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TRIBOLOGICAL EVALUATION OF BORIDED Ti6Al4V ALLOY FOR BIOMEDICAL APPLICATIONS

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Abstract. *Ti6Al4V alloys are frequently used in joint prosthesis, due to their biocompatibility and corrosion resistance, as a result of their naturally formed oxide layer. Despite the alloy being present in a wide range of applications, it has poor tribological properties, which limits its lifespan. By this reason, this study was conducted to evaluate the effects of boriding on improving the tribological properties of the alloy. The thermochemical and electrochemical treatments of boriding were performed obtaining significantly better properties, and increasing wear resistance. For both types of treatment, it was used Ekabor and Borax boriding agents, to compare the efficiencies of the modified layer. Borided samples were evaluated by optical microscopy, scanning electron microscopy, energy dispersive spectroscopy and X-ray diffraction. Also, surface hardness test and the microhardness profile test were carried out, to verify the changes in the mechanical properties. Tribological test was done using the reciprocal linear mode, on samples with and without thermochemical treatment. Borided samples presented the formation of layers with higher hardness and more resistant to wear. Borided samples also showed a higher coefficient of friction, due to the higher roughness resulting from the treatment.*

Keywords: *Biomaterial, boriding, titanium, wear resistance, tribology.*

1. INTRODUCTION

Titanium and its alloys are widely used in biomedical devices because they have superior mechanical, biological and chemical properties compared to other materials (Marino et al., 2006). The most commonly used titanium alloy for biomedical applications is Ti6Al4V (6% aluminium and 4% vanadium) (Craig et al., 2002). Although titanium and its alloys have good properties, there is still the problem of having low resistance to adhesive wear and, consequently, high coefficient of friction. Thus, cellular damage can occur by debris release, inflammatory reactions and even rejection of the material within the body (Maloney et al., 1993). Surface engineering represents an attractive method to improve the surface of the materials. From the existing treatments, the boriding is effective in improving the hardness in the titanium alloys, forming layers of TiB and TiB₂ on its surface (Fenghua et al., 2010).

2. EXPERIMENTAL PROCEDURE

Ti6Al4V samples were cut (9mm x 13mm x 3mm), then they were sanded using silicon carbide sandpapers, up to #600. Following, samples were ultrasonically cleaned in acetone. Samples were borided using two different techniques: the thermochemical and electrochemical methods, changing the process parameters, such as temperature, time, heating rate and boriding agent. After the process, samples were cooled to room temperature, except for the sealed crucible condition, where the samples were not removed from the oven, until it reaches the room temperature. The boriding conditions are shown on Table 1.

Table 1. Boriding parameters.

Type	Boronizing Agent	Atmosphere	Temperature (°C)	Heating rate (°C/min)	Duration (h)	Electric Current (mA/cm ²)	Electric Tension (V)
Thermochemical	Ekabor® 1-V2 (90% SiC + 5% B ₄ C + 5% KBF ₄)	Argon (4.5l/min, 70psi)	1000	50	7.5	--	--
Electrochemical	Ekabor® 1-V2 (90% SiC + 5% B ₄ C + 5% KBF ₄)	Ambient	970	40	4	125	4
Thermochemical (sealed crucible)	Borax (Na ₂ B ₄ O ₇)	Ambient	1000	40	8	--	--

2.1 Substrate and surface characterization

Samples were prepared for the optical microscopy analysis, where their cross sections were sanded on silicon carbide sandpapers, using different granulometries, up to #2400. Then, they were polished with a diamond paste (9 µm), followed by an alcohol cleaning. Samples were etched using the Kroll's solution (10% HNO₃ + 2% HF + 88% H₂O) during 15 seconds. Following, another polishing was made, but using a solution composed by 85% colloidal silica + 15% H₂O₂. One last chemical attack using the Kroll's solution was performed, during 3 minutes, to show the details of the microstructure of the samples.

