanical elements currently leads to economic losses of approximately 0.5% of the gross domestic product (GDP) of industrialized countries [2]. These losses occur primarily because sufficient knowledge has not yet been accumulated to reduce friction, either by using more suitable materials or by applying better lubricants. On the other hand, wear is a phenomenon that presents as a consequence of friction in practically every piece of equipment having moving components that are in contact with one another, and it involves the loss of material.

The main conditions leading to wear include surface-surface contact (friction wear), surface contact with a strange substance (abrasive wear), and erosion by corrosive materials (corrosive wear). Depending on the wear system in question, different methods to prevent wear have been developed. The use of lubricants between two sliding solids can help to reduce friction and, thus, the wear of the materials.

The problem of wear is not limited only to industrial applications, where machine elements are affected and must

Table 1: Chemical composition of the AISI 316L steel.

Element	Weight (%)
C	0.03
Si	1.0 max
Mn	2.0 max
Cr	16.7–18.0
Ni	10.0–14.0
Mo	2.0–3.0
P	0.045 max
S	0.03 max
Fe	Balance

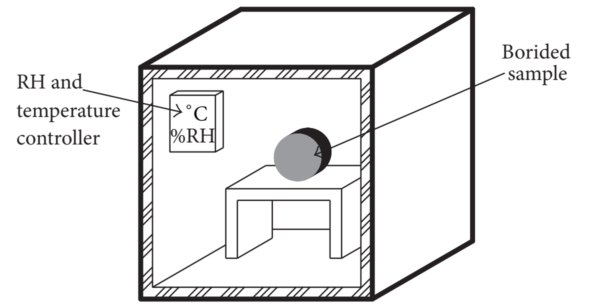


Figure 1: Schematic representation of the cooling process in a moisture controlled chamber.

be continuously replaced. In orthopedic surgery, one of the main problems encountered with hip and knee prostheses is aseptic loosing, which has been associated with the tissue reaction to wear particles of the implant material that are produced by friction between the contacting surfaces [3]. Nevertheless, the metallic materials used to manufacture prosthetic joints are exposed to corrosion and friction wear conditions, as it is not possible to use conventional methods to prevent wear when working in contact with living tissue. For this reason, several researchers have sought to develop surface modification techniques to reduce the friction coefficient of the materials and, thus, reduce wear and the shedding of particles to living tissue [4]. In addition, Erdemir et al. [5] studied the behavior of a self-lubricating film of boric acid, generated at the surface of materials rich in boron. When those materials are heated, the boron reacts with oxygen and is oxidized to form a boron oxide (B_2O_3) film on the exposed surface [6]. During cooling, the boron oxide film undergoes a secondary chemical reaction upon contact with environmental moisture to form a thin boric acid film, which exhibits self-lubricating behavior because of its crystalline structure.

This study was focused on understanding the influence of the environmental humidity present during cooling on the features of the boric acid film generated by means of a short annealing process (SAP). The aim of the work was to determine the best moisture conditions for generating a boric acid film with capability of meeting the need for self-lubricating materials.

2. Experimental Details

2.1. Boriding Treatment. Cylindrical samples of AISI 316L steel with the chemical composition shown in Table 1 were cut to a size of 12.7-mm diameter and 5.0 mm of thickness. The surfaces were carefully prepared by a traditional metallographic procedure using SiC abrasive paper.

The samples were cleaned in an ultrasonic bath for 5 min in acetone and dried in hot air. The samples were then embedded in a boron powder source, Hef-Durferrit. The boriding process was carried out at a constant temperature of 1223 K for 6 h. The treatment conditions were established to ensure the formation of a compact and homogenous layer of iron boride [7, 8]. Once the boriding treatment was completed, the samples were cooled to room temperature inside the furnace. Prior to SAP, one face of each sample was metallographically prepared for optical examination to evaluate the thickness of the iron boride layer using a GX-51 optical microscope. At least 50 measurements were performed on the surfaces of different sections of borided samples. The mean thickness value of the iron boride layer ($Fe_2B + FeB$) was estimated to be $45.15 \pm 3.8\,\mu$m. The hardness and Young's modulus of the borided layers were evaluated by indentation on a nanohardness tester (TTX-NHT, CSM Instruments) using a Berkovich indenter, according to the methodology established by Oliver and Pharr [9]. To obtain a profile of the physical and mechanical characteristics of the borided layers, ten indentations were performed with a constant indentation load of 250 mN at distances of 10, 25, 45, 60, 75, 90, and 120 μm from the surface of the borided layers to the substrate.

2.2. Short Annealing Process (SAP). The SAP was performed in a conventional furnace at 1023 K for 5 minutes in open air [6]. First, the samples were cleaned to remove impurities remaining from the boriding process. After the SAP, the samples were cooled to room temperature in a controlled moisture chamber at five different conditions of relative humidity (RH): 20, 40, 60, 75, and 85%. Figure 1 shows a schematic representation of the cooling process.

2.3. Characterization of the Boric Acid Films. The presence of boric acid films on the surface of the borided layers was confirmed by optical microscopy and scanning electron microscopy (SEM). Raman spectroscopy and X-ray diffraction (XRD) were also used to corroborate the nature of the thin boric acid films. The Raman spectroscope was a Labram, model HR-800, Horiba Jobin Yvon. The XRD patterns of borided steel were obtained using D8 FOCUS diffractometer with Cu-Kα radiation with a wavelength of 1.5418 Å.

2.4. Coefficient of Friction. The self-lubricating nature of the boric acid films was characterized by evaluating their friction coefficient using a CSM pin-on-disk tribometer. The pins were secured to a stationary holder, and the AISI 316L samples were attached to a horizontal chuck driven by a variable-speed electric motor. All tests were performed at controlled temperature of 19°C and 40% of relative humidity using a

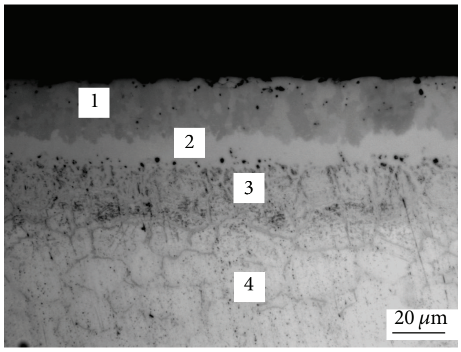


Figure 2: Cross-sectional view of borided AISI 316L steel showing the four zones in the sample.

constant rotational speed of 10 rpm. The sliding velocity was held constant at 0.05 m s^{-1} for a sliding distance of 50 m, and the normal load applied to the wear tungsten carbide (WC) pins was 1 N.

To determine the effect of the SAP, the friction coefficient tests were conducted on annealed, borided, and nonborided samples. Five tests were performed under the same conditions to show reproducibility of the results.

3. Results and Discussion

3.1. Microstructure. Figure 2 shows optical micrographs of the cross section of borided SS-316L steel, which reveal a microstructure typical of boride coatings with a polyphase structure and flat morphology.

This morphology is expected in stainless steel because of the high concentration of alloying elements in the substrate [7, 10]. Four different zones can also be observed in the cross sections of the borided samples. Outermost zone is a FeB phase with high boron content (16.23 wt.%), a second zone which is mainly Fe_2B phase with 8.83 wt.% in boron content. A third zone is the region below boride layers, which is called diffusion zone. Fourth is the steel substrate, which is not affected by boron diffusion. The nature of the surface layers was corroborated by X-ray diffraction (see Figure 3).

In addition, small traces of CrB and Ni_3B can be seen in Figure 3. During the boriding process, alloying elements, especially Cr, tend to diffuse from the steel to form chromium borides (CrB and/or Cr_2B). Ni also diffuses from the steel but in a smaller amount and is located beneath the layer [10].

The presence of a boron-rich surface (FeB/Fe_2B) is expected to promote the formation of a uniform film of boric acid, due to more boron atoms being available to enhance the reaction with the environmental humidity.

The hardness and Young's modulus values of the borided layers are shown in Table 2 and Figure 4.

Figure 4(a) shows a hardness profile from the surface of the layer to the substrate.

It can be seen that while the hardness of the boride layers is approximately 22500 MPa, the hardness of the unborided steel substrate is approximately 2500 MPa. Similarly, it is possible to correlate the hardness profile to the four distinct regions observed in Figure 2. The highest hardness corresponds to the layer with the highest boron content [11]. Thus, it is valid to assume that the amount of available boron at the surface is sufficient for the formation of the boric acid film.

In addition, according to Figure 4(b), Young's modulus of the layers was also influenced by boron diffusion, as the layers near the surface tended to be harder and less susceptible to plastic deformation. Thus, it is expected that Young's modulus values increase when the boron content in the layer increases [12]. Likewise, the four zones described earlier could also be correlated with Young's modulus behavior of the layers (Figure 4(b)).