After the preparation, the samples were observed on an Olympus BX60 optical microscope, when the phases alpha and beta were noticed on the untreated sample. For higher detailing, it was used Scanning Electronic Microscopy (SEM, Tescan, Vega3), and an Energy Dispersive Spectroscopy (EDS, Oxford Instruments). The X-Ray Diffraction (XRD) was also performed (Shimadzu XRD-7000), using the thin film mode, with the incident angle of 2.5° to 5° and 10°, using a speed of 2°/min, applying a scanning angle ranging from 10° to 110°, to determine the crystalline structure of the samples.

2.2 Hardness

The surface hardness test was performed to compare the surface hardness of the untreated samples with the treated samples, using the HR30N scale, where a 30 kgf is applied to measure its hardness, using the Instron series 600 equipment. This procedure was repeated 10 times per sample, which were used three samples of each condition.

The other hardness test performed was the Vickers microhardness test profile, realized on samples that were prepared as the others used on the SEM analysis, using the HMV micro hardness tester (Shimadzu). Starting from the surface, going to the middle of the sample, there were made 17 indentations in each sample, to check the influence of the borided layer.

2.3 Tribology

The linear reciprocal tribology test was performed on all the samples, using an Al₂O₃ ball of 6mm diameter, with an applied load of 3N over the Ti6Al4V sample and 10N for the borided samples. The amplitude of the movement was 1.5mm, the total length chosen was 10 m and the frequency of 1 Hz. Three tracks were made for each sample, to determine the friction coefficient and the wear rate, with the aid of a perfilometer (Taylor/Hobinson surtronic 25). These tracks were analysed on SEM to check if the substrate of the samples was exposed.

3. RESULTS AND DISCUSSION

The optical micrograph images show the differences between the original sample and the borided samples (Figure 1).

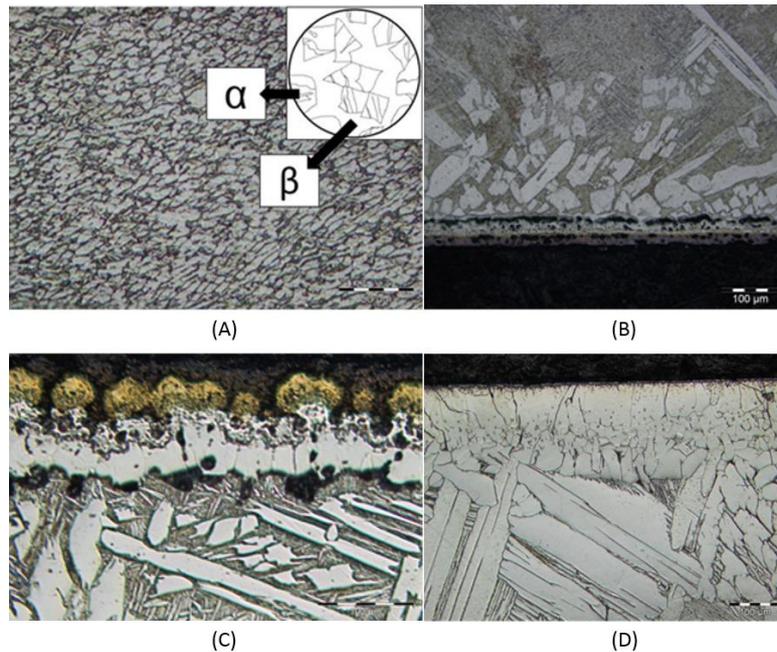


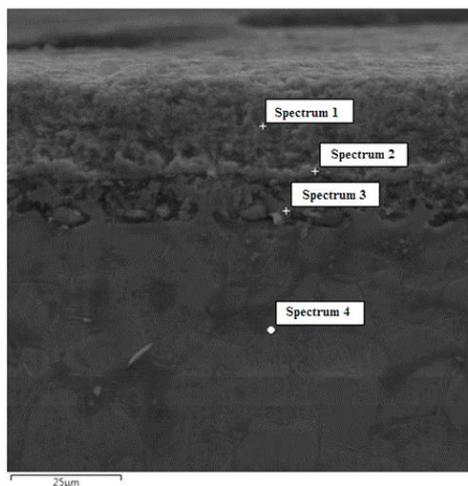
Figure 1. Comparison between the original alloy and the borided samples. (A) Ti6Al4V (50X); (B) Thermochemically borided sample (20X); (C) Electrochemically borided sample (20X); (D) Sealed crucible borided sample (20X).