3.2. Short Annealing Process (SAP). The evolution of the boric acid films as a function of the RH is shown in Figure 5, which shows that the proportion of boric acid crystals (white particles) tended to increase as RH increased. These results can be explained by the spontaneous reaction between the

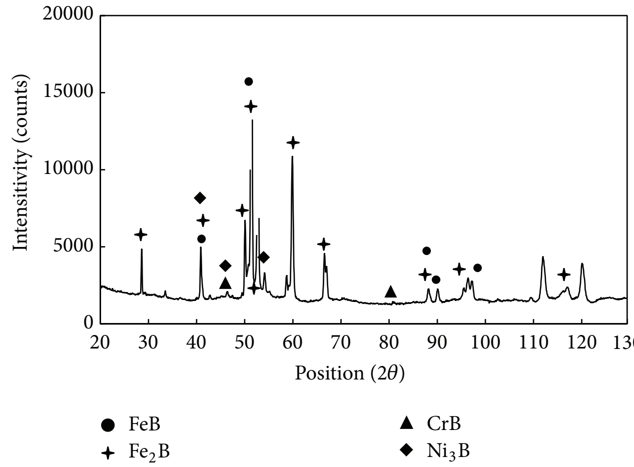


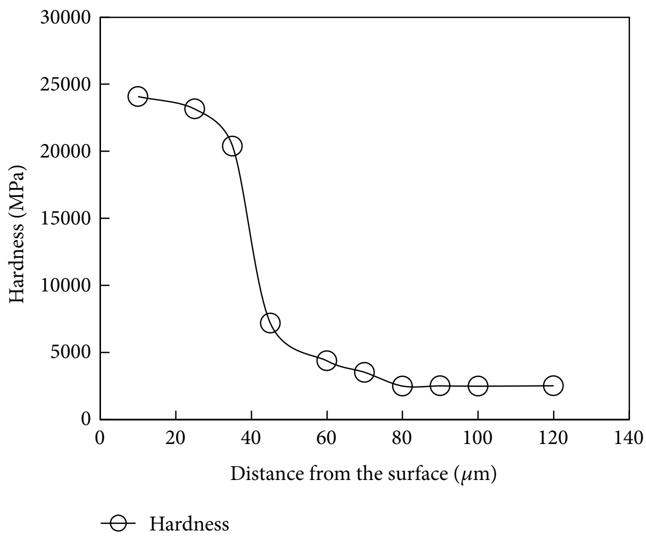
Figure 3: XRD pattern of AISI 316L stainless steel borided for 6 h at a temperature of 1273 K.

Table 2: Hardness and Young's modulus profiles for borided AISI 316L steel.

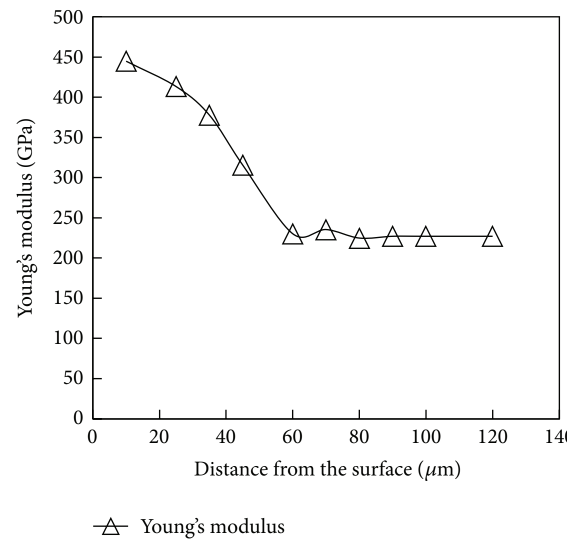
Distance from surface (μm)	Hardness (MPa)	Young's modulus (GPa)
10	24085.1 ± 1220.2	444.75 ± 37.1
25	23150.4 ± 2345.3	413.23 ± 32.2
35	20387.5 ± 1123.8	377.67 ± 28.4
45	7187.8 ± 632.3	315.56 ± 29.3
60	4377.9 ± 545.2	230.20 ± 21.6
70	3520.4 ± 254.1	235.40 ± 20.4
80	2500.5 ± 198.4	224.80 ± 19.2
90	2512.6 ± 212.1	227.01 ± 19.7
100	2489.3 ± 206.4	227.01 ± 18.2
120	2520.2 ± 184.2	227.01 ± 19.1

Table 3: Friction coefficients for the different RH conditions.

Unborided samples	Borided samples	Annealed samples relative humidity (%)				
		20	40	60	75	85
0.62	0.52	0.164 ± 0.013	0.125 ± 0.012	0.026 ± 0.0015	0.050 ± 0.0027	0.074 ± 0.0064



(a)



(b)

Figure 4: Behavior of (a) hardness and (b) Young's modulus of borided AISI 316L steel as a function of the distance from the surface.

boron oxide and the hydrogen of the environment as follows [5]:

$$2B + \frac{3}{2}O_2 \longrightarrow B_2O_3 \quad \text{(Heating process)}$$
$$\frac{1}{2}B_2O_3 + \frac{3}{2}H_2O \longrightarrow H_3BO_3 \quad \text{(Cooling process)} \tag{1}$$

It should be noted that as the RH increases during the cooling process, there will be more hydrogen atoms available. Thus, because the formation of the boric acid films occurs quickly, a slight increase in RH could produce a significant increase in the resultant films.

The presence of the H_3BO_3 film generated on the surface of the boride layers was corroborated by X-ray diffraction (XRD). Figure 6 shows the XRD pattern, and the presence of boric acid (H_3BO_3) and boron oxide (BFe_2O_4), which did not react with the environmental hydrogen and were remaining after the SAP, can be seen. XRD pattern in Figure 6 was achieved by applying the grazing incidence X-ray diffraction technique (GIXRD) to avoid intense signal from the borided layers and get stronger signal from the film of H_3BO_3 and BFe_2O_4 at the surface of the borided steel. Comparing with Figure 3, where the XRD study was applied to the borided steel before the SAP to evidence the presence of borided phases (FeB, Fe_2B, CrB and Ni_3B), Figure 6 shows mainly H_3BO_3 peaks and some indications of BFe_2O_3 with only small indications of the borided phases FeB and Fe_2B. So that, it is possible to assume that a thin film of H_3BO_3 was formed at the surface of the borided steel.

The XRD study also showed the triclinic crystalline microstructure of the boric acid films, which was expected for these materials [5].

Raman spectroscopy analysis revealed the presence of two well-defined Raman bands. The first was at approximately 498 cm^{-1}, and the second was at approximately 879 cm^{-1} (Figure 7). The values exhibited by the Raman pattern were compared to those exhibited by H_3BO_3 in natural conditions [5], also presented in Figure 7. It can be seen that the Raman spectrum of H_3BO_3 is similar to that of the film formed on the surface of the AISI 316L steel.

This result confirmed that a compact and continuous film of H_3BO_3 was formed on the surface of the borided samples and increased as the RH was increased. According to these results, it is apparent that the RH present during the cooling process is of great importance for boric acid film formation.

3.3. Pin-On-Disk Tests. Figure 8 shows the effect of the RH conditions on the friction coefficient. In addition to the profiles of the annealed samples, the profiles of borided samples and as-received AISI 316L steel are also shown (Figure 8(b)).

According to the results, the friction coefficient of the samples was reduced by an order of magnitude from values of 0.49 for unborided steel to 0.026 in the samples prepared at 60% RH (see Table 3).

These results were compared with those reported in the literature for boric acid films (see Table 4).

Table 4: Solid materials with self-lubricating properties.

Material	Sliding condition	RH (%)	Friction coefficient	Reference
H_3BO_3 on VB_2	440C Pin-on-disk	40–50	0.1–0.05	[5]
H_3BO_3 on B_4C	Zirconia Pin-on-disk	38–84	0.04	[6]
B_2O_3 on C/C	Ni60-friction and wear tester	—	0.06–0.08	[13]
H_3BO_3 on AISI 316 steel	WC Pin-on-disk	60	0.02	Present study