The Figure 1A shows the alpha and beta phases of the alloy, what characterizes its bimodal microstructure. In the image B, it is possible to see the formation of a new layer on the surface of the sample: the porous layer between the surface and the substrate. It is also possible to see the platelets formed, with different sizes, varying from thick on the surface and thin on the substrate. The low speed cooling process generated the Widmanstätten structure on the substrate, which is characterized by having an acicular shape.

In the image C, it is possible to see the formation of a new layer on the surface, the Widmanstätten structure and a porous structure in the medium layer. In the last case (D), no porous layer formation was observed, but it is possible to see the Widmanstätten structure, with different size grains, due to the slow cooling process.

In general, all the samples had their equiaxial structures transformed into the Widmanstätten structure. In the case of the samples that were borided using the Ekabor, a porous layer was formed, but when the Borax was used it did not happen.

The EDS analysis showed the chemistry composition of each borided sample, the figures 2, 3 and 4 indicates the analyzed points and the tables present its compositions.



Spectrums	Ti	O	B	Al	V	Si
Spectrum 1	52.60%	30.00%	15.90%	0.30%	0.70%	0.40%
Spectrum 2	83.40%	-	13.60%	0.90%	1.80%	0.30%
Spectrum 3	82.70%	-	8.40%	7.20%	1.20%	0.50%
Spectrum 4	90.00%	-	-	7.90%	2.10%	-

(B)

(A)

Figure 2. Thermochemically borided sample (A) SEM image showing the analyzed points by EDS. (B) Chemical composition of the sample.

The analysis of the chemical composition of the thermochemically borided sample shows a percentage of Boron on the surface of the sample, but its detection is not reliable, because the equipment is just reliable on the detection of higher energies, such as those coming from the Nitrogen.

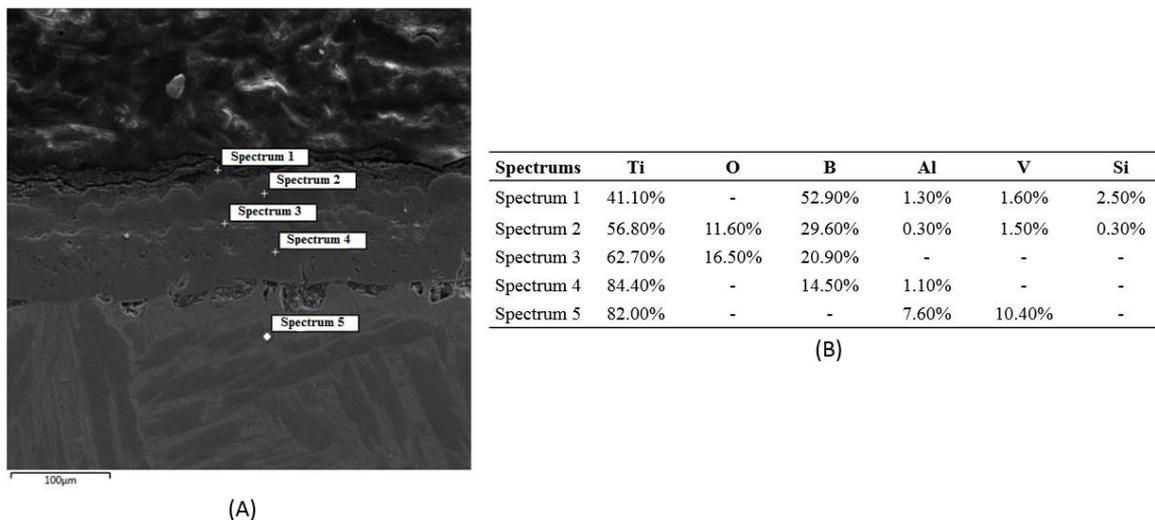


Figure 3. Electrochemically borided sample (A) SEM image showing the analyzed points by EDS. (B) Chemical composition of the sample.

In this case, the Boron percentage is too high, making this result not reliable.