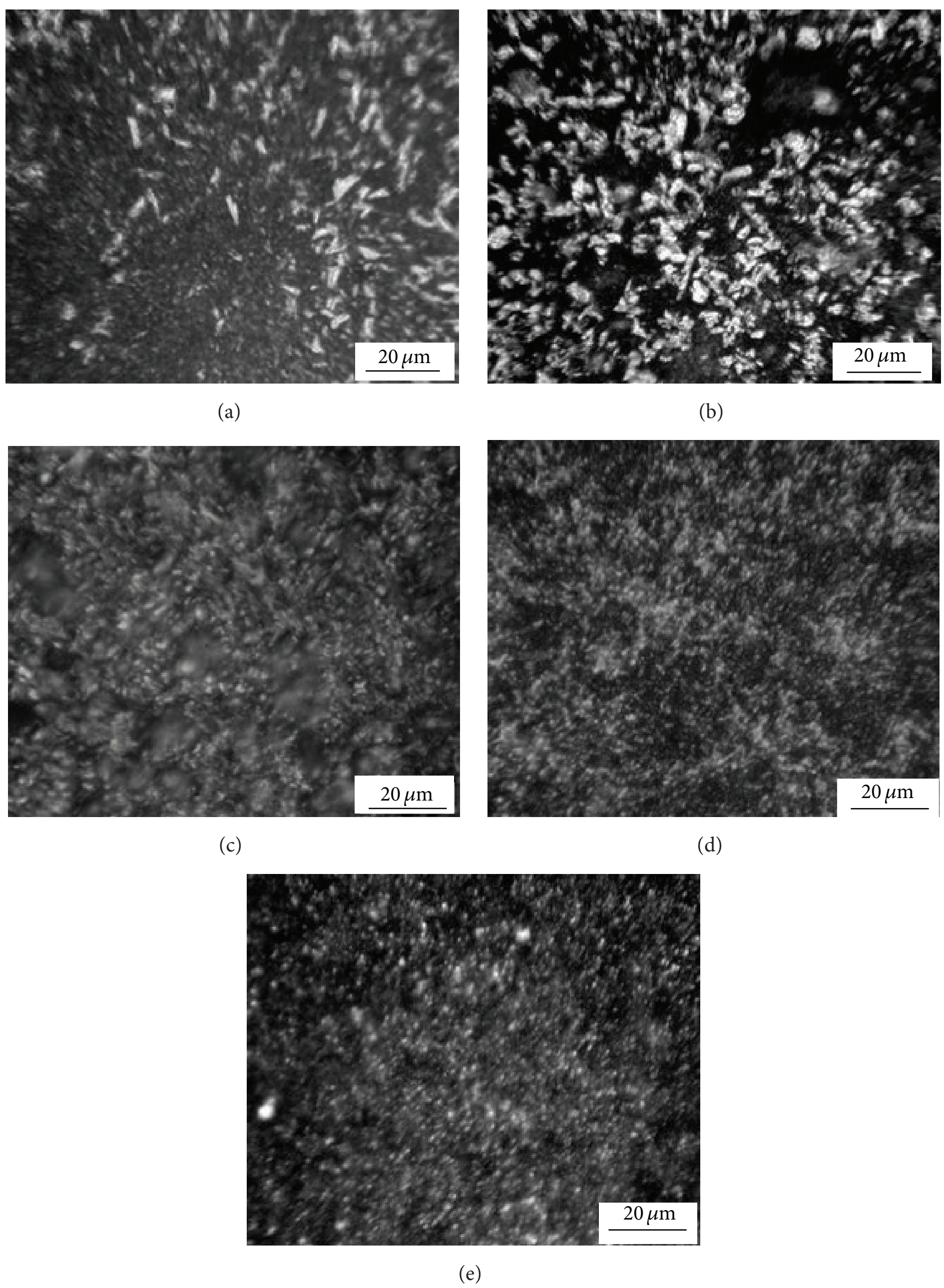


Figure 5: Evolution of the boric acid films as a function of relative humidity: (a) 20%, (b) 40%, (c) 60%, (d) 75%, and (e) 85% RH.

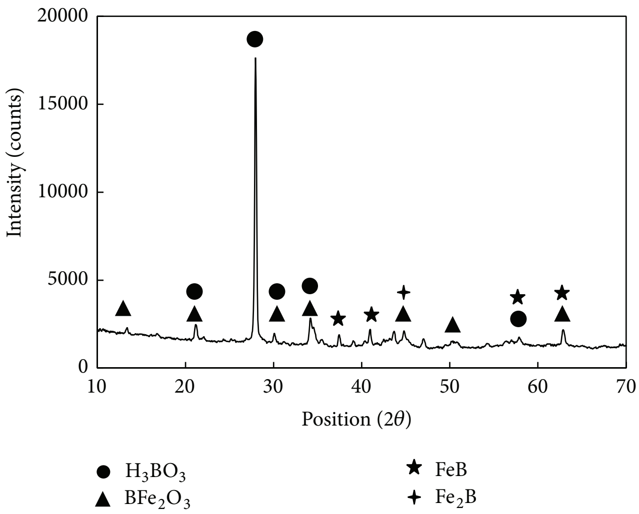


Figure 6: XRD pattern of the sample after a short annealing process (SAP) in the presence of 40% of RH.