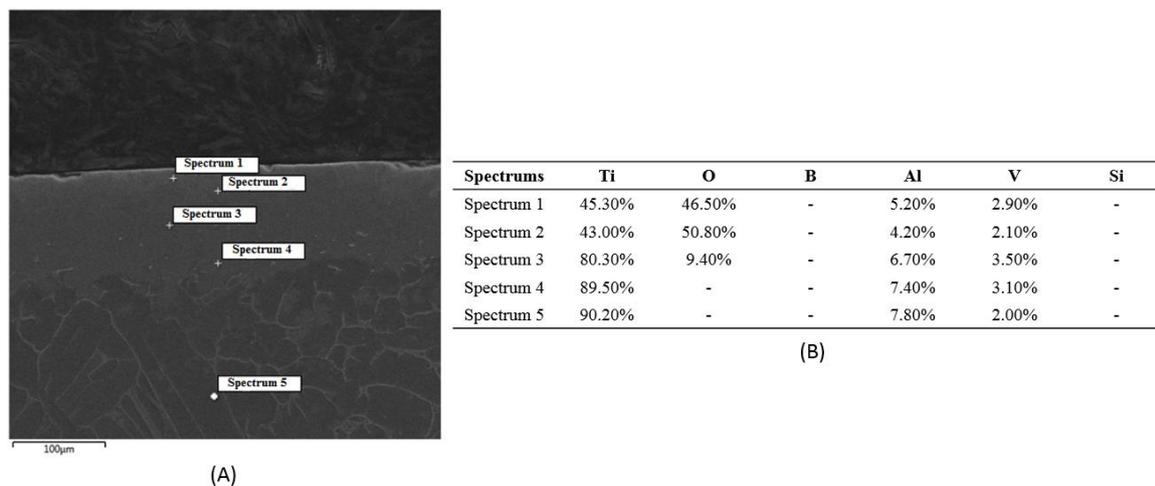


Figure 4. Sealed crucible borided sample (A) SEM image showing the analyzed EDS points. (B) Chemical composition of the sample.

The detection of the Boron was not reliable, because of its low energy emission, so in the sealed crucible condition it was discarded from the analysis, increasing the other elements amount.

The X-ray diffraction was performed to characterize the crystalline microstructure of the modified layers of the samples, as it is shown below, on figures 5, 6 and 7.

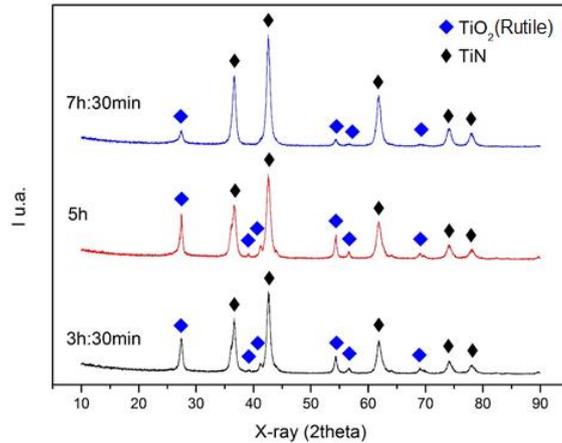


Figure 5. XRD analysis of the thermochemically borided sample, using a 10° incidence angle.

The titanium boride was not formed because of the use of Nitrogen instead of Argon, forming titanium nitride. The other samples formed the titanium boride layer, but the electrochemically sample formed Rutile and the electrochemically borided sample formed titanium diboride.

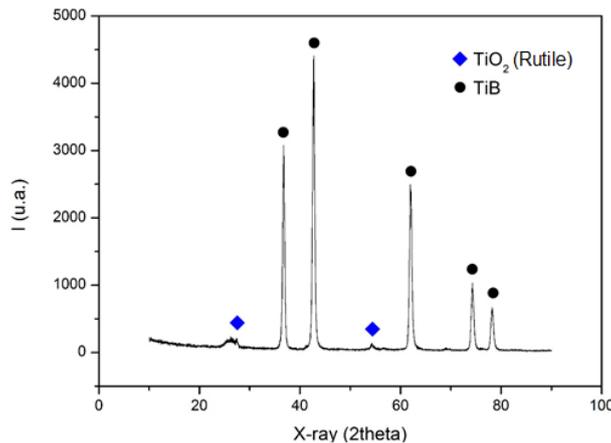


Figure 6. XRD analysis of the electrochemically borided sample, using a 10° incidence angle.

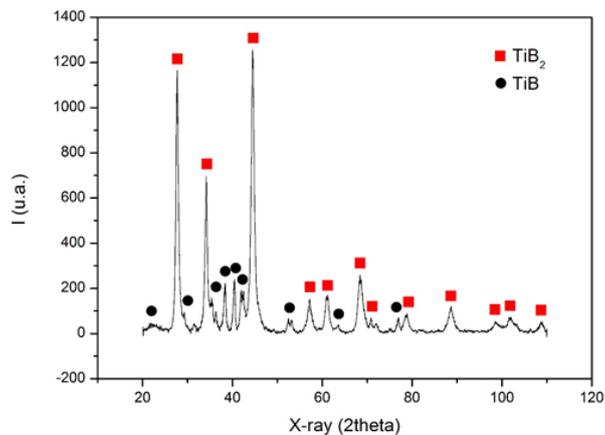


Figure 7. XRD analysis of the sealed crucible borided sample, using a 5° incidence angle.

The use of Ekabor boriding agent was not favorable to the process, because of the Fluorine on its composition, that reacted with the oxide protective layer on the alloy's surface, destroying it and attacking the titanium, starting the corrosion process, formatting the porosities, as its shown on Figure 8. For 7h30min, the porosities vary from 10µm to 12µm.

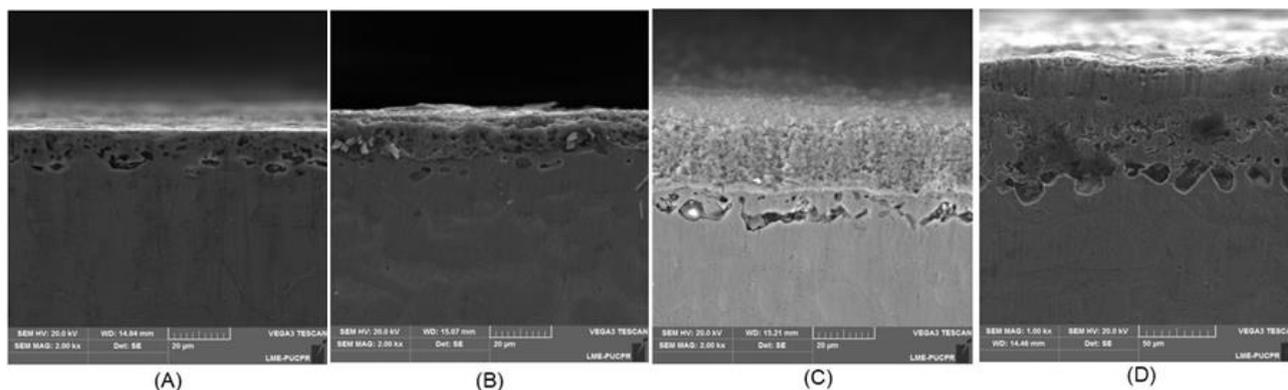


Figure 8. SEM image of the thermochemically borided sample. (A) 3h:30min (2000x); (B) 5h (2000x); (C) 6h:30min (2000x); (D) 7h:30min (1000x).

The thickness of the formed layers was measured by SEM, as it is shown on Table 2.

Table 2. Thickness of the formed layers.

Sample	Thickness [μm]
Ekabor® 1-V2 – Argon atmosphere (1000 °C; 7h30min)	29.21 ± 0.66
Ekabor® 1-V2 – Electrochemical process (970°C; 4h)	107.60 ± 6.08
Borax – Sealed crucible (1000 °C; 8h)	112.17 ± 6.03

As can be seen, the most efficient way to form bigger layers was the sealed crucible technique. Otherwise, the samples borided in Argon atmosphere formed the smaller layers. The superficial hardness of all the samples was measured, and then compared, as can be seen in Table 3.