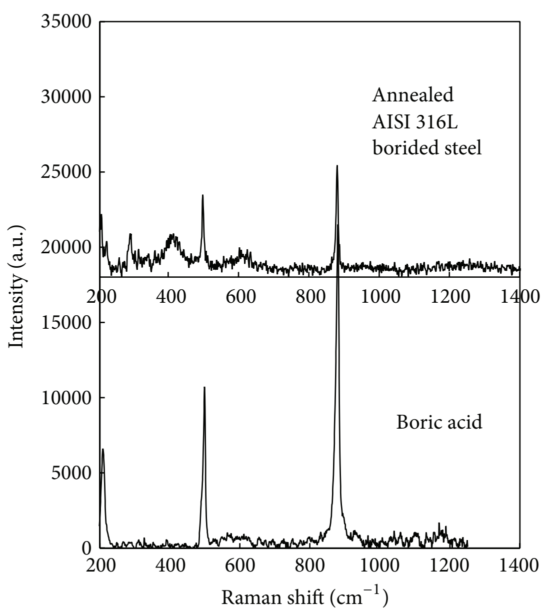


Figure 7: Raman spectra of annealed of AISI 316L borided steel samples and the H_3BO_3 (boric acid) surface film.

The low friction coefficient values of boric acid films can be explained by their triclinic crystalline structure. This type of crystalline structure is considered to function as a solid lubricant because of the unique layered structure, in which the atoms in the same layer are strongly bonded to each other, as show in Figure 9.

However, even though the layers are relatively far apart (0.318 nm), they are only bonded by weak van der Waals forces. Thus, when these materials are present between sliding surfaces, they tend to align parallel to the direction of relative movement and slide over one another with relative ease, thereby providing low friction [13].

Because the samples in this study showed a behavior similar to that exhibited by solid lubricants, and in particular boric acid films, the data support that a film of boric acid was generated at the surface of the borided AISI 316L steel. In addition, the lowest friction coefficient values (0.026) were achieved for samples prepared in the presence of 60% RH, which reflects the strong influence of RH on the formation of the boric acid films as well as their performance under wear conditions.

As can be observed in Figure 10, the friction coefficient of the H_3BO_3 films tended to decrease as a function of the RH to the value achieved at 60% RH. Nevertheless, when the RH was further increased, the friction coefficient increased again to a value of 0.074 at 85% RH.

This behavior can be explained by the fact that the spontaneous reaction resulting in the formation of the boric acid film has more available hydrogen atoms as RH increases. Thus, once the RH has reached a saturation value (60%), an oversaturated film is achieved, in which the boric acid crystals are superimposed, and the film becomes more brittle. Figure 11 shows SEM micrographs of the boric acid films, and it can appreciated that the boric acid films tended to be more compact as the RH was increased (20, 40, and 60%). Nevertheless, after 60% RH (75 and 85%), the boric acid films exhibited larger cracks and holes than what was observed at lower RH.

Therefore, once the relative humidity exceeds 60%, the friction coefficient increased again. Likewise, the adhesion theory [14, 15] provides an explanation for understanding the phenomenon of sliding wear. The actual contact area between two bodies is too small and is formed by the highest points of the asperities in contact. Even when the surfaces are perfectly polished, they present an irregular microtopography with roughness in the form of ridges and valleys [15]. Thus, when two surfaces make contact with each other under the influence of a load, the contact is only produced at the peaks of the roughness, and the true contact area is much smaller than the apparent contact area. The pressure at the true contact points is higher than that expected from the apparent contact area. Consequently, the coefficient of friction between the moving surfaces is also higher than expected. In the case of the surface with a small film of H_3BO_3, the film acts as a lubricant that occupies the valleys of the rough surface and generates a smoother surface (see Figure 12).

This condition and the fact that the boric acid film is considered as a self-lubricating film both improve the ability of the surface to withstand sliding wear.

4. Conclusions

The following conclusions can be derived from the present study:

(a) By boriding AISI 316L, it is possible to achieve a hard surface layer with enough free boron atoms to form a compact and homogenous H_3BO_3 surface film.