Table 3. Average superficial hardness of the samples.

Sample	Ti6Al4V	Ekabor® 1-V2 Argon atmosphere (1000 °C; 7h30min)	Ekabor® 1-V2 Electrochemical process (970°C; 4h)	Bórax – Sealed cucible (1000 °C; 8h)
1°	47.50 ± 0.97	54.08 ± 1.96	49.28 ± 4.69	56.12 ± 2.55
2°	47.25 ± 0.97	53.62 ± 1.09	51.55 ± 10.10	54.45 ± 14.34
3°	47.64 ± 1.05	53.02 ± 1.98	52.06 ± 6.23	50.81 ± 11.06

The original alloy presented the lower values of standard deviation, indicating uniform properties along the sample, otherwise, the sealed crucible borided sample presented the higher hardness, but also presented the higher standard deviation, indicating a not uniform hardness property along the sample.

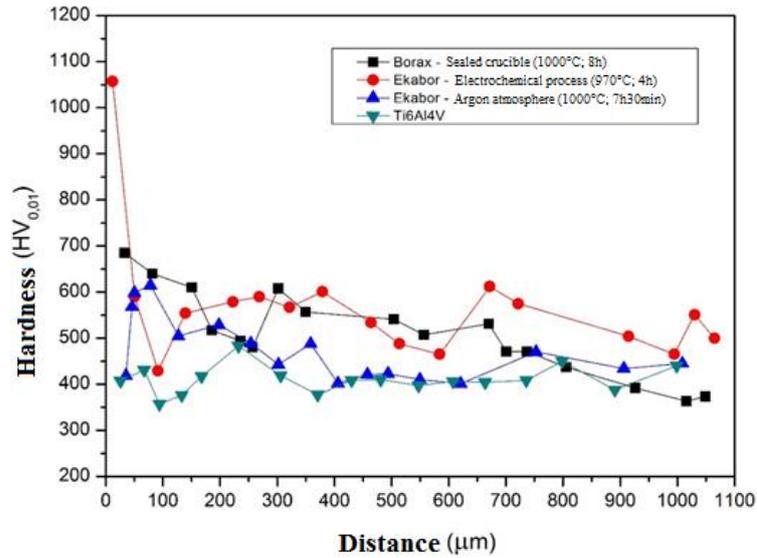


Figure 9. Vickers microhardness profile of the samples.

The Vickers microhardness profile shows that the higher average hardness was presented by the sample borided by the electrochemical process, as the higher hardness value, about 1060HV_{0,01}. The Argon atmosphere borided sample presented a low average hardness, being very similar to the original alloy.

The reciprocal linear tribology test was performed, then, the trails were analyzed by SEM, as can be seen in the Figure 10.

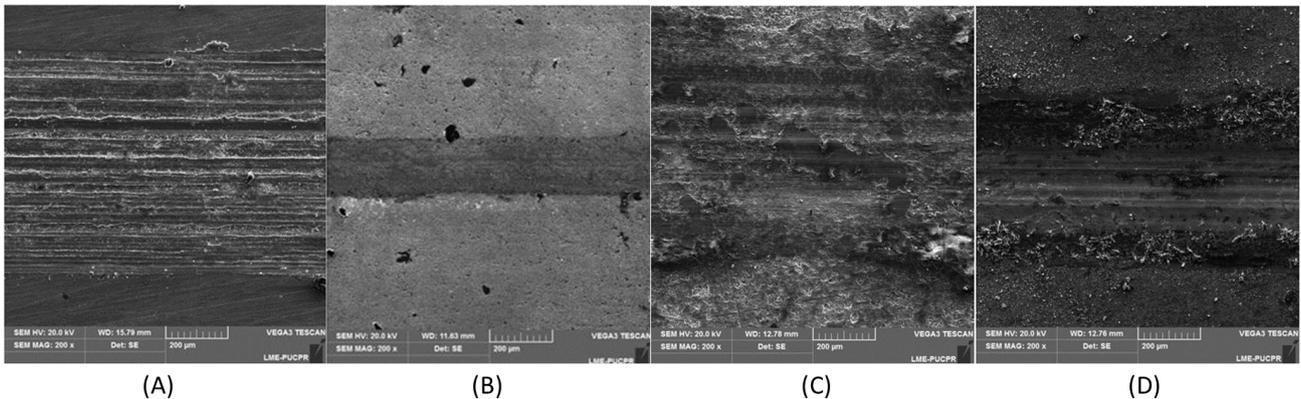


Figure 10. Trails formed on the surface of the samples (200x magnification). (A) Original alloy; (B) Thermochemically borided sample; (C) Electrochemically borided sample; (D) Sealed crucible borided sample.