(b) By performing a posttreatment that was referred to as a short annealing process (SAP), it was possible to generate a thin film of boric acid through the

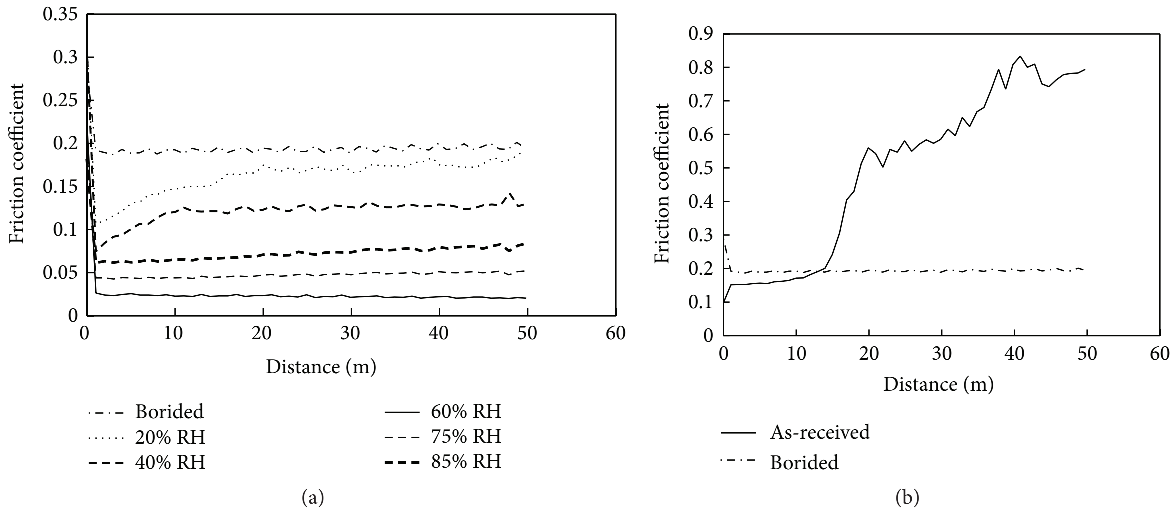


FIGURE 8: Variation of friction coefficient for a tungsten carbide pin sliding against (a) annealed 316L borided steel as a function of RH and (b) borided and as-received AISI 316L steel.

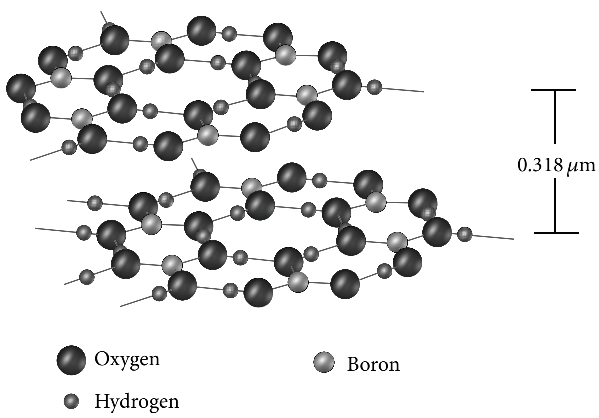


FIGURE 9: Schematic representation of the layered crystalline structure of H_3BO_3.

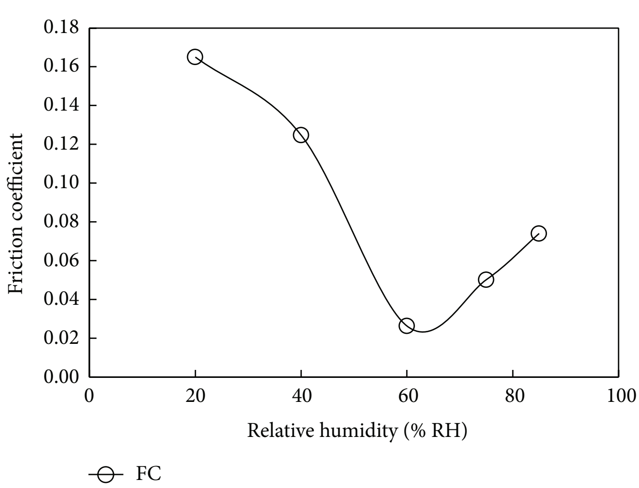


FIGURE 10: Behavior of the friction coefficient as a function of the RH present during the cooling process.

spontaneous reaction between free boron in the boride layers and the environmental humidity.

(c) The tribological properties of the boric acid film were dependent on the relative humidity (RH) during the cooling step of the SAP.

(d) The influence of RH on the formation of the boric acid films was clearly reflected in the friction coefficient values, as the lowest value achieved was 0.026 at 60% RH, whereas the friction coefficient at 20% RH was 0.19.

(e) Finally, the lower limit of the friction coefficient of the boric acid film seems to be at 60% RH because the friction coefficient values tended to increase once this value was exceeded. Thus, according to the results of the present research, the best RH condition for generating a self-lubricating H_3BO_3 film at the surface of AISI 316L borided steel is 60% RH.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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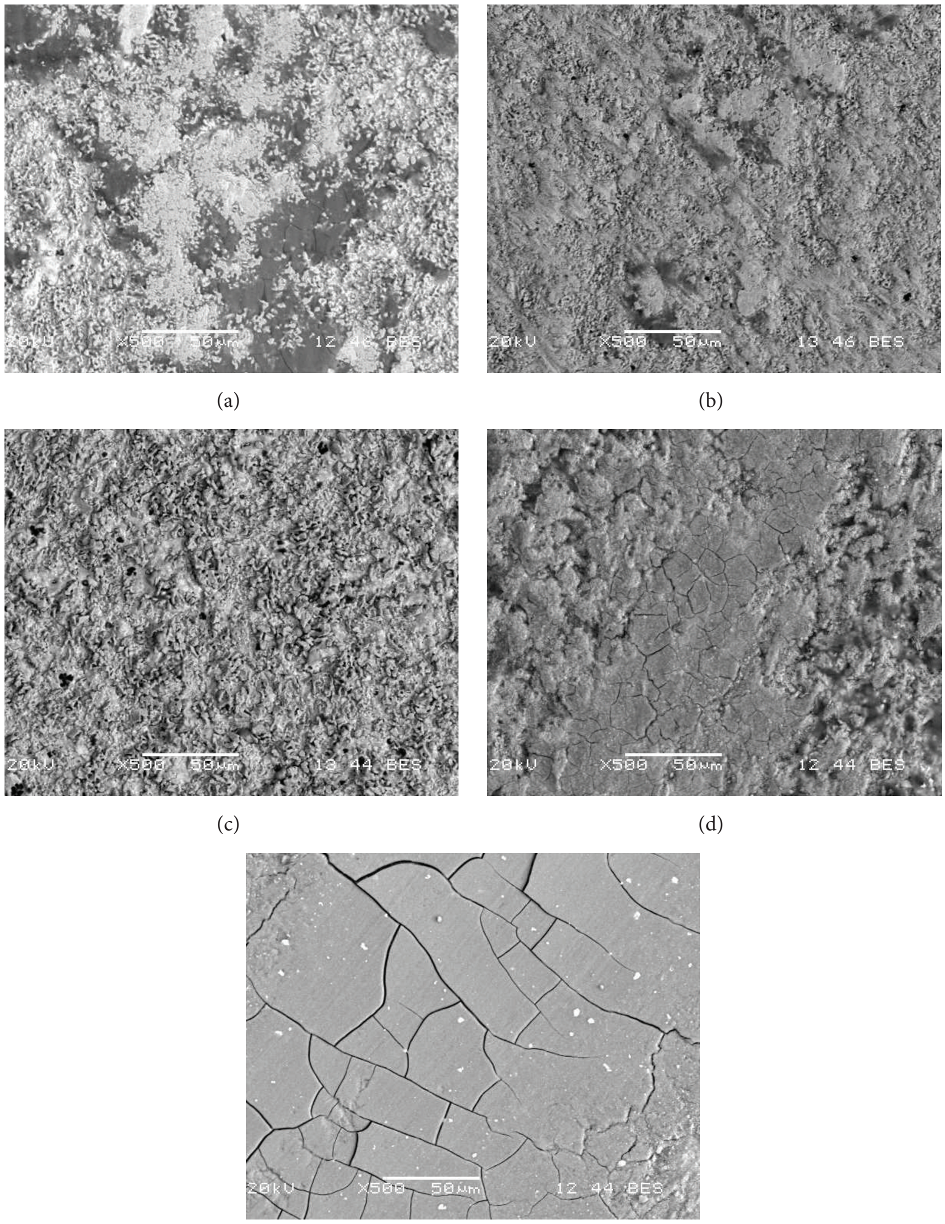

(a) (b) (c) (d) (e)

Figure 11: SEM micrographics of the annealed samples at conditions of (a) 20%, (b) 40%, (c) 60%, (d) 75%, and (e) 85% of RH.

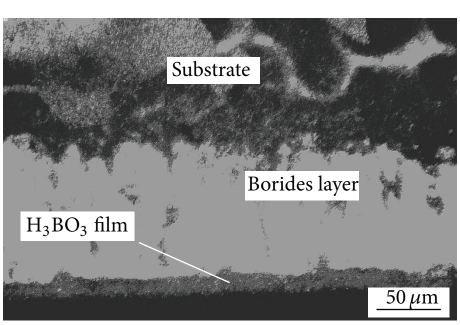

Figure 12: H_3BO_3 surface film covering the surface roughness of borided AISI 316L steel samples.

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