In the first case, it is possible to see that a severe adhesive wear happened, where some particles were deposited on the material's surface, leading to an abrasive wear, leaving scratches on the trail. The second image shows that no particles were released on the material's surface, only the adhesive wear happened, but in a minor scale, even with a major load. The third image reveals that adhesive and abrasive wear happened on the sample, the particles can be seen, as the almost imperceptible scratches on the trail. In the last image, it is possible to see the particles deposited on the material's surface, occurring an adhesive wear.

The test also registered the friction coefficients of the samples, which are shown on the table below.

Table 4. Average friction coefficients of the samples.

Trail	Ti6Al4V	Thermochemically borided sample	Electrochemically borided sample	Thermochemically borided sample (sealed crucible)
1	0.44 ± 0.04	0.11 ± 0.01	0.65 ± 0.02	0.81 ± 0.09
2	0.44 ± 0.04	0.11 ± 0.01	0.61 ± 0.02	0.68 ± 0.10
3	0.43 ± 0.04	0.14 ± 0.01	0.64 ± 0.03	0.64 ± 0.11

In comparison to the original alloy, the electrochemical borided sample and the sealed crucible borided sample have increased their roughness due to the treatment, while the thermochemically boride sample had a reduction of 25%, approximately, on its friction coefficient.

The profile of the trails was measured, making possible to obtain the wear rates that are shown on table 5.

Table 5. Wear rates of the samples.

Trail	Ti6Al4V	Thermochemically borided sample	Electrochemically borided sample	Thermochemically borided sample (sealed crucible)
1	5.48×10^{-4}	-	1.95×10^{-4}	6.90×10^{-5}
2	6.67×10^{-4}	-	2.02×10^{-4}	9.61×10^{-5}
3	6.36×10^{-4}	-	5.11×10^{-4}	1.70×10^{-5}

The borided samples presented lower wear rates, comparing to the original sample, but the electrochemically borided sample presented a slightly significant difference. The trail formed on the surface of the thermochemically borided sample was very small, so, the profilometer used was not able to measure the trail, due to its limited sensitivity.

4. CONCLUSIONS

It was possible to see the transformation of the equiaxial grains into the Widmanstätten structure, with variations on their size. It was also possible to see the formation of the porous layer on the samples borided using Ekabor, due to its composition that contains Fluoride, that destroys the passive layer and attack the Titanium. The sealed crucible borided sample did not have a porous layer, because of the use of the Borax boriding agent.

All the borided samples reached higher hardness values, but they were not stable as the original alloy. Regarding the microhardness profile, the behavior of the borided samples was the expected, showing higher hardness values on the surface and lower values on the substrate.

The tribological test revealed that the Ti6Al4V alloy have poor tribological properties, but the boriding process may reduce the wear rate, despite having higher friction coefficient in some cases.

Analyzing the results obtained, it is possible to see that the best surface treatment used in this study, which could be done in orthopedic prostheses, would be the nitriding process, to form the TiN layer, because even though it reached the lowest layer of the tests, it presented a reduction in the value of the friction coefficient and did not generate particles when supposed to the tribological test, which is ideal for prostheses, since the generated debris can cause problems, such as inflammation, intoxication and even prosthesis rejection. This analysis was done taking into account only the values obtained by the tribological studies. We know that the boriding element used for this treatment (Ekabor) generated porosities in the material, compromising the properties of the alloy. Among the boriding processes studied, the one that used Borax was the one that presented better resistance to the wear, without the formation of porosities between the borate layer and the substrate.

5. REFERENCES

